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Jonathan Dunn, Adrian Dobbs

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Synthesis and Reactions of Donor Cyclopropanes: efficient routes to *cis*- and *trans*- tetrahydrofurans

Jonathan Dunn[a] and Adrian Dobbs[a,b]

[a]School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK.
[b]School of Science, University of Greenwich, Central Avenue, Chatham Maritime, KENT ME4 4TB, UK

a.dobbs@gre.ac.uk

Keywords

donor-cyclopropane; silylmethylcyclopropane; silicon-stabilised carbocation; β-effect; tetrahydrofuran; Lewis acid promoted reaction

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[a]**School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK.**

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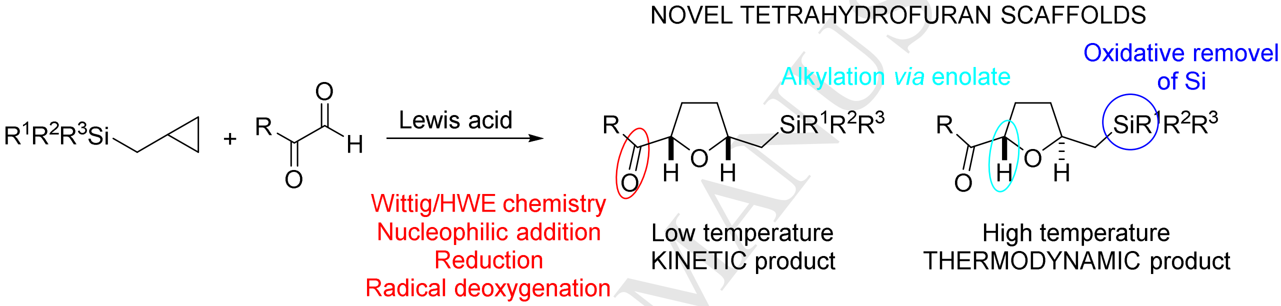
Graphical Abstract



Abstract

A detailed study on the synthesis and reactions of silylmethylcyclopropanes is reported. In their simplest form, these donor-only cyclopropanes undergo Lewis acid promoted reaction to give either *cis*- or *trans*-tetrahydrofurans, with the selectivity being reaction condition-dependant. The adducts themselves are demonstrated to be an important scaffold for structural diversification. The combination of a silyl-donor group in a donor-acceptor cyclopropane with novel acceptor groups is also discussed.

Keywords

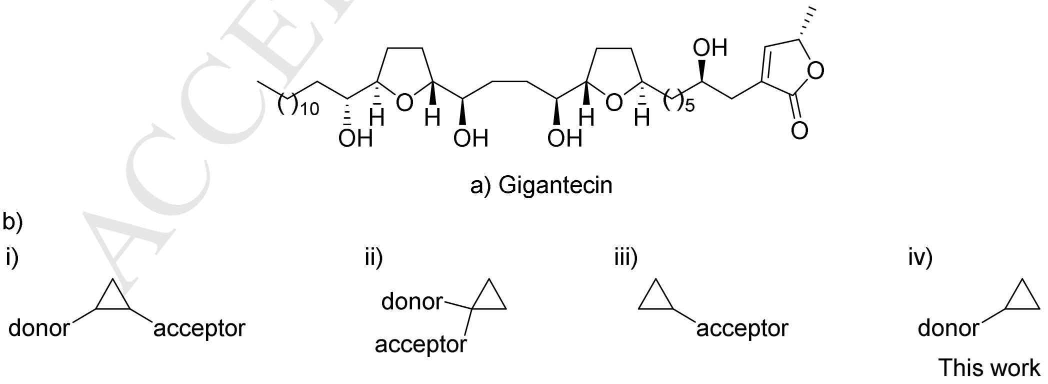
donor-cyclopropane; silylmethylcyclopropane; silicon-stabilised carbocation; β-effect; tetrahydrofuran; Lewis acid promoted reaction

Dedicated, from the current Secretary & Treasurer of the Royal Society of Chemistry's Heterocyclic and Synthesis Group, with deepest respect, to one of the founding members of the Group, Professor Alan Katritzky

Introduction

The 2,5-disubstituted tetrahydrofuran (THF) motif is found widely throughout nature, notably appearing in highly topical and active Annonaceous acetogenins[1-3] and many polyether-containing compounds and antibiotics.[1-8] Robust and rapid routes to access this motif are thus of great interest. Herein we report one such route, and subsequent transformations of the resultant 2,5-disubstituted THFs.

The use of donor–acceptor (D–A) substituted cyclopropanes (Scheme 1b (i) & b (ii)) in synthesis is well documented[9-14] and more recently, acceptor-group only substituted cyclopropanes (Scheme 1b (iii)) have also been utilised in a number of transformations.[15,16] However, until our work, reports and applications of donor-only cyclopropanes (Scheme 1b (iv)) were almost non-existant.[17-19] Herein, we report the first detailed study of the synthesis, reactions and applications of one class of donor-only cyclopropanes – silylmethylcyclopropanes – in the synthesis of 2,5-disubstituted tetrahydrofurans. It should be noted that the use of silicon moieties within D–A cyclopropanes has been reported: the silicon group aids the stabilisation of a β-carbocation, via the β-effect, but this has always been coupled with an anion stabilising group – most frequently a carbonyl or dicarbonyl (malonate) function simultaneously to stabilise the anion. Recent studies have suggested that the role of the anion stabilising group may be more subtle, including complexation of the Lewis acid between the 1,3-dicarbonyl groups when employing malonate.[20,21] Given our long standing interest in organosilicon chemistry[22-27] and the use of silyl groups to stabilise cationic intermediates in particular, we have turned our attention to study the chemistry and reactions of highly novel donor-only cyclopropanes, namely silylmethylcyclopropanes, and herein reveal their contrastingly different behaviour to donor-acceptor cyclopropanes.



Scheme 1. a) examples of Annonaceous acetogenins. b) classes of cyclopropanes: i) – iii) are known in the literature;[12] iv) is reported herein.

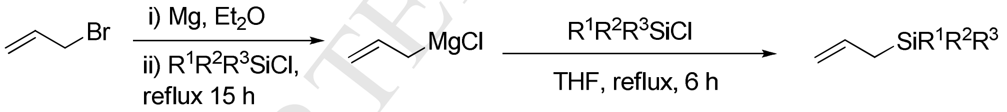
Results and Discussion

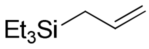
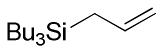
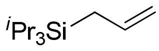
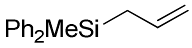
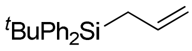
Synthesis of silylmethylcyclopropane precursors

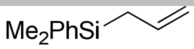
Unlike D-A cyclopropanes, there is no general reported method for the synthesis of simple silylmethylcyclopropanes. Initial attempts examined the reaction of cyclopropylmagnesium bromide and a chloromethylsilane as the most direct route. However, the reaction between chloromethyldimethylphenylsilane with cyclopropylmagnesium bromide was unsuccessful, irrespective of temperature, even after 92 hours, with quantitative recovery of chloromethyldimethylphenylsilane. Finkelstein conversion of the chloride to the iodide prior to addition of the Grignard reagent also failed to yield any substituted cyclopropane.[28] The alternative Grignard-based approach, forming a Grignard reagent from a chloromethylsilane and reacting it with bromocyclopropane, similarly failed to give any of the desired product, with high yields of reduced starting material obtained.[28]

The Simmons-Smith reaction was viewed as a viable alternative route to access a range of silylmethylcyclopropanes. The majority of the prerequisite allylsilanes had to be prepared; this was achieved *via* the method of Soderquist, involving adding allylbromide to a suspension of activated magnesium turnings in diethyl ether, followed by the chlorosilane, before heating the mixture at reflux temperature.[29] This method was used effectively for the synthesis of a variety of allylsilanes (Table 1).

Table 1 Synthesis of allylsilanes using a Grignard methodology



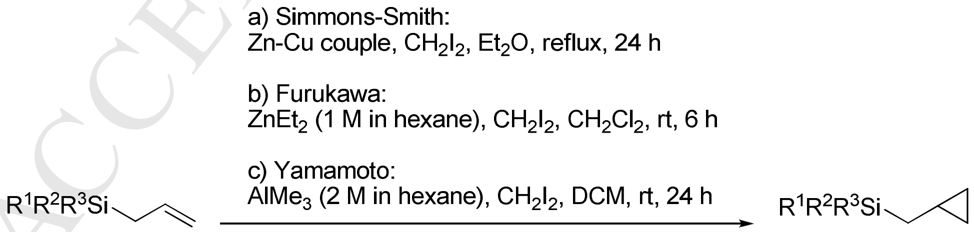
Entry	R^1	R^2	R^3	Product	Yield (%)[a]
1	Et	Et	Et		90[b]
2	Bu	Bu	Bu		88
3	^{i}Pr	^{i}Pr	^{i}Pr		81
4	Me	Ph	Ph		59[b]
5	^{t}Bu	Ph	Ph		92

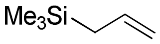
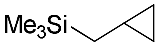
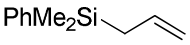
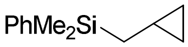
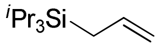
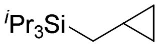
6	Me	Me	Ph		86

[a] Purified and isolated yields; [b] Grignard reagent was prepared (from the allyl bromide and activated magnesium turnings) prior to the addition of the chlorosilane

Initial attempts at the Simmons-Smith reaction using allyltrimethylsilane, zinc-copper couple (3 equivalents) and diiodomethane (1.5 equivalents) in diethyl ether disappointingly only gave 24% of the cyclopropane after 24h at reflux temperature, with unreacted allylsilane recovered. The non-aqueous work-up modification of Mironov gave no improvement in isolated yield.[30] Utilising freshly prepared (rather than commercial) zinc-copper couple, from the method of Rawson[31] gave cyclopropylmethyltrimethylsilane in an improved yield of 51% (Table 2 entry 1). Employing a sterically more congested silyl group – the dimethylphenylsilyl group – gave cyclopropylmethyldimethylphenylsilane in 54% yield (Table 2, entry 2). As the original Simmons-Smith reaction generated the desired cyclopropanes in only moderate yields, alternative methods were examined. Yamamoto's modified version of the Simmons-Smith reaction – using trimethylaluminium and diiodomethane – with allyltriisopropylsilane and allyldimethylphenylsilane gave the desired cyclopropanes in 56% and 63% respectively (Table 2 entries 4 and 6). Finally, the Furukawa methodology employing $ZnEt_2$, in place of the Zn/Cu couple, with allylphenyldimethylsilane gave the corresponding cyclopropane in 61% yield (Table 2 entry 3), although it should be noted that this method has been reported to be sufficiently exothermic to cause explosions if performed on larger scales.

Table 2 Summary of different cyclopropanation methodologies used for the synthesis of silylmethylcyclopropanes

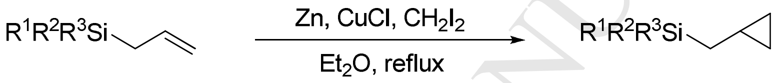


Entry	Allylsilane	Product	Method	Yield (%)
1			Simmons Smith[a]	51
2			Simmons Smith[a]	54
3			Furukawa[b]	61
4			Yamamoto[c]	63
5			Simmons Smith	60

[a] 1 eq. of allylsilane, 2 eq.diiodomethane, 5 eq. of copper chloride and 5 eq. of zinc powder in diethyl ether were heated at reflux temperature for 24 h. [b] 1eq. allylsilane, 5 eq. diiodomethane and 5 eq. of diethyl zinc in DCM were stirred at room temperature for 6 h. [c] 1eq. allylsilane, 2 eq. diiodomethane and 2 eq. of trimethylaluminium in DCM were stirred at room temperature for 24 h.

All three methods failed to go to completion, even with a large excess of reagents and longer reaction times. The separation of cyclopropane and allylsilane was frequently challenging, but this was overcome using silver nitrate-impregnated silica gel.[32] Despite the better yields from other methods, the original Simmons-Smith methodology was the most robust for the large scale production of the cyclopropanations required and was applied to a range of allylsilanes (Table 3).

Table 3. Summary of silylmethylcyclopropanes synthesised using the Simmons-Smith reaction

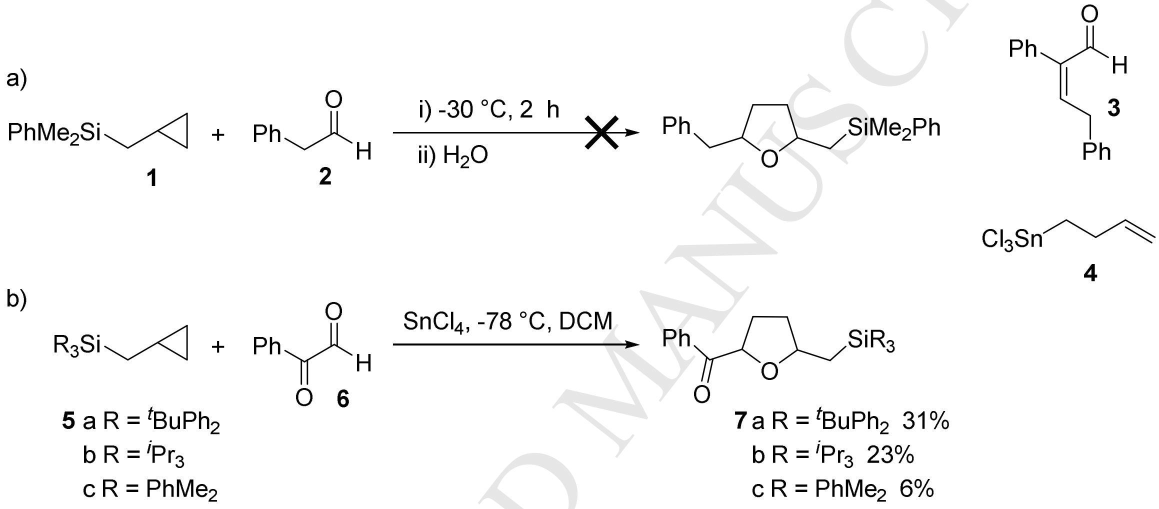


Entry	R^1	R^2	R^3	Isolated yield of cyclopropane (%)	Recovered allylsilane (%)[a]
1	Et	Et	Et	42	7 (12)[b]
2	Bu	Bu	Bu	65	9 (13)
3	*i*Pr	*i*Pr	*i*Pr	77	8 (9)
4	Me	Me	Ph	82	6
5	Me	Ph	Ph	71	5
6	*t*Bu	Ph	Ph	86	5

[a] In several cases the recovered starting material could not be cleanly separated from the cyclopropane, the value in brackets is the percentage of silylmethylcyclopropane that eluted with starting material determined by ^1H NMR analysis. [b] The remaining material was identified as hexaethyldisiloxane by GCMS.

Cyclisation studies and optimisation

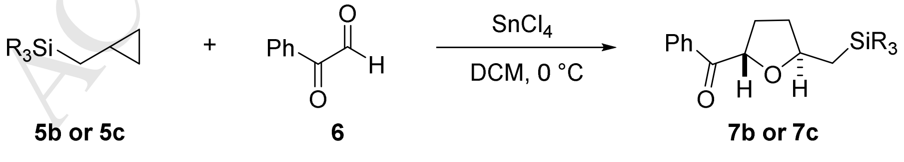
A plethora of successful catalysed cyclisation reactions have been reported for D-A cyclopropanes.[9-12,14] The same optimised conditions were first attempted here: between dimethylphenylsilylmethylcyclopropane **1** and phenylacetaldehyde **2** using titanium tetrachloride as the Lewis acid, owing to its oxophilic nature and success in many Lewis acid promoted reactions. No tetrahydrofuran was obtained, with the main products recovered being choromethylphenyldimethylsilane and the aldol condensation product **3**. Numerous attempts at this reaction, varying reaction conditions, molar equivalents, concentration, work-up procedure and the aldehyde component all failed to yield any product.[28] Changing the silane or the Lewis acid also failed to produce any THF, with either starting materials or aldol product being obtained. Varying the aldehyde similarly had no effect on the reaction outcome. When employing tin tetrachloride, an additional product, homoallyl tin trichloride **4**, was obtained, presumably through ring opening and nucleophilic attack followed by elimination of the silicon group (Scheme 2a). Yadav has reported to prevent this type of nucleophilic attack at silicon, bulky substituents should be incorporated on the silicon: disappointingly, utilising *tert*-butyldiphenylsilylmethylcyclopropane with any aliphatic aldehyde failed to yield any THF, but with starting material now being recovered.



Scheme 2

However, reaction of *tert*-butyldiphenylsilylmethylcyclopropane **5a** with phenyl glyoxal **6** activated by tin tetrachloride in dichloromethane at -78 °C and avoiding an aqueous work up afforded the cyclised THF adduct **7a** in an isolated yield of 31% (Scheme 2b). Repeating this with dimethylphenylsilylmethylcyclopropane **5c** gave the THF adduct **7c** in a disappointing 6% yield, the major product being the disilylether, suggesting that the steric properties of the silyl group did indeed influence the product of the reaction. Given that the triisopropyl group is smaller than the *tert*-butyldiphenyl group and larger than the dimethylphenyl group, an intermediate yield was expected, and indeed the TIPS substituted THF **7b** was obtained in 23% yield, thus confirming the importance of bulk around silicon. Since the triisopropyl-substituted silylmethylcyclopropane **5b** was the easiest of the three to handle, this was chosen for optimisation studies. A range of Lewis acids were screened for promoting the reaction, both in different equivalents and under varying reaction conditions. Initially, all reactions were performed using 1 equiv. of the Lewis acid, with respect to the phenyl glyoxal and triisopropylsilylmethylcyclopropane. Any Lewis acids containing a triflate counter ion failed to afford any of the desired THF and in most cases led to decomposition of the silylmethylcyclopropane, except for $Zn(OTf)_2$ where the starting material was recovered (80%). Brønsted acids were also ineffective at promoting the reaction. Titanium tetrachloride, aluminium chloride, germanium chloride and magnesium bromide all gave trace amounts of the THF in the reaction mixture (by GC-MS), but in insufficient amounts to warrant isolation. Tin tetrabromide gave a comparable yield of product to tin tetrachloride although the reaction was slower at -78 °C (5 hr, *c.f.* 3 hr for $SnCl_4$) and the Lewis acid harder to handle. The only other Lewis acids that promoted the reaction in any significant yield were the zinc halides, in particular zinc bromide. Thus zinc halides and tin (IV) halides were the only Lewis acids found to promote the reaction, although with zinc Lewis acids having the considerable drawback of requiring longer reaction times and heating, plus giving less diastereocontrol. However, one thing that soon became apparent was that both the order in which the reagents were added and the concentration of the reaction were found to have an important influence on the product obtained, with the best yields being obtained when the Lewis acid was added to a solution of phenyl glyoxal, and the silylmethylcyclopropane being added later.[33] The quantity of Lewis acid was also significant (Table 4). The desired THF was still obtained in good yields with sub-stoichiometric amounts of tin tetrachloride, although less than 0.6 eq. gave significantly reduced yields, with unreacted cyclopropane recovered. Rather than the reaction being catalytic, the tin tetrachloride is thought to coordinate with two molecules of the glyoxal. Therefore, reducing the amount of tin tetrachloride only becomes significant once the number of moles is less than half that of the aldehyde, corresponding to 0.75 eq. or a 2:1 ratio of glyoxal to tin tetrachloride. The same pattern was observed with the phenyldimethylsilyl group.

Table 4. Cyclisation of triisopropylsilylmethylcyclopropane 5b using sub-stoichiometric quantities of tin tetrachloride



Equivalents of $SnCl_4$	$R^1,R^2,R^3 = {}^i$Pr **7b** %Yield	R^1,R^2,R^3 = $PhMe_2$ **7c** %Yield
0.7	85	71
0.6	71	56

0.4	55	41
0.3	46	29
0.2	38	10

The temperature of the reaction was found to control the relative stereochemistry of the THF product. When the reaction was run at temperatures below 0 °C, two compounds were always obtained from the reaction, which were inseparable by column chromatography: the *cis* and *trans* diastereoisomers of the THF. At 0 °C, only one diastereoisomer was obtained. The C-5 proton was particularly useful in determining which diastereoisomer was formed, since it had distinctly different chemical shifts in the two different diastereoisomers (δ=5.13 and 5.30 ppm) while the C-2 proton signals overlapped with each other (δ=4.23-4.30 ppm). NOE measurements permitted the determination of which diastereisomer was formed at each temperature, with the single product formed at 0 °C found to be the *trans* adduct, while at -78 °C a mixture of *cis* and *trans* diastereoisomers, favouring the *cis*.

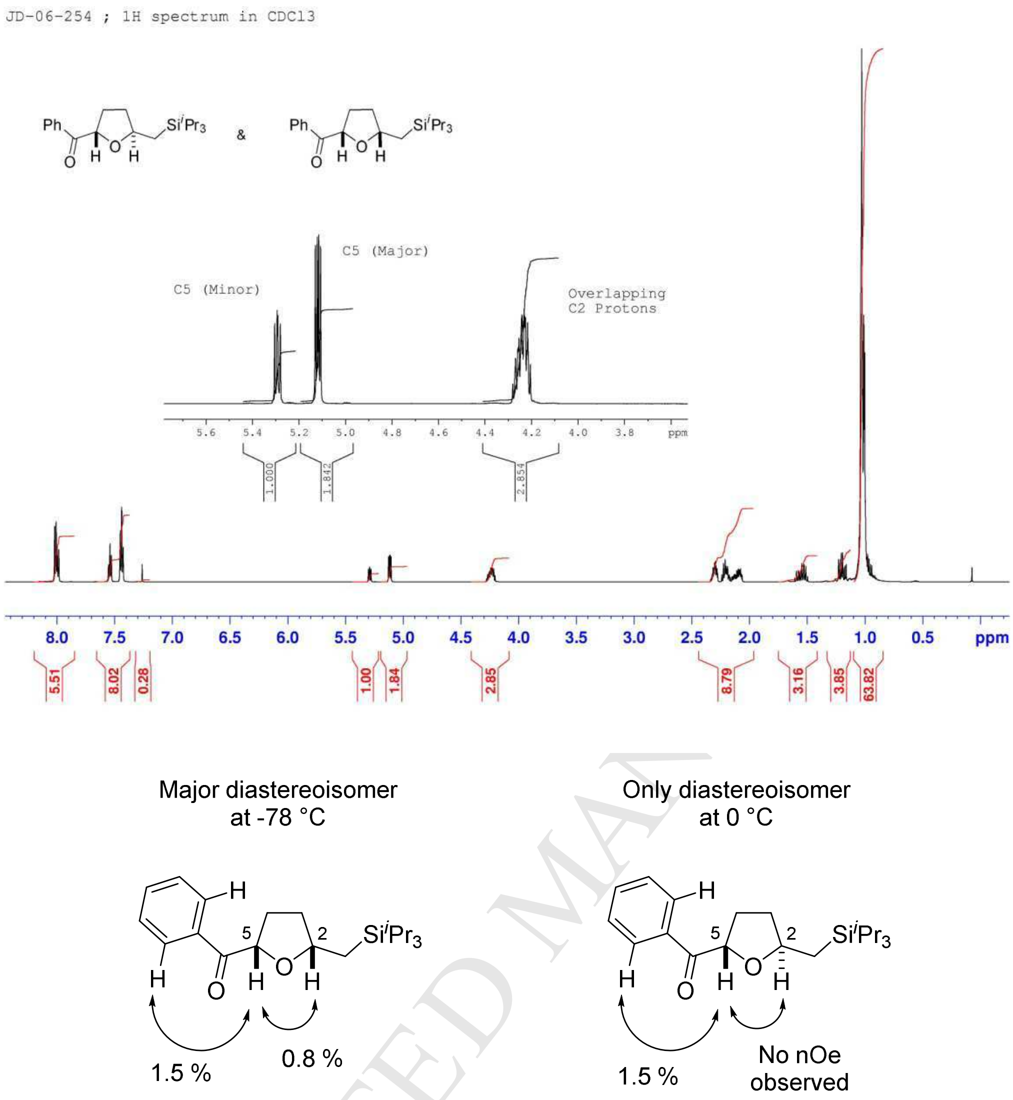
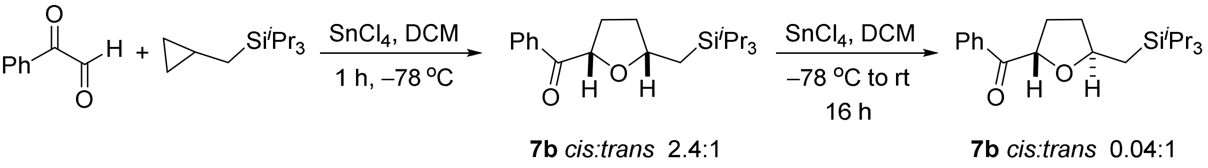


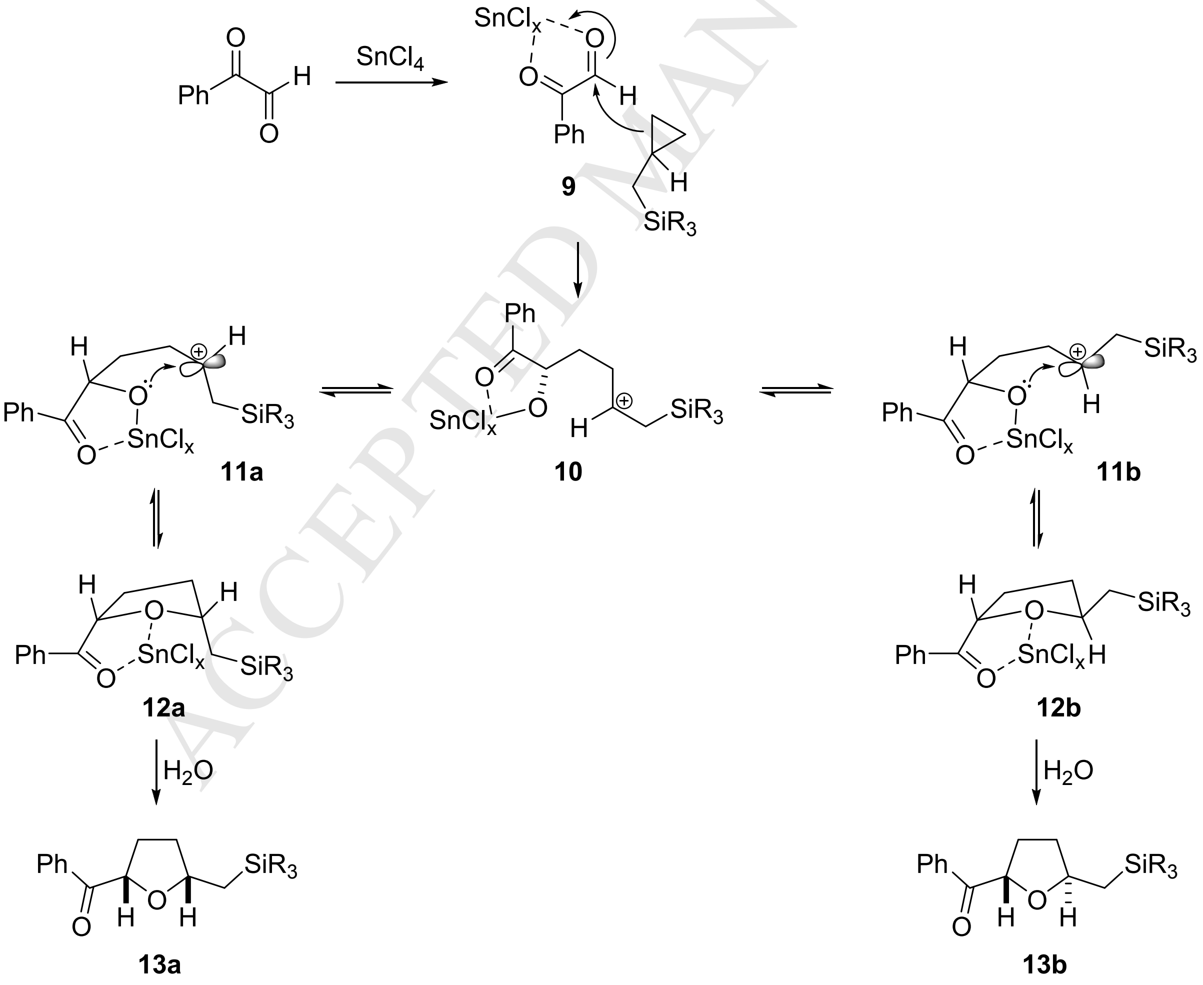
Figure 1. ^{1}H NMR spectrum of the mixture of diastereoisomers of the THF 7b formed at -78 °C.

Believing the *cis* product to be the reaction kinetic product and the *trans* adduct the thermodynamic product, a sample of the 2,5-disubstituted THF **7b** was prepared at -78 °C (*cis:trans* 2.4:1), re-dissolved in DCM, cooled to -78 °C and tin tetrachloride added, and the reaction then warmed to room temperature. The two diastereisomers were now found in a ratio *cis:trans* 0.04:1, indicating that they had indeed undergone equilibration and interconversion to the thermodynamically more stable *trans*-THF upon warming under the reaction conditions (Scheme 3).



Scheme 3. Interconversion of *cis* and *trans* THF, **7b**

The reaction is postulated to proceed initially *via* $SnCl_4$ coordination between the two carbonyl oxygen atoms of the glyoxal, thus activating the aldehyde. The cyclopropane acts as a nucleophilic pseudo π-donor forming a carbon-carbon bond, and driven by the β-carbocation stabilising effect of the silyl group (**10**). To reduce steric hindrance, the bulky silyl group would be expected to be directed away from the glyoxal. The ring opening of the cyclopropane places the 2- and 5-substituents in a *cis* orientation (**11a**). At -78 °C, the ring-closing reaction is faster than rotation around the C-C bond, and thus the kinetic product, the *cis* stereoisomer (**13a**), is the major product. Given the temperature dependence of the reaction, the ring closing must be reversible. This allows the ring to open (**10**), and as the temperature increases, and the rate of rotation around the C-2/C-3 bond increases, positioning the silyl group in a *trans* relationship to the α-keto group (**11b**), thus giving the *trans* stereoisomer after ring closure (**13b**). The $SnCl_4$ is thought to remain coordinated to the THF and carbonyl oxygen (**12a** and **12b**) until the reaction is quenched with water.

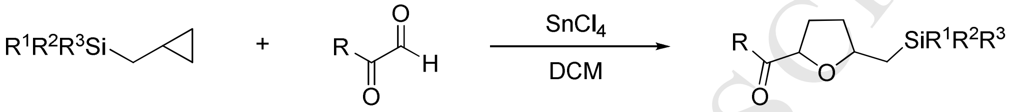


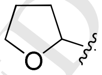
Scheme 4. Mechanistic explanation for the formation of *cis* and *trans* adducts

In summary, the optimum reaction conditions for promoting the reaction between glyoxals and silylmethylcyclopropanes involved using 0.7 eq of tin tetrachloride at -78 °C to give a mixture of *cis* and *trans* products, or after warming to 0 °C to give solely the *trans* diastereomer.

Given the success of phenyl glyoxal and the optimised reaction conditions, a range of other α-keto aldehydes were successfully employed in the cyclisation (Table 5), with a variety of the silylmethylcyclopropanes.

Table 5. Cyclisations of silylmethylcyclopropanes with α-ketoaldehydes promoted by tin tetrachloride.



Entry	R^1	R^2	R^3	R	Temperature (°C)[a]	Yield (%)	*dr* (*cis/trans*)
1	^{i}Pr	^{i}Pr	^{i}Pr	Ph	-78	67	1.6 : 1
2	^{i}Pr	^{i}Pr	^{i}Pr	Ph	-78 to 0	85	Only *trans*
3	^{i}Pr	^{i}Pr	^{i}Pr	tBu	-78 to 0	5[b]	
4	^{i}Pr	^{i}Pr	^{i}Pr	OEt	-78 to 0/2 h	42[c]	
5	^{i}Pr	^{i}Pr	^{i}Pr		-78 to 0/ 6 h	0[d]	
6	^{t}Bu	Ph	Ph	Ph	-78	66	2.1 : 1
7	^{t}Bu	Ph	Ph	Ph	-78 to 0	72	1 : 1.1
8	Me	Me	Ph	Ph	-78	53	2.1 : 1
9	Me	Me	Ph	Ph	-78 to 0	18	Only *trans*
10	Me	Me	Ph	OEt	-78 to 0	53	Only *trans*
11	Me	Me	Ph	p-NO$_2$-C$_6$H$_4$	-78	25	2.6:1
12	Me	Me	Ph	p-NO$_2$-C$_6$H$_4$	-78 to 0	3	Only *trans*
13	Me	Me	Ph	p-Br-C$_6$H$_4$	-78	55	1.8:1
14	Me	Me	Ph	p-Br-C$_6$H$_4$	-78 to 0	34	Only *trans*
15	Me	Ph	Ph	Ph	-78	40	2 : 1
16	Me	Ph	Ph	Ph	-78 to 0	38	1 : 2.4
17	Et	Et	Et	Ph	-78	21	2.3 : 1
18	Et	Et	Et	Ph	-78 to 0	53	1 : 10
19	^{n}Bu	^{n}Bu	^{n}Bu	Ph	-78	43	1 : 1.4

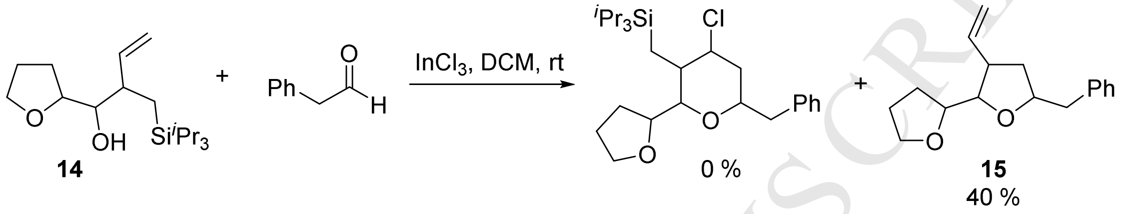
20	^{n}Bu	^{n}Bu	^{n}Bu	Ph	-78 to 0	31	1 : 11

[a] Conditions: A solution of tin tetrachloride in DCM was added to a solution of phenyl glyoxal in DCM at -78 °C. After stirring at this temperature for approx. 5 min a solution of silylmethylcyclopropane in DCM was added. The reaction was either kept at -78 °C or allowed to warm to 0 °C and the product was isolated by column chromatography.

[b] Additionally 63% TiPs-Cl and 26% TiPS-OH were recovered.

[c] Additionally 11% TiPs-Cl and 10% TiPS-OH were recovered.

[d] While none of the desired adduct was obtained, the following were isolated: 26% TiPs-Cl and 6% TiPS-OH and 5% unreacted cyclopropane were recovered. A further additional product **14** was observed in 23% yield (combined diastereomers). As an aside, this was utilised in a Prins reaction utilising our established method employing $InCl_3$ as the Lewis acid,[34] and gave a bis-THF product **15** in 40% yield.



The reaction proceeded in modest to very good yields for a variety of α-ketoaldehydes and silylmethylcyclopropanes. In many cases, where lower yields are reported, this was frequently due to not knowing the exact quantity of α-ketoaldehyde that had been added to the reaction, as these were cracked and their water content removed immediately prior to use. However, when this was not an issue, the yields were good. The previously observed mixture of *cis* and *trans* furans were observed at low temperatures but almost exclusively *trans* at room temperature was observed in all cases.

The yields also varied significantly between the different silyl groups and appear to correspond to the size of the substituents on the silicon. If the silyl groups are arranged in a decreasing order of yield based on an average of the two temperatures the following pattern emerges: TIPS > TBDPS > Bu_3Si ≈ MDPS ≈ DMPS ≈ TES. This order could be compared to the relative stabilities of different trialkylsilyl ethers towards base-catalysed hydrolysis: DTBMS > TIPS > TDS > TBS ≈ TBDPS > MDIPS > Bu_3Si > Pr_3Si > DMIPS ≈ TES > TMS ≈ MDPS ≈ DMPS. The similarities can be explained if it is assumed the most likely side reaction is addition of the silylmethylcyclopropane to tin tetrachloride and elimination of the silicon by nucleophilic attack of the chloride ion. By comparison, the relative stabilities of different trialkylsilyl ethers towards base-catalysed hydrolysis is a measure of resistance to nucleophilic addition of the hydroxyl ion. Once the silyl group is smaller than the tri-*n*-butylsilyl group all the groups give similar yields and the size of the substituents seems to make only a small difference to the yield.

The stereochemical outcome was identical to that recorded earlier, irrespective of the silicon substituents: if the reaction was performed at -78 °C and warmed to 0 °C the *trans* diastereoisomer predominated (the exception being TBDPS, which showed equal amounts of the *cis* and *trans* diastereoisomer). However, if the reaction was quenched at -78 °C, the *cis* diastereoisomer predominated in a ratio of approximately 2:1 for all silyl groups except $^{n}Bu_3Si$, suggesting that the *cis* diastereoisomer is the kinetic product while the *trans* is the thermodynamic product. It is probable that in the cases where two products were isolated at 0 °C, insufficient time was allowed to establish the temperature dependent equilibrium before the reaction was quenched, since increasing the reaction time gave improved ratios of the *trans* adduct.

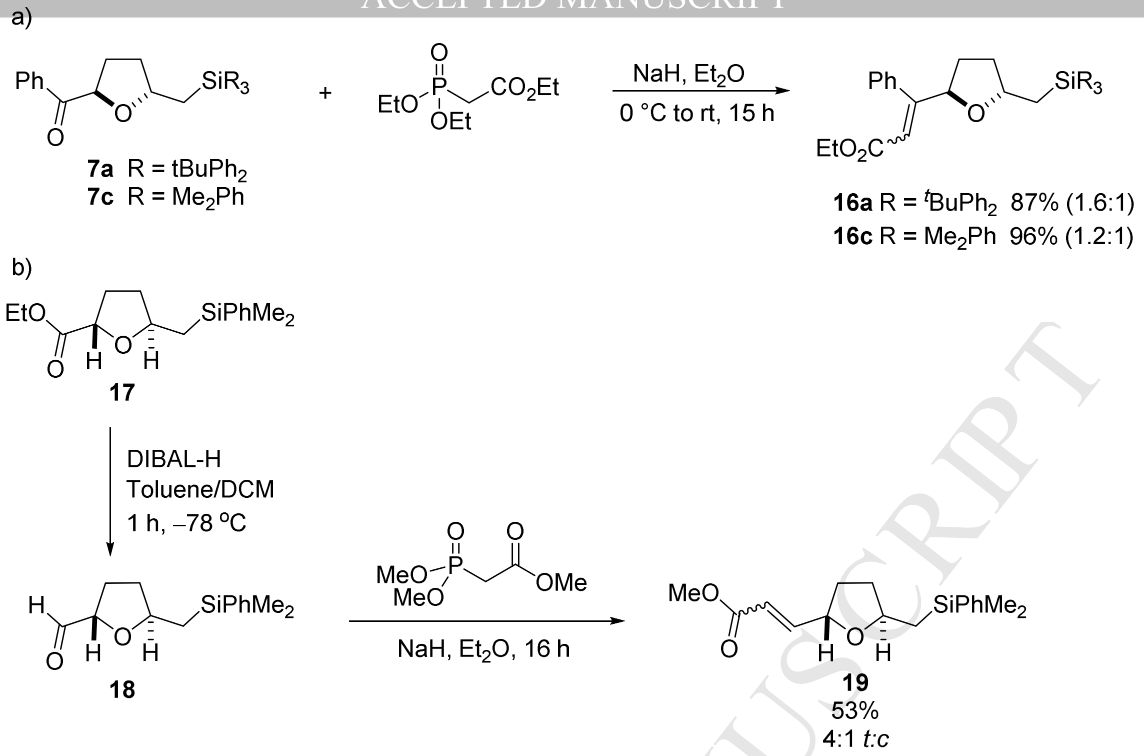
To expand the scope of the cyclisation, a further series of non-glyoxal derived aldehydes were attempted, including a range of aromatic aldehydes containing either electron-donating or electron-withdrawing substituents at the *para* position, but none produced any of the desired THF and the isolated products were always the chlorotriisopropylsilane, triisopropylsilanol and recovered aldehyde, thus demonstrating that the cyclopropane had reacted directly with the tin tetrachloride. Similarly, employing phenylacetaldehyde or butanal also resulted in rapid decomposition of the cyclopropane.

In summary, we have reported both the scope and limitations of donor silylmethylcyclopropanes in the synthesis of substituted tetrahydrofurans.

Transformations of the THF adducts

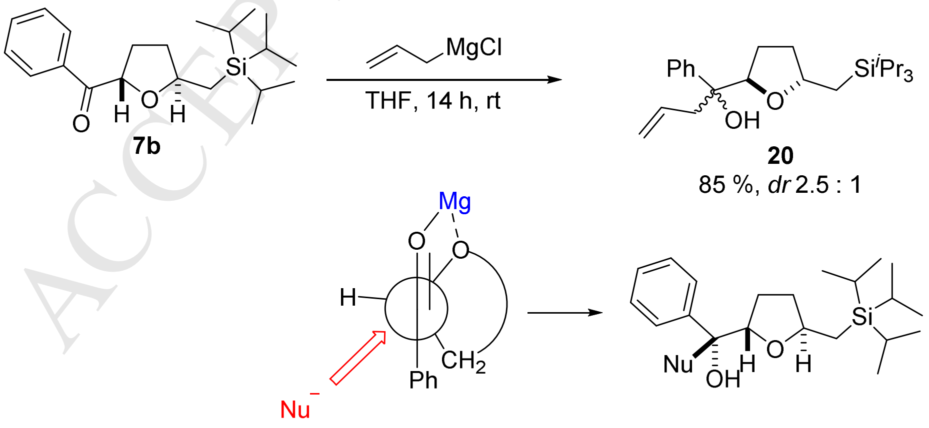
Additionally, we wished to demonstrate the usefulness of the 2,5-disubstituted THFs produced as scaffolds for further transformation. The incorporation of the α-ketone and the silicon moieties, during the cyclisation, were seen as the key handles for further elaboration.

It was envisaged that the α-ketone moiety could be utilized in a number of different transformations. The *trans* α-ketones **7a** and **7c** readily underwent Horner-Wadsworth-Emmons (Scheme 5a). Deprotonation of triethyl phosphonoacetate with sodium hydride in diethyl ether followed by addition of the *trans* THFs **7a** and **7c** gave the corresponding alkenes **16a** and **16c** in excellent 87% and 96% yields respectively and both as a 1:1.2 mixture of alkene geometric isomers. NOE studies confirmed that no epimerisation of the C-5 proton had occurred and the relative stereochemistry of the THF ring remained *trans* but identification of the different alkene geometries was inconclusive, and thus impossible to state which isomer was the major one (Scheme 5a). In contrast, DiBALH reduction of ethyl 2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carboxylate **17** gave the aldehyde **18** in 78% yield (Scheme 5b). This aldehyde has huge potential for a variety of transformations. First, it also was used in a Horner-Wadsworth-Emmons reaction with trimethyl phosphonoacetate, giving the alkene **19** in 53% yield and 4:1 *trans:cis* ratio (Scheme 5b).



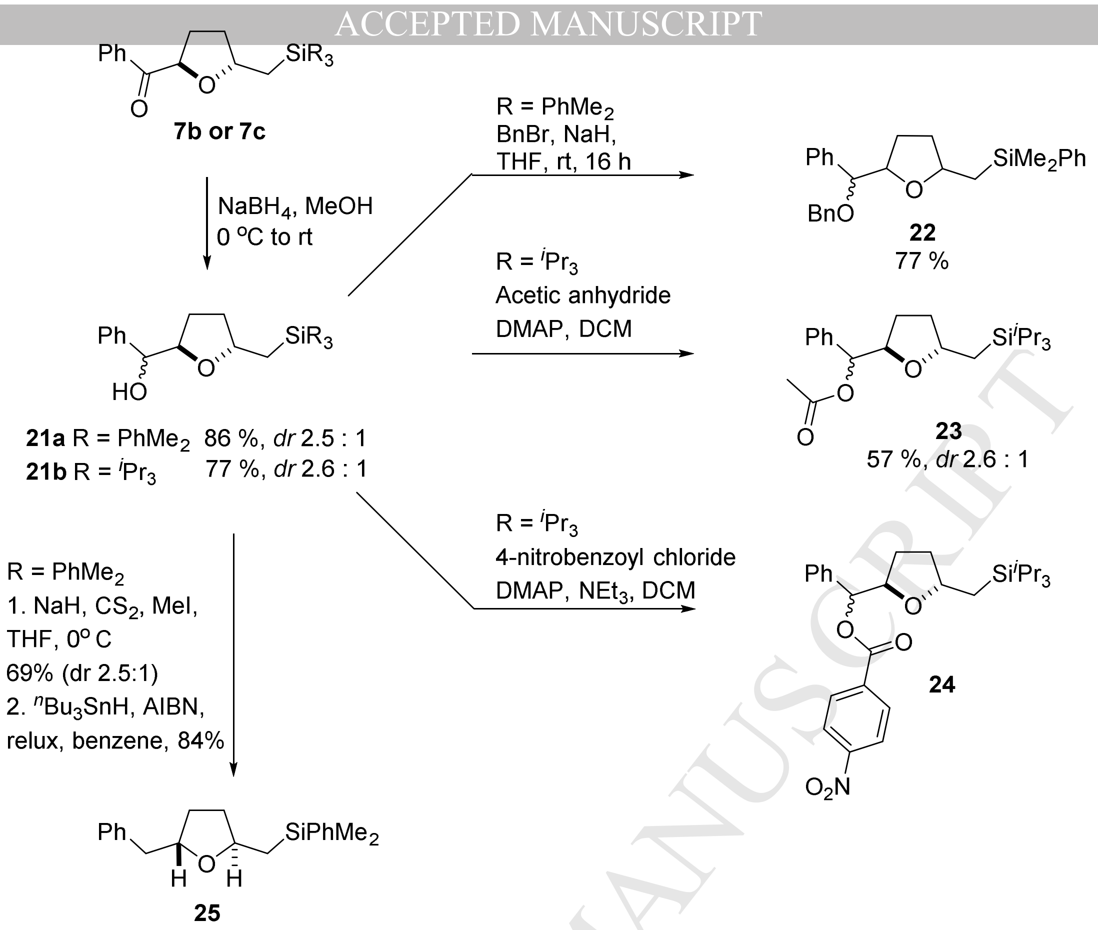
Scheme 5

Nucleophilic addition of allylmagnesium chloride to the *trans* THF diastereoisomer **7b** gave the desired tertiary alcohol **20** in 85% (Scheme 6) as a mixture of diastereoisomers (2.5:1). Speculatively, we propose that chelation control is operating in the reaction, giving the predicted *anti* arrangement of C-5 proton and hydroxyl group as the major product, although it was impossible to confirm this as the major product by NMR.



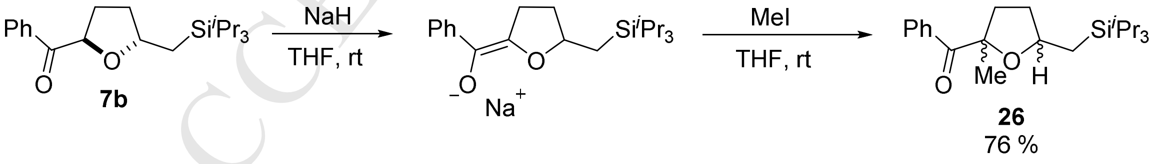
Scheme 6

Hydride addition to the ketones **7b** and **7c** also occurred readily using sodium borohydride. The resulting secondary alcohol **21b** could be converted to the corresponding acetate **23** or 4-nitrobenzoyl esters **24**, or alternatively the benzyl ether **22**, all in good yields and with the diastereoselectivity across the oxygen of the ring being maintained (Scheme 7). Interestingly, both Grignard and hydride addition gave the resultant alcohol in the same 2.5:1 diastereomeric ratio (starting from a pure sample of the *trans* THF diastereomer). This is somewhat surprising, given that sodium borohydride is known to be only a weakly chelating reducing agent (and we cannot rule out the possibility of Felkin-Anh operating in both cases). The one step reduction of the α-ketone to the methylene group using a Clemmensen reduction (Zn(Hg), HCl (conc) in benzene) resulted in the decomposition of the starting material, as did the milder sonochemical Clemmensen reduction developed by Salvador[35,36] (Zn in acetic acid/water). The strongly basic conditions of the Wolff-Kishner reduction also resulted in decomposition. However, it was possible to achieve complete reduction of the ketone *via* the alcohol **21a** previous reported, followed by a Barton-McCombie radical deoxygenation. Conversion of the diastereomeric mixture of alcohols **21a** derived from the $NaBH_4$ reduction to the methyl xanthate was achieved with carbon disulfide, methyl iodide and sodium hydride in tetrahydrofuran at 0 °C. Treatment of the methyl xanthate with tri-*n*-butyltin hydride and AIBN in toluene at reflux gave the 2,5-disubstituted THF **25** in an overall yield of 50% from the ketone and as still a single diastereoisomer. This overall transformation has given, in effect, the product from the cycloaddition with a simple aldehyde (phenylacetaldehyde) rather than phenyl glyoxal, and thus opens this methodology to access many non α-keto THFs. No epimerisation was observed in any of these reactions.



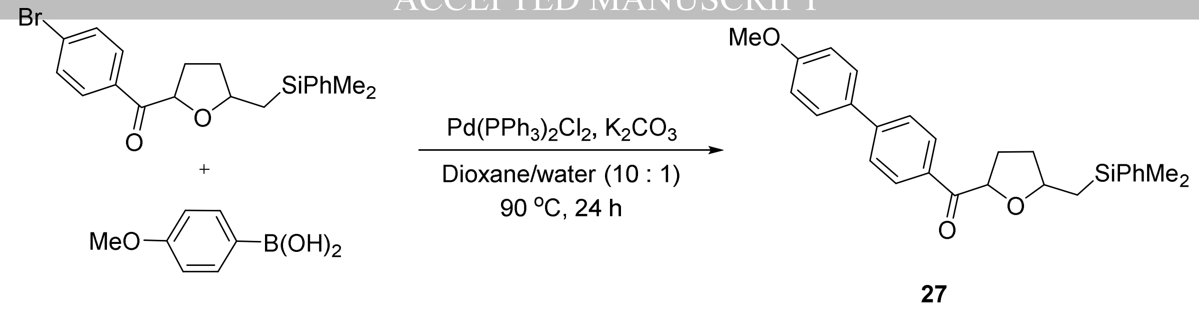
Scheme 7

Functionalisation α- to the ketone was possible *via* the corresponding enolate. Disappointingly, use of LDA (THF, -78 °C) only led to decomposition of the THF. Pleasingly, however, employing sodium hydride as the base and quenching with methyl iodide gave the methyl substituted THF **26** in 76% as two inseparable diastereoisomers (1.5:1).



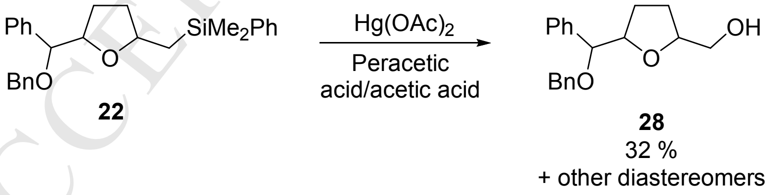
Scheme 8

Having previously employed 4-bromophenyl glyoxal in the synthesis of THF (Table 5, entries 13 and 14), to demonstrate the usefulness of the bromine substituent, this was successfully utilised in a Suzuki coupling reaction with 4-methoxyboronic acid, to give the biaryl-coupled product in 82% yield.



Scheme 9

In the design of silylmethylcyclopropanes, the presence of the silicon moiety was not only as a donor to aid stabilization of positive charge built-up at the β-carbon during the cyclisation step, but also to act as a masked alcohol, remaining chemically inert throughout a range of other transformations, before being unmasked.[37] Fleming has reported several methods for the oxidation of the phenyldimethylsilyl group. No product was isolated from the reaction of the α-keto THFs **7b** or **7c** with mercuric acetate and peracetic acid, although the reaction mixture showed the presence of several phenylmercury species indicating that the electrophilic aromatic substitution had occurred. This is consistent with Fleming's work, where the presence of a ketone elsewhere in the molecule was reported to be problematic.[38] Pleasingly, however, oxidation (desilylation) occurred readily when employing the benzyl-protected reduced compound **22**, yielding the primary alcohol **28** as a mixture of diastereoisomers in high yield. One of these diastereomers was separated pure in 32%, with the remainder mass balance comprising the other inseparable diastereomers. The unprotected primary alcohol now offers the scope for further manipulation, before later unmasking the secondary alcohol.

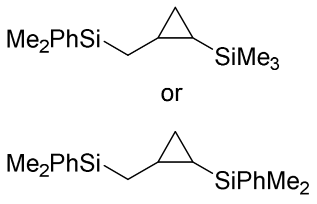


Scheme 10

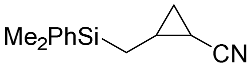
In summary, we have reported, for the first time, the synthesis of simple silylmethylcyclopropanes and the scope and limitations of their reactions with aldehydes to give THFs.

Disubstituted silylmethylcyclopropanes

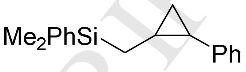
To conclude our study of the cycloaddition reactions of cyclopropylmethylsilanes with α-keto aldehydes, it was decided to investigate novel donor-acceptor cyclopropanes. Although not the original aim of this work, it was reasoned that such cyclopropanes would be more reactive than the donor-only silylmethylcyclopropanes, participating in reactions with a wider range of substrates. Three hitherto unreported acceptor groups were targeted: the nitrile group **30**, the trialkylsilyl group (making use of the α-effect) **29** and the phenyl group **31**.



29

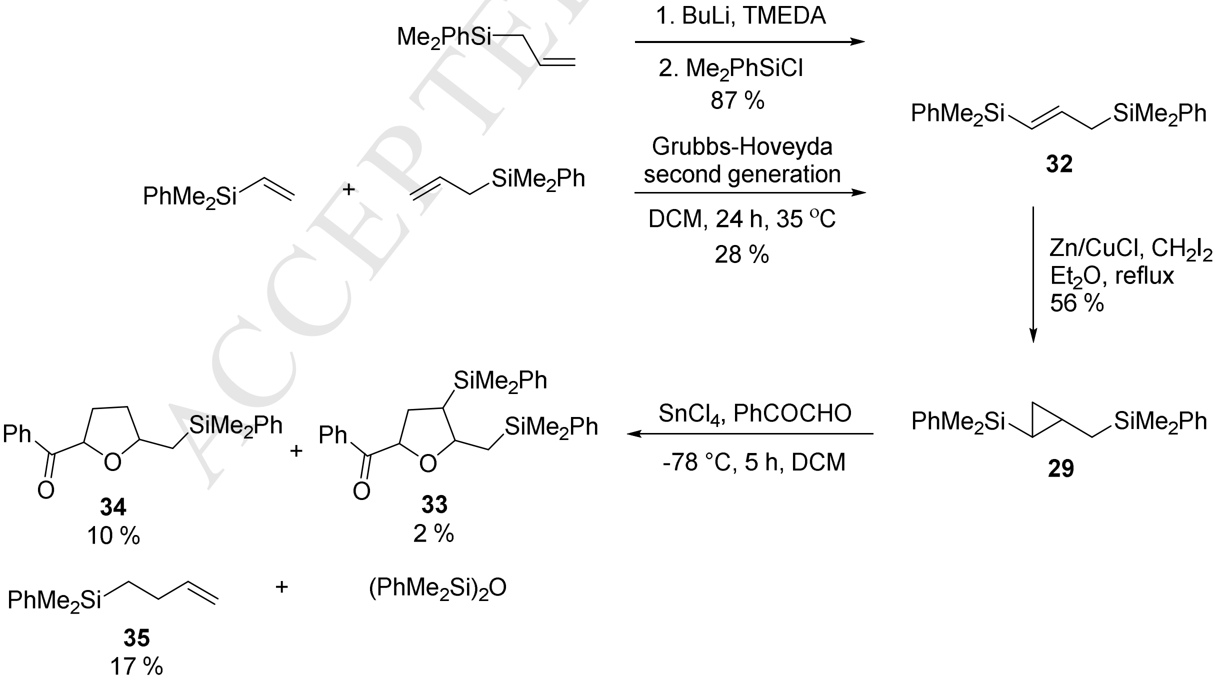


30



31

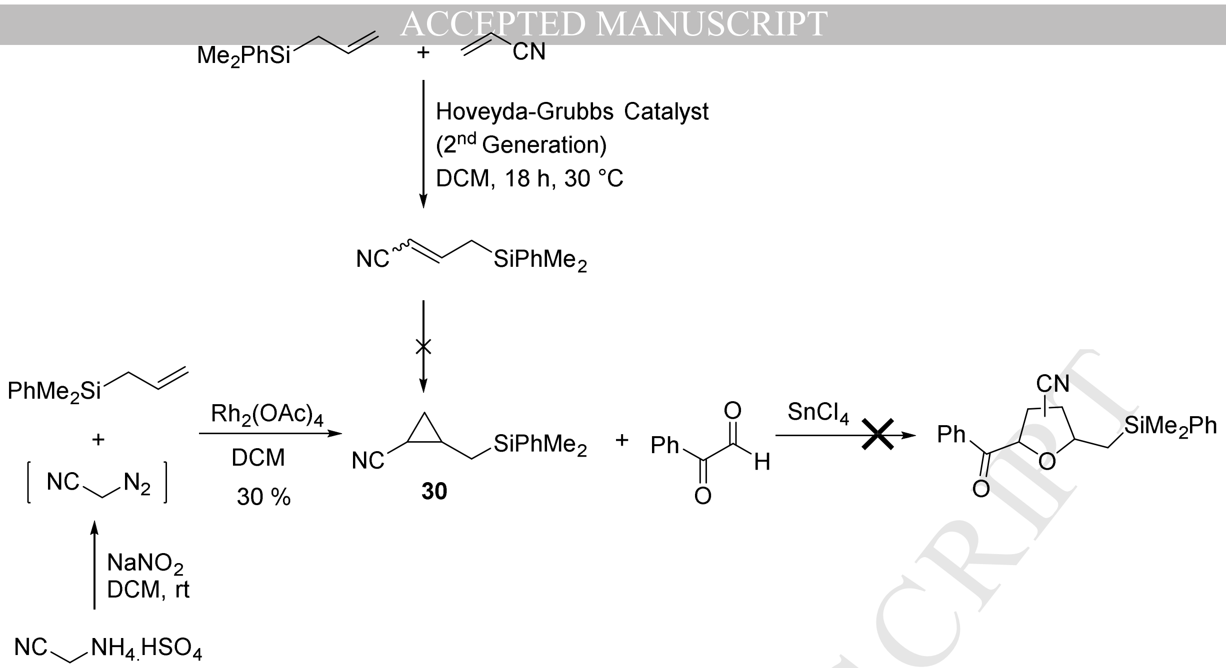
Using the method of Fleming, **32** was prepared as the *trans* isomer in 87% yield by the reaction of allyldimethylphenylsilane with *n*-butyllithium and quenching of the resultant anion with chlorodimethylphenylsilane.[39] It was also possible to prepare the same target *via* cross olefin metathesis using the second generation Grubbs-Hoveyda catalyst, although the yield was much lower. Simmons-Smith reaction, under the conditions reported above, gave the corresponding cyclopropane **29** in 56% yield (Scheme 11).



Scheme 11

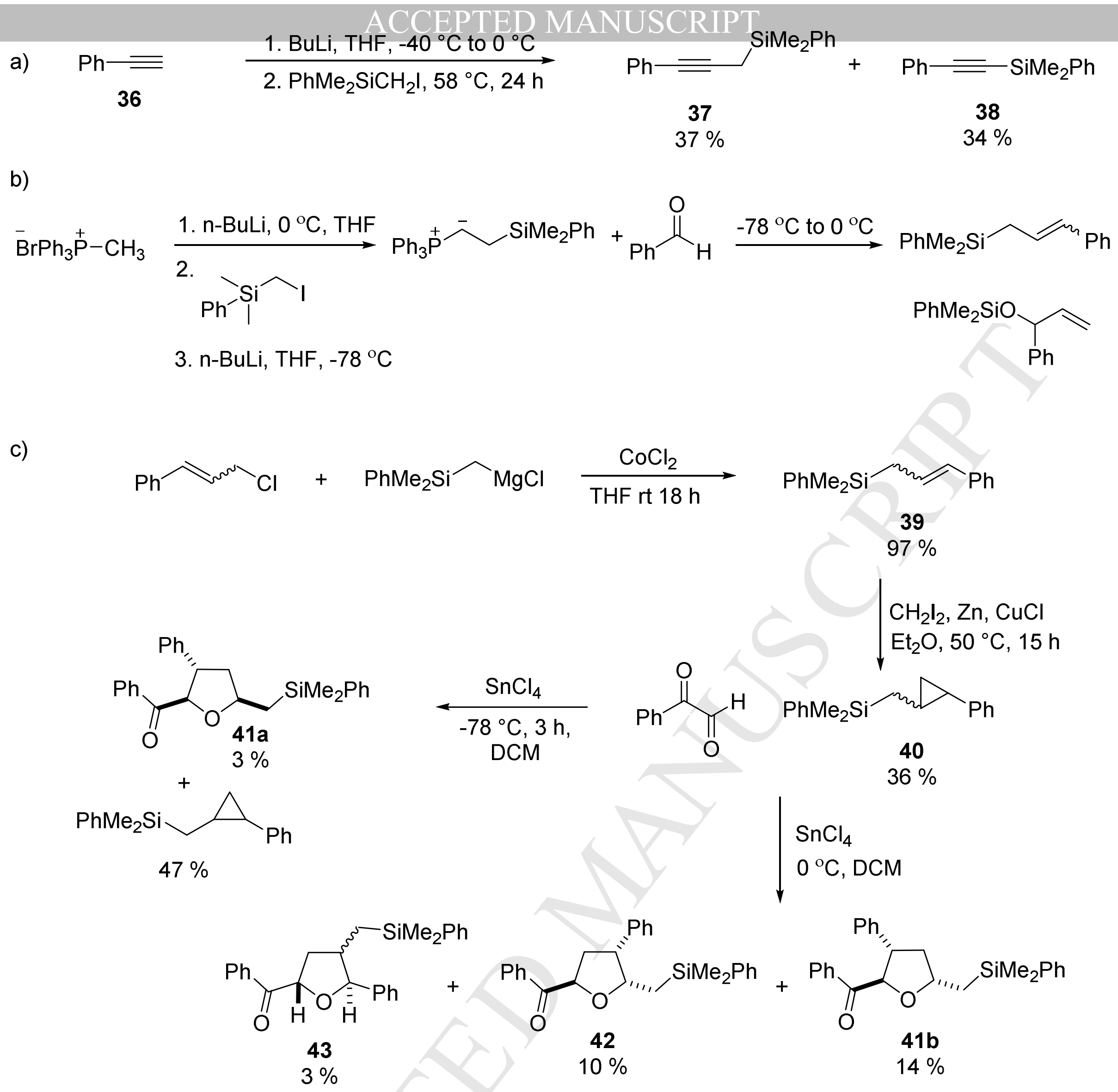
Under the reaction conditions developed above, at -78 °C, **29** gave a trace amount (2%) of the desired product **33**, together with a number of byproducts, which included 2,5-disubstituted THF **34** and homoallylic silane **35** but mainly unreacted starting material and disilylether. None of the desired product could be detected when the reaction was carried out at -78 °C and allowed to warm to 0 °C or when tin tetrachloride was added at 0 °C; the disilyl ether being the major product of reactions using these conditions. Disappointingly, the second silyl group appeared to make the cyclopropane more susceptible to decomposition with tin tetrachloride.

Attention was turned to 2-((dimethylphenyl)silylmethyl)cyclopropanecarbonitrile **30**. Several methods were attempted to prepare the pre-requisite alkene to this, including from a Wittig reaction of cyanomethylphosphonium chloride with *tert*-butyl(diphenyl)silylacetaldehyde (prepared in turn from *n*-butyllithium and tetravinyltin to form tetravinyl lithium *in situ* followed by the addition of *tert*-butylchlorodiphenylsilane to give the vinylsilane; epoxidation with *m*CPBA and Lewis acid catalysed rearrangement with $BF_3.OEt_2$ in THF to give the α-silyl-aldehyde, 21% over the 3 steps), which gave the alkene in only trace amounts, and as a mixture of *E/Z* isomers and second via cross metathesis of acrylonitrile and allylphenyldimethyl silane with the Grubbs-Hoveyda second generation catalyst, giving the alkene in 64% and an isomeric ratio of 3.4 : 1 (*trans*:*cis*; Scheme 12). However, all attempts at cyclopropanation failed, including the three conditions applied so successfully earlier (Table 2). An alternative Horner-Wadsworth-Emmons cyclopropanation reaction approach also failed to give **30**. Finally, the product was obtained *via* a rhodium-catalysed carbenoid insertion, using diazoacetonitrile and dimethylphenylallylsilane. No reaction was observed under either of the previously optimised conditions at -78 °C or 0 °C, with quantitative recovery of stating material. Even heating the reaction to reflux temperature for 48 h gave 60% recovered cyclopropane. The nitrile substituted cyclopropane was not only unreactive towards phenyl glyoxal using the previously developed conditions, but also substantially reduced the side reaction between silylmethylcyclopropane and tin tetrachloride. The Lewis basic nature of the nitrogen in the nitrile had been expected to coordinate to the Lewis acid making the ring opening a favourable process, but this was not observed. Thus nitriles would not appear to be good acceptors on cyclopropanes.



Scheme 12

Finally, we examined 2-phenyl-1-methyl-dimethylphenylsilylcyclopropane **31**. The prerequisite phenyl-substituted allylsilane could not be prepared by the reduction of the corresponding alkyne (Scheme 13a; deprotonation of phenylacetylene with *n*-butyllithium/quenching with iodomethyl(dimethylphenyl)silane gave a mixture of **37** and **38** which could not be separated[40]) or by a Wittig-based approach, which gave primarily the product of a Brook rearrangement (Scheme 13b).



Scheme 13

The cobalt-catalysed Heck-type reaction of alkenyl halides and silylmethyl Grignard reagents, as reported by Oshima, successfully gave the desired allylsilane **39** in 97%, as a 10:1 ratio of *trans:cis* isomers.[41] Cyclopropanation using the Simmons-Smith conditions gave the phenyl substituted cyclopropane (**40**, 36%). Cyclisation of **40** with phenyl glyoxal and tin tetrachloride at -78 °C, yielded a small amount of the tri-substituted THF (**41**, 3%), together with recovered starting material (47%). When the reaction was carried out at 0 °C, three tri-substituted THFs were isolated: **41 (**14%), **42** (10%) and **43** (3%) yields, along with unreacted cyclopropane, disilyl ether and polymerised aldehyde. All three THFs had different ^{1}H NMR spectra to the previously isolated tri-substituted THF. The structures of the two THFs obtained in greater quantity were determined, but unfortunately there was not enough material to determine absolutely the third one, although it is proposed to have the phenyl group at the C-5 position while the methylsilyl substituent is at the four position. The nOe data indicated a *trans* relationship between the C-2 and C-5 substituents while the data was ambiguous for the C-4 substituent. This minor product could only arise from the cyclopropane opening with the formation of the carbocation α- to the phenyl group instead of β- to the silyl group. This is slightly surprising as, although, the phenyl group can stabilise the positive charge though the π-system, the carbanion has no additional stabilising functionality. The low yield of this product shows that the intermediate is less stable than that with the carbocation β to the silicon atom.

CONCLUSIONS

In conclusion, we have reported a detailed study on the synthesis and reactions of donor-only substituent cyclopropanes and their uses in heterocycle synthesis. Further, we have also considered the reactions of a number of novel donor-acceptor cyclopropanes.

EXPERIMENTAL

General Methods

All reactions were carried out under an atmosphere of nitrogen or argon unless otherwise stated, using oven or flame-dried glassware and all transfers were performed using either plastic or glass syringes. Petroleum ether or petrol refers to the fraction of petroleum ether boiling between 40 °C and 60 °C. Anhydrous THF, diethyl ether, dichloromethane, toluene and DMF were purified using a MBRAUN MB SPS-800 solvent purification system; dichloromethane and 1,2-dichloroethane were freshly distilled over calcium hydride. Ethyl glyoxalate was distilled from commercially available 1:1 ethyl glyoxalate toluene solution according to the procedure reported by Evans *et al*.[30] Mechanically activated magnesium turnings were prepared by vigorous dry stirring with a Teflon-coated stirrer bar for 24 h under an atmosphere of nitrogen as reported in the literature. Flash column chromatography was carried out using silica gel (220-240 mesh) (Brockmann 2-3); samples were applied as a concentrated solution in an appropriate solvent. Thin layer chromatography (TLC) was performed on pre-coated aluminium backed plates with either Merck Kieselgel 60 F254 or Merck Aluminium Oxide 60 F254. Visualisation was either by ultraviolet light (λ = 254 nm) or by staining with acidified aqueous potassium permanganate solution followed by heating. Preparative layer chromatography was performed on pre-coated glass backed plates with Merck silica gel 60 F254 (thickness 1000 μm). Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Low resolution mass spectra were recorded on an Agilent 6890 Series GC System with a 5973 mass spectrometry detector. High and low resolution mass spectra were recorded on a Thermofisher LTQ Orbitrap XL, Finnigan MAT 95 XP, Thermofisher DSQ-II, Agilent 5975C Inert XL GC/MSD or Micromass Quattro II instrument (EPSRC Mass Spectrometry

Service, Swansea). Infrared spectra were recorded using either a Shimadzu FTIR-8300 spectrometer, with samples prepared as thin films between NaCl plates or on KBr disks, or on a Perkin Elmer Spectrum 65 FT-IR spectrometer with universal ATR sampling accessory. FTIR spectra were recorded in the range of 600-4000 cm^{-1} and only selected absorbances (ν_{max}) are reported. Elemental analyses (CHN) were obtained using an Exeter Analytical EA44 analyser from the micro analysis service at University College London. X-ray crystal structures were obtained at QMUL using a KAPPA APEX ii DUO diffractometer with dual Cu and Mo Sources and APEX ii CCD area detector. NMR spectra were recorded on one of the following spectrometers: a JEOL JNM-EX270 operating at 270 MHz (^{1}H), 67.8 MHz (^{13}C) and 109.3 MHz (^{31}P); a Bruker AMX-400 operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) fitted with a variable temperature probe controlled by a Bruker B-VT-2000 controller; a Bruker Avance 400 operating at 400 MHz (^{1}H), 100 MHz (^{13}C), 162 MHz (^{31}P) and 149.2 MHz (^{119}Sn); a Bruker Avance III operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) or a Bruker AV600 operating at 600 MHz (^{1}H) and 150 MHz (^{13}C). Chemical shift values (δ_H and δ_C) are reported as values in parts per million (ppm) relative to either tetramethylsilane or the residual protic solvent as the internal standard reference for ^{1}H NMR spectra and from the solvent peaks for ^{13}C NMR using values from the literature. Coupling constants (*J* values) are quoted to one decimal place with values in hertz and are quoted twice where possible, each being recorded as observed in the spectrum without averaging. Multiplets are reported over the range at which they appear. ^{1}H NMR data is presented in the form δ_H (integration, multiplicity, coupling constants, assignment). The multiplicity of the signal is designated by the following abbreviations: s-singlet, d-doublet, t-triplet, q-quartet, and m-multiplet. The abbreviation br refers to a broad signal and app refers to apparent. ^{13}C NMR spectra are recorded in the form δ_C (assignment) or (multiplicity, coupling constants, assignment) where appropriate.

Notes

A number of the unsuccessful reactions, together with tables listing the outcomes of all screening and optimisation reactions are included in the Supporting Information.[28]

General Procedure A - Preparation of allylsilanes

A solution of chlorosilane (1 eq.) in anhydrous THF (0.3 mL/mmol) was added cautiously to a stirred solution of allylmagnesium chloride (1.4 eq., 2 M solution in THF) at room temperature under an atmosphere of argon and the resulting mixture stirred at 55 °C for 15 h. The mixture was cooled to 0 °C, quenched with 10% *w*/*v* aqueous ammonium chloride solution (1.5 mL/mmol), warmed to room temperature and partitioned between water and diethyl ether. The organic phase was separated and the aqueous phase extracted with diethyl ether. The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The products were purified by flash column chromatography.

Allyltriethylsilane (Table 1 Entry 1)

To a stirred suspension of magnesium turnings (1.82 g, 75.0 mmol) in anhydrous diethyl ether (50 mL) under an atmosphere of argon was added several crystals of iodine, upon which the solution turned brown. After 10 min the solution became clear and allylbromide (8.47 g, 6.10 mL, 70.0 mmol) was cautiously added dropwise at a rate sufficient to maintain gentle reflux during the addition. The mixture was stirred for a further 30 min before chlorotriethylsilane (4.06 g, 4.53 mL, 27.0 mmol) was added dropwise at a rate sufficient to maintain gentle reflux. The mixture was heated to reflux temperature for 15 h. After this time, the reaction mixture was cooled to approximately −15 °C and a 10% *w*/*v* aqueous ammonium chloride solution (90 mL) was added dropwise with efficient stirring over a period of 30 min. Two layers developed and the organic phase was separated. The aqueous phase was extracted with diethyl ether (3 × 20 mL) and the combined organic portions were washed with brine (20 mL), separated, dried ($MgSO_4$) and filtered. The diethyl ether and allylbromide were removed by distillation at atmospheric pressure. Purification of the resulting residue by either Kugelrohr distillation or flash column chromatography [silica gel, hexane] gave the desired product (3.78 g, 24.2 mmol, 90%) as a colourless oil; bp 81-83 °C/35 mmHg, (lit.[42] 37 °C/3 mmHg); R_f 0.75 [hexane]; ν_{max}(film)/cm^{-1} 2953, 2875, 1630 (C=C), 1416, 1237, 1153, 1011, 891; δ_H (400 MHz; $CDCl_3$) 0.54 (6H, q, *J* 8.0, 3 × CH_2), 0.94 (9H, t, *J* 8.0, 3 × CH_3), 1.54 (2H, dt, *J* 8.2 and 1.2, $\mathrm{C\underline{H}_2CH{=}CH_2}$), 4.81 (1H, ddt, *J* 10.1 2.2 and 0.9, $\mathrm{CH_2CH{=}C\underline{H}_{\mathit{cis}}H_{\mathit{trans}}}$), 4.87 (1H, ddt, *J* 16.9 2.2 and 1.4, $\mathrm{CH_2CH{=}CH_{\mathit{cis}}\underline{H}_{\mathit{trans}}}$), 5.81 (1H, ddt, *J* 16.9 10.1 and 8.2, $\mathrm{CH_2C\underline{H}{=}CH_{\mathit{cis}}H_{\mathit{trans}}}$); δ_C (100.6 MHz; $CDCl_3$) 3.3 (3 × CH_2), 7.5 (3 × CH_3), 19.6 ($\mathrm{\underline{C}H_2CH{=}CH_2}$), 112.6 ($\mathrm{CH_2CH{=}\underline{C}H_2}$), 135.6 ($\mathrm{CH_2\underline{C}H{=}CH_2}$); LRMS (EI$^+$, *m/z*) 156 ([M]$^+$, 4%), 127 (4), 115 (87), 99 (31), 87 (100), 57 (38); HRMS (EI$^+$, *m/z*) 156.1329 [M]$^+$, $C_9H_{20}Si$ requires 156.1329. The data is in good agreement with previously reported values.[43]

Allyltri-*n*-butylsilane (Table 1 entry 2)

Following the general procedure A, chlorotributylsilane (4.93 g, 21.0 mmol) furnished the impure product (4.96 g) as a colourless oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (4.45 g, 18.5 mmol, 88%) as a colourless oil; R_f 0.82 [hexane]; ν_{max}(film)/cm^{-1} 2956, 2918, 1630 (C=C), 1195, 890; δ_H (400 MHz; $CDCl_3$) 0.50-0.54 (6H, m, 3 × CH_2 $SiCH_2$), 0.89 (9H, t, *J* 7.0, 3 × CH_3), 1.22-1.37 (12H, m, 6 × CH_2), 1.53 (2H, d, *J* 8.2, $\mathrm{C\underline{H}_2CH{=}CH_2}$), 4.80 (1H, dd, *J* 10.1 and 2.2, $\mathrm{CH{=}C\underline{H}_{\mathit{cis}}H_{\mathit{trans}}}$), 4.84 (1H, dd, *J* 16.9 and 2.2, $\mathrm{CH{=}CH_{\mathit{cis}}\underline{H}_{\mathit{trans}}}$), 5.79 (1H, ddt, *J* 16.9 10.1 and 8.2, $\mathrm{CH_2C\underline{H}{=}CH_{\mathit{cis}}H_{\mathit{trans}}}$); δ_C (100.6 MHz; $CDCl_3$)

12.0 (3 × CH_2, $SiCH_2$), 14.0 (3 × CH_3, Bu), 20.7 ($\underline{C}H_2CH=CH_2$), 26.2 (3 × CH_2, Bu), 26.9 (3 × CH_2, Bu), 112.6 ($CH_2CH=\underline{C}H_2$), 135.7 ($CH_2\underline{C}H=CH_2$); LRMS (EI^+, *m/z*) 199 ($[M-Allyl]^+$, 72%), 143 (100), 127 (28), 101 (18), 87 (15); HRMS (EI^+, *m/z*) 239.2190 $[M]^+$, $C_{15}H_{32}Si$ requires 239.2189.

Allyltriisopropylsilane (Table 1 entry 3)

Following the general procedure A, chlorotriisopropylsilane (6.75, 7.92 mL, 35.0 mmol) furnished the impure product (7.17 g) as a pale yellow oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (6.52 g, 32.8 mmol, 94%) as a colourless oil; R_f 0.79 [hexane]; bp 74-79 °C/0.4 mmHg, (lit.[44] 45-50 °C/0.2 mmHg); δ_H (400 MHz; $CDCl_3$) 0.97-1.11 (21H, m, overlapping doublet and septet 3 × ^{i}Pr), 1.64 (2H, dt, *J* 8.2 and 1.2, $C\underline{H}_2CH=CH_2$), 4.81 (1H, ddt, *J* 10.0 2.2 and 1.2, $CH_2CH=C\underline{H}_{cis}H_{trans}$), 4.92 (1H, ddt, *J* 16.9 2.2 and 1.2, $CH_2CH=CH_{cis}\underline{H}_{trans}$), 5.89 (1H, ddt, *J* 16.9 10.0 and 8.2, $CH_2C\underline{H}=CH_2$); δ_C (100.6 MHz; $CDCl_3$) 11.2 (3 × CH, ^{i}Pr), 17.5 ($SiCH_2$), 18.8 (6 × CH_3), 112.9 ($CH_2CH=\underline{C}H_2$), 136.3 ($CH_2\underline{C}H=CH_2$); LRMS (EI^+, *m/z*) 198 ($[M]^+$, 3%), 157 (100), 115 (60), 85 (52). The data is in good agreement with previously reported values.[44]

Allyldiphenylmethylsilane (Table 1 entry 4)

Dimethyl(iodomethyl)phenylsilane was prepared based on the procedure reported by Soderquist *et al*.[29] To a mixture of mechanically activated magnesium turnings (0.36 g, 15.0 mmol) and chloromethyldiphenylsilane (2.79 g, 2.53 mL, 12.0 mmol) in THF (15 mL) was added dropwise allylbromide (1.45 g, 1.01 mL, 12.0 mmol) at a rate to maintain gentle reflux. After being stirred at 25 °C for 15 h, the reaction mixture was poured onto ice. The aqueous layer was extracted with diethyl ether (2 × 20 mL) and the combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford a pale yellow oil (2.90 g). Purification by either Kugelrohr distillation or flash column chromatography [silica gel, hexane] gave the desired product (1.68 g, 7.05 mmol, 59%) as a colourless oil; bp 115-119 °C/1 mmHg, (lit.[45] 93 °C/0.1 mmHg); R_f 0.23 [hexane]; ν_{max}(film)/cm^{-1} 3069, 2953, 2875, 1629 (C=C), 1427, 1251, 1112, 895; δ_H (400 MHz; $CDCl_3$) 0.59 (3H, s, $SiC\underline{H}_3$), 2.12 (2H, dt, *J* 8.0 and 1.1, $C\underline{H}_2CH=CH_2$), 4.89-4.97 (2H, m, overlapping signals $CH_2CH=C\underline{H}_2$), 5.83 (1H, ddt, *J* 17.0 10.1 and 8.0, $CH_2C\underline{H}=CH_2$), 7.36-7.43 (6H, m, Ar), 7.54-757 (4H, m, Ar); δ_C (100 MHz; $CDCl_3$) −4.7 (2 × CH_3), 22.3 ($\underline{C}H_2CH=CH_2$), 114.2 ($CH_2CH=\underline{C}H_2$), 128.0 (4 × *m*-CH, Ar), 129.4 (2 × *p*-CH, Ar), 134.2 ($CH_2\underline{C}H=CH_2$), 134.7 (4 × *o*-CH, Ar), 136.7 (2 × C, Ar); LRMS (EI^+, *m/z*) 238 ($[M]^+$, 2%), 223 (3), 197 (100), 181 (19), 165 (20), 119 (10), 105 (27); HRMS (EI^+, *m/z*) 238.1170 $[M]^+$, $C_{16}H_{18}Si$ requires 238.1172. The data is in good agreement with previously reported values.[45]

Allyl-*tert*-butyldiphenylsilane (Table 1 entry 5)

Following the general procedure A, *tert*-butyldiphenylchlorosilane (7.15 g, 6.76 mL, 26.0 mmol) furnished the impure product (7.02 g) as a pale yellow oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (6.67 g, 23.8 mmol, 92%) as a colourless oil; R_f 0.42 [hexane]; ν_{max}(film)/cm^{-1} 2929, 2857, 1630 (C=C), 1427, 1104, 895, 820; δ_H (400 MHz; $CDCl_3$) 1.09 (9H, s, ^{t}Bu), 2.21(2H, dt, *J* 7.8 and 1.2, $C\underline{H}_2CH=CH_2$), 4.82 (1H, ddt, *J* 10.0 2.0 and 1.2, $CH_2CH=C\underline{H}_{cis}H_{trans}$), 4.92 (1H, ddt, *J* 16.9 2.0 and 1.2, $CH_2CH=CH_{cis}\underline{H}_{trans}$), 5.79 (1H, ddt, *J* 16.9 10.0 and 7.8, $CH_2C\underline{H}=CH_{cis}H_{trans}$), 7.35-7.44 (6H, m, Ar), 7.62-7.64 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 18.6 ($Si\underline{C}(CH_3)_3$), 18.9 ($\underline{C}H_2CH=CH_2$), 28.0 ($SiC(\underline{C}H_3)_3$), 114.7 ($CH_2CH=\underline{C}H_2$), 127.7 (4 × *m*-CH, Ar), 129.2 (2 × *p*-CH, Ar), 134.6 (2 × C, Ar), 134.8 ($CH_2\underline{C}H=CH_2$), 136.16 (4 × *o*-CH, Ar); LRMS (EI$^+$, *m/z*) 280 ([M]$^+$, 1%), 239 (71), 223 (100), 197 (52), 181 (36), 135 (100), 105 (40); HRMS (EI$^+$, *m/z*) 280.1643 [M]$^+$, $C_{19}H_{24}Si$ requires 280.1642. The data is in good agreement with previously reported values, where reported.[46]

Allyldimethylphenylsilane (Table 1 entry 6)

Following the general procedure A, chlorodimethylphenylsilane (4.27 g, 5.01 mL, 25.0 mmol) furnished the impure product (5.22 g) as a pale yellow oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (3.79 g, 21.5 mmol, 86%) as a colourless oil; R_f 0.49 [hexane]; bp 44-45 °C/0.07 mmHg, (lit.[29] 96-97 °C 14 mmHg); ν_{max}(film)/cm^{-1} 3071, 2956, 1630 (C=C), 1427, 1248, 1195, 890; δ_H (400 MHz; $CDCl_3$) 0.30 (6H, s, $SiMe_2$), 1.77 (2H, dt, *J* 8.1 and 1.0, $C\underline{H}_2CH=CH_2$), 4.86 (1H, ddt, *J* 10.1 2.1 and 1.0, $CH_2CH=C\underline{H}_{cis}H_{trans}$), 4.87 (1H, ddt, *J* 16.9 2.1 and 1.0, $CH_2CH=CH_{cis}\underline{H}_{trans}$), 5.79 (1H, ddt, *J* 16.9 10.1 and 8.1, $CH_2C\underline{H}=CH_2$), 7.35-7.38 (3H, m, Ph), 7.52-7.54 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −3.3 (3 × CH_3), 23.8 ($\underline{C}H_2CH=CH_2$), 113.6 ($CH_2CH=\underline{C}H_2$), 127.9 (2 × *m*-CH, Ph), 129.1 (*p*-CH, Ph), 133.8 (2 × *o*-CH, Ph), 134.8 ($CH_2\underline{C}H=CH_2$), 138.8 (C, Ph); LRMS (EI$^+$, *m/z*) 176 ([M]$^+$, 7%), 161 (6), 135 (100), 119 (11), 105 (15), 91 (7); HRMS (EI$^+$, *m/z*) 176.1017 [M]$^+$, $C_{11}H_{16}Si$ requires 176.1016. The data is in good agreement with previously reported values, where reported.[29]

General Procedure B - Preparation of (cyclopropylmethyl)silanes (Simmons-Smith reaction)

To a stirred suspension of zinc powder (5 eq.) and copper chloride (5 eq.) in anhydrous diethyl ether (5 mL/mmol), which had been heated at reflux temperature for 30 min and allowed to cool to room temperature, was added allylsilane (1 eq.) and diiodomethane (2 eq.). The reaction was heated at reflux temperature for 15 h, cooled to room temperature and filtered through celite washing with diethyl ether (2 mL/mmol). The filtrate was washed with 1 M HCl followed by 10% *w*/*v* sodium bicarbonate solution until pH 7. The combined aqueous layers were extracted with diethyl ether and the combined organic layers were washed with brine, 10% *w*/*v* sodium thiosulfate solution, separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product. Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica (1:3) eluting with hexane gave the desired product.

[Preparation of silver nitrate impregnated silica gel: Silver nitrate (3 g) and methanol (300 mL) was stirred vigorously until the all the solid had dissolved. To this solution was added silica gel (30 g) and the resulting mixture stirred for 5 min. The slurry was then transferred to a round bottom flask covered with silver foil and the solvent removed *in vacuo* to give the impregnated silica gel as a bright white powder/gel. The column was made by pre-forming a slurry of silica gel (50 g) in hexane. Once this had settled the silver nitrate impregnated silica gel was added as a slurry in hexane creating a band of silver nitrate impregnated silica at the top of the column. The column was washed with three column lengths of hexane to wash through any residual methanol and run in the usual way.]

(Cyclopropylmethyl)triethylsilane (Table 3 entry 1)

Following the general procedure B, allytriethylsilane (3.78 g, 24.0 mmol) furnished the impure product as a brown oil (2.90 g). Purification by flash column using 10% silver nitrate impregnated silica and standard silica eluting with hexane gave desired product (1.61 g, 9.45 mmol, 40%) as a colourless oil; R_f 0.81 [hexane]; ν_{max}(film)/cm^{-1} 3071 (CH cyclopropyl), 2952, 2875, 1457, 1416, 1239, 1013, 891; δ_H (400 MHz; $CDCl_3$) −0.06 to −0.02 (2H, m, CH_2 cyclopropyl), 0.41-0.45 (2H, m, CH_2 cyclopropyl), 0.49 (2H, d, *J* 6.9, 3 × CH_2), 0.56 (6H, q, *J* 8.0, 3 × $C\underline{H_2}CH_3$), 0.54-0.61 (1H, m, CH cyclopropyl); 0.95 (9H, t, *J* 8.0, 3 × CH_3); δ_C (100.6 MHz; $CDCl_3$) 3.7 (3 × CH_2), 6.3 (CH), 6.9 (2 × CH_2 cyclopropyl), 7.6 (3 × CH_3), 17.3 ($SiCH_2$); LRMS (EI$^+$, *m/z*) 170 ([M]$^+$ 1%), 141 (34),115 (61), 87 (100), 59 (35); HRMS (EI$^+$, *m/z*) 170.1483 [M]$^+$, $C_{10}H_{22}Si$ requires 170.1485.

(Cyclopropylmethyl)tri-*n*-butylsilane (Table 3 entry 2)

Following the general procedure B, allyltri-*n*-butylsilane (3.78 g, 16.5 mmol) furnished the impure product as a colourless oil (3.78 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (2.73 g, 10.7 mmol, 65%) as a colourless oil; R_f 0.93 [hexane]; ν_{max}(film)/cm^{-1} 2918, 1463, 1197 (Si-C), 1081, 886 (Si-C); δ_H (600 MHz; $CDCl_3$) −0.06 to −0.03 (2H, m, CH_2 cyclopropyl), 0.42-0.45 (2H, m, CH_2 cyclopropyl), 0.49 (2H, d, *J* 7.0, $SiC\underline{H_2}CH$), 0.54-0.63 (7H, m, $SiCH_2C\underline{H}$ and 3 × CH_2 overlapping signals), 0.89 (9H, t, *J* 7.0, 3 × $C\underline{H_3}$), 1.26-1.36 (12H, m, 6 × $C\underline{H_2}$ Bu); δ_C (100.6 MHz; $CDCl_3$) 6.4 (CH cyclopropyl), 6.9 (2 × CH_2 cyclopropyl), 12.5 (3 × CH_2, Bu), 14.0 (3 × CH_3), 18.3 ($Si\underline{C}H_2CH$), 26.4 (3 × CH_2), 27.1 (3 × CH_2); LRMS (EI$^+$, *m/z*) 199 ([M−C_4H_7]$^+$, 45%), 143 (100), 101 (29), 87 (22), 59 (29); HRMS (EI$^+$, *m/z*) 253.2348 [M−H]$^+$, $C_{16}H_{33}Si$ requires 253.2346.

(Cyclopropylmethyl)triisopropylsilane (Table 3 entry 3)

Following the general procedure B, allyltriisopropylsilane (5.77 g, 21.0 mmol) furnished the impure product as a yellow oil (5.04 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (3.45 g, 16.2 mmol, 77%) as a colourless oil; R_f 0.88 [hexane]; ν_{max}(film)/cm^{-1} 3074 (C-H cyclopropyl), 2941 (C-H), 1464, 1015, 881 (Si-C); δ_H (400 MHz; CDCl$_3$) 0.00-0.03 (2H, m, CH$_2$ cyclopropyl), 0.46-0.49 (2H, m, CH$_2$ cyclopropyl), 0.58 (2H, d, *J* 6.5, SiC$\underline{H}_2$CH), 0.61-0.71 (1H, m, SiCH$_2$C$\underline{H}$), 1.04-1.12 (21H, m, overlapping signals 6 × CH$_3$ and 3 × CH, ^{i}Pr); δ_C (100.6 MHz; CDCl$_3$) 6.6 (CH cyclopropyl), 8.0 (2 × CH$_2$ cyclopropyl), 11.1 (3 × CH, ^{i}Pr), 15.1 (Si$\underline{C}$H$_2$CH), 19.0 (6 × CH$_3$); LRMS (EI$^+$, *m/z*) M$^+$ not visible, 169 ([M−^{i}Pr]$^+$, 13%), 157 (80), 127 (88), 115 (100), 99 (56), 87 (58), 73 (78), 59 (81); HRMS (EI$^+$, *m/z*) 213.2034 [M+H]$^+$, $C_{13}H_{29}Si$ requires 213.2033.

(Cyclopropylmethyl)dimethylphenylsilane (Table 3 entry 4)

Following the general procedure B, allyldimethylphenylsilane (3.88 g, 22.0 mmol) furnished the impure product as a yellow oil (3.24 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (2.79 g, 14.7 mmol, 67%) as a colourless oil; R_f 0.53 [hexane]; ν_{max}(film)/cm^{-1} 3070 (C-H cyclopropyl), 2956, 1426, 1247, 1113, 835; δ_H (400 MHz; CDCl$_3$) −0.03-0.01 (2H, m, CH$_2$ cyclopropyl), 0.34 (6H, s, 2 × CH$_3$), 0.43-0.47 (2H, m, CH$_2$ cyclopropyl), 0.61-0.71 (1H, m, SiCH$_2$C$\underline{H}$), 0.75 (2H, d, *J* 6.9, SiC$\underline{H}_2$CH),7.36-7.39 (3H, m, Ph), 7.54-7.58 (2H, m, Ph); δ_C (100.6 MHz; CDCl$_3$) −2.6 (2 × CH$_3$), 6.3 (CH cyclopropyl), 6.6 (2 × CH$_2$ cyclopropyl), 21.4 (Si$\underline{C}$H$_2$), 127.8 (2 × *m*-CH, Ph), 128.9 (*p*-CH, Ph), 133.7 (2 × *o*-CH, Ph), 139.9 (C, Ph); LRMS (EI$^+$, *m/z*) 190 ([M]$^+$, 2%), 175 (9), 135 (100), 105 (12); HRMS (EI$^+$, *m/z*) 190.1173 [M]$^+$, $C_{12}H_{18}Si$ requires 190.1172.

(Cyclopropylmethyl)(methyl)diphenylsilane (Table 3 entry 5)

Following the general procedure B, allyl(methyl)diphenylsilane (4.32 g, 18.0 mmol) furnished the impure product as a yellow oil (3.94 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (3.21 g, 12.7 mmol, 71%) as a colourless oil; R_f 0.32 [hexane]; ν_{max}(film)/cm^{-1} 3069 (C-H cyclopropyl), 2998 (CH$_3$), 1427, 1250, 1108, 802, 727, 697; δ_H (400 MHz; CDCl$_3$) 0.01-0.05 (2H, m, CH$_2$ cyclopropyl), 0.43-0.47 (2H, m, CH$_2$ cyclopropyl), 0.65 (3H, s, SiMe), 0.68-0.77 (1H, m, CH cyclopropyl), 1.09 (2H, d, *J* 7.0, $\mathrm{SiC\underline{H}_2}$), 7.35-7.42 (6H, m, Ar), 7.54-7.60 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −4.0 ($SiMe_2$), 6.2 (CH cyclopropyl), 6.9 (2 × CH_2 cyclopropyl), 20.0 ($\mathrm{Si\underline{C}H_2}$), 127.9 (4 × *m*-CH, Ar), 129.2 (2 × *p*-CH, Ar), 134.7 (4 × *o*-CH, Ar), 137.7 (2 × C, Ar); LRMS (EI^+, *m/z*) 252 ($[M]^+$, 8%), 237 (4), 224 (13), 197 (100), 181 (13), 165 (11), 105 (20); HRMS (EI^+, *m/z*) 252.1329 $[M]^+$, $C_{17}H_{20}Si$ requires 252.1329.

(Cyclopropylmethyl)-*tert*-butyldiphenylsilane (Table 3 entry 6)

Following the general procedure B, allyl-*tert*-butyldiphenylsilane (3.50 g, 12.5 mmol) furnished the impure product as a colourless oil (3.65 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (2.16 g, 7.33 mmol, 59%) as a colourless oil; R_f 0.62 [hexane]; ν_{max}(film)/cm^{-1} 3072, 2929, 2856, 1427, 1103, 818; δ_H (600 MHz; $CDCl_3$) 0.08-0.12 (2H, m, CH_2 cyclopropyl), 0.45-0.49 (2H, m, CH_2 cyclopropyl), 0.76-0.86 (1H, m, CH cyclopropyl), 1.21 (9H, s, 3 × CH_3), 1.31 (2H, d, *J* 6.6, $\mathrm{SiC\underline{H}_2CH}$), 7.44-7.54 (6H, m, Ar), 7.79-7.81 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 6.6 (CH cyclopropyl), 7.9 (2 × CH_2 cyclopropyl), 16.7 ($\mathrm{Si\underline{C}H_2CH}$), 18.2 ($\mathrm{Si\underline{C}(CH_3)_3}$), 28.1 (3 × CH_3), 127.6 (4 × *m*-CH, Ar), 129.1 (2 × *p*-CH, Ar), 135.5 (2 × C, Ar), 136.3 (4 × *o*-CH, Ar); LRMS (EI^+, *m/z*) M^+ not visible, 237 ($[M-{}^tBu]^+$, 100%), 197 (54), 183 (100), 159 (62), 135 (100), 105 (44); HRMS (CI^+, *m/z*) 312.2141 $[M+NH_4]^+$, $C_{20}H_{30}NSi$ requires 312.2142.

General Procedure C - Cyclisation of silylmethylcyclopropanes with α-keto-aldehydes

To a stirred mixture of freshly distilled glyoxal or glyoxalate (1.5 eq.) and silylmethylcyclopropane (1 eq.) in anhydrous dichloromethane (9 mL/mmol of silylmethylcyclopropane) cooled to the required temperature (−78 or 0 °C) and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.8 eq.) in anhydrous dichloromethane (3 mL/mmol of tin tetrachloride). The reaction was stirred at the required temperature and monitored by TLC, after 3 h the reaction was quenched by the addition of wet acetone (1 mL/mmol of silylmethylcyclopropane) if the reaction was performed at −78 °C or water (1 mL/mmol of silylmethylcyclopropane) if the reaction was at 0 °C. The organic layer was separated and the aqueous layer further extracted with dichloromethane. The combined organic phases were washed with brine, separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a yellow oil. The products were purified by flash column chromatography.

(±)-Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanone (Table 5 entry 1)

Following the general procedure C, (cyclopropylmethyl)tri*iso*propylsilane (0.13 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at −78 °C furnished the impure product (0.27 g) as a yellow oil.

Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.14 g, 0.40 mmol, 67%, *dr* (*trans* : *cis*) 1 : 1.6) as a colourless oil; R_f 0.63 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2947 (C-H), 1690 (C=O), 1430 (C-H), 1230 (Si-C), 1115 (C-O), 885; *cis* diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.93-1.05 (22H, m, overlapping signals $Si(C\underline{H}(C\underline{H}_3)_2)_3$ and $SiC\underline{H}_aH_b$), 1.23 (1H, dd, *J* 12.5 and 6.6, $SiCH_a\underline{H}_b$), 1.46-1.63 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 2.05-2.38 (3H, m, overlapping signals CH$_2$ C-4 and $CH_a\underline{H}_b$ C-3 THF), 4.19-4.29 (1H, m, CH C-2 THF), 5.13 (1H, dd, *J* 8.7 and 5.0, CH C-5 THF), 7.42-7.57 (3H, m, Ph), 7.98-8.02 (2H, m, Ph); δ_C (100.6 MHz; CDCl$_3$) 11.4 (SiCH, ^{i}Pr), 16.8 (SiCH$_2$), 18.9 (6 × CH$_3$, ^{i}Pr), 29.2 (CH$_2$, C-4 THF), 34.4 (CH$_2$, C-3 THF), 79.8 (CH, C-2 THF), 79.8 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 198.3 (C=O); *trans* diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.96 (1H, dd, *J* 14.4 and 7.5, $SiC\underline{H}_aH_b$), 1.02-1.04 (21H, m, overlapping signals 3 × CH and 6 × CH$_3$), 1.20 (1H, dd, *J* 14.4 and 6.6, $SiCH_a\underline{H}_b$), 1.53-1.64 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 2.09-2.23 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 2.27-2.37 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.23-4.30 (1H, m, CH C-2 THF), 5.31 (1H, dd, *J* 8.3 and 6.1, CH C-5 THF), 7.45 (2H, app t, *J* 7.7, 2 × *m*-CH, Ph), 7.55 (1H, app tt, *J* 7.4 and 1.4, *p*-CH, Ph), 7.99 (2H, app dd, *J* 8.3 and 1.4, 2 × *o*-CH, Ph); δ_C (100.6 MHz; CDCl$_3$) 11.4 (3 × CH, ^{i}pr), 16.9 (SiCH$_2$), 19.0 (6 × CH$_3$, ^{i}Pr), 29.3 (CH$_2$, C-4 THF), 35.1 (CH$_2$, C-3 THF), 78.7 (CH, C-2 THF), 79.3 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 303 ([M−^{i}Pr]$^+$, 14%), 261 (100), 241 (7), 157 (22), 105 (30), 77 (22); HRMS (CI$^+$, *m/z*) 347.2405 [M+H]$^+$, $C_{21}H_{35}O_2Si$ requires 347.2401. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.13 *cis* and 5.30 *trans*.

(±)-(Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanone (Table 5 entry 2)

Following the general procedure C, (cyclopropylmethyl)tri*iso*propylsilane (0.13 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at 0 °C furnished the impure product (0.25 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.18 g, 0.51 mmol, 85%) as a colourless oil; R_f 0.63 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2947 (C-H), 1690 (C=O), 1430 (C-H), 1230 (Si-C), 1115 (C-O), 885; *trans*-diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.96 (1H, dd, *J* 14.4 and 7.5, $SiC\underline{H}_aH_b$), 1.02-1.04 (21 H, m, overlapping signals 3 × CH and 6 × CH$_3$), 1.20 (1H, dd, *J* 14.4 and 6.6, $SiCH_a\underline{H}_b$), 1.53-1.64 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 2.09-2.23 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 2.27-2.37 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.23-4.30 (1H, m, CH C-2 THF), 5.31 (1H, dd, *J* 8.26 and 6.1, CH C-5 THF), 7.45 (2H, app t, *J* 7.7, 2 × *m*-CH Ph), 7.55 (1H, app tt, *J* 7.4 and 1.4, *p*-CH Ph), 7.99 (2H, dd, *J* 8.3 and 1.4, 2 × *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH, ^{i}Pr), 16.9 ($SiCH_2$), 19.0 (6 × CH_3, ^{i}Pr), 29.3 (CH_2, C-4 THF), 35.1 (CH_2, C-3 THF), 78.7 (CH, C-2 THF), 79.3 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 303 ([M−^{i}Pr]$^+$, 14%), 261 (100), 241 (7), 157 (22), 105 (30), 77 (22); HRMS (CI$^+$, *m/z*) 347.2405 [M+H]$^+$, $C_{21}H_{35}O_2Si$ requires 347.2401.

(±)-2,2-Dimethyl-1-(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)propan-1-one (Table 5 entry 3)

To a stirred solution of freshly distilled *tert*-butyl glyoxal (0.17 g, 1.50 mmol) in anhydrous DCM (2 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at 0 °C for 5 min followed by the dropwise addition of a solution of (cyclopropylmethyl)tri*iso*propylsilane (0.13 g, 0.60 mmol) in anhydrous DCM (3 mL). Stirring was continued at 0 °C for 3.5 h and the reaction was monitored by TLC. After this time the reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.12 g) as a colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.01 g, 0.03 mmol, 5%) as a colourless oil; R_f 0.67 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2942 (C-H), 2866 (C-H), 1716 (C=O), 1464, 1059, 883 (Si-C); δ_H (400 MHz; $CDCl_3$); 0.90 (1H, dd, *J* 14.4 and 8.1, $SiC\underline{H}_aH_b$), 1.02-1.08 (21H, m, overlapping signals: 6 × CH_3 and 3 × CH), 1.17 (1H, dd, *J* 14.4 and 6.2, $SiCH_a\underline{H}_b$), 1.18 (9H, s, CH_3 ^{t}Bu), 1.49 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.86-1.95 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 2.08-2.21 (2H, m, $CH_a\underline{H}_b$ C-3 and $CH_a\underline{H}_b$ C-4 THF), 4.32 (1H, app tt, *J* 8.1 and 5.7, CH C-2 THF), 4.84 (1H, t, *J* 7.4, CH C-5 THF); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH, ^{i}Pr), 16.8 ($SiCH_2$), 19.0 (6 × CH_3, ^{i}Pr), 26.4 (CH_3, ^{t}Bu), 30.5 (CH_2, C-4), 35.3 (CH_2, C-3 THF), 40.5 (C, ^{t}Bu), 77.5 (CH, C-5 THF), 78.9 (CH, C-2 THF), 215.9 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 283 ([M-^{i}Pr]$^+$, 37%), 241 (66), 199 (53), 157 (100), 115 (58), 87 (35), 57 (98); HRMS (CI$^+$, *m/z*) 344.2979 [M+NH$_4$]$^+$, $C_{19}H_{42}O_2NSi$ requires 344.2979.

(±)-Ethyl-2-((triisopropylsilyl)methyl)tetrahydrofuran-5-carboxylate (Table 5 entry 4)

To a stirred solution of freshly distilled ethyl glyoxalate (0.10 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of a solution of (cyclopropylmethyl)triisopropylsilane (0.13 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 1 h the reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.15 g) as a colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.08 g, 0.25 mmol, 42%) as a colourless oil; R_f 0.50 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2940 (C-H), 2865 (C-H), 1752 (C=O), 1735 (C=O), 1264, 1230 (Si-C), 1183 (C-O), 1094 (C-O), 882 (Si-C); δ_H (400 MHz; $CDCl_3$); 0.92 (1H, dd, *J* 14.4 and 8.1, $SiC\underline{H}_aH_b$), 1.00-1.10 (21H, m, overlapping signals: 6 × CH_3 and 3 × CH), 1.18 (1H, dd, *J* 14.4 and 6.1, $SiCH_a\underline{H}_b$), 1.27 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$), 1.48 (1H, dq, *J* 11.7 and 8.0, $C\underline{H}_aH_b$ C-3 THF), 1.98 (1H, app dtd, *J* 12.6 8.6 and 6.3, $C\underline{H}_aH_b$ C-4 THF), 2.10 (1H, dddd, *J* 11.7 8.0 5.3 and 3.5, $CH_a\underline{H}_b$ C-3 THF), 2.34 (1H, app dtd, *J* 12.5 8.4 and 3.2, $CH_a\underline{H}_b$ C-4 THF), 4.18 (2H, qd, *J* 7.1 and 2.4, $OC\underline{H}_2CH_3$), 4.32 (1H, app tt, *J* 8.3and 5.8, CH C-2 THF), 4.49 (1H, dd, *J* 8.4 and 6.3, CH C-5 THF); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH, ^{i}Pr), 14.3 (O $CH_2\underline{C}H$-$_3$), 16.7 ($SiCH_2$), 19.0 (6 × CH_3, ^{i}Pr), 30.8 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 60.8 ($O\underline{C}H_2CH_3$), 76.1 (CH, C-5 THF), 78.9 (CH, C-2 THF), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 271 ([M−^{i}Pr]$^+$, 100%), 241 (11), 225 (15), 198 (19), 157 (58), 145 (42), 131 (88), 103 (59); HRMS (CI$^+$, *m/z*) 332.2615 [M+NH$_4$]$^+$, $C_{17}H_{38}O_3NSi$ requires 332.2615.

1-(Tetrahydrofuran-2-yl)-2-((triisopropylsilyl)methyl)but-3-en-1-ol (Table 5 entry 5)

To a stirred solution of tetrahydrofurfuryl aldehyde (0.09 g, 0.90 mmol) and triisopropylsilylmethylcyclopropane (0.13 g, 0.61 mmol) in DCM (6 mL) at 0 °C was added dropwise using a syringe pump (rate = 9 mL/h) a solution of tin tetrachloride (0.19 g, 0.73 mmol) in DCM (3 mL). The reaction was allowed to warm to room temperature and monitored by TLC, after 18 h TLC and GCMS analysis showed all the staring material had been consumed and the reaction was quenched by the addition of water (5 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.20 g) as a brown oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% ethyl acetate : hexane] afforded a separable mixture of two diastereoisomers of the *title compound* (combined yield 0.04 g, 0.14 mmol, 23%), rather than the expected adduct, as colourless oils:

Major diastereoisomer (0.04 g, 0.11 mmol, 19%); R_f 0.25 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3450 (br), 2941(C-H), 2867 (C-H), 2362, 1465 (O-H bend), 1245 (Si-C), 1059 (C-O), 1000, 883; δ_H (400 MHz; CDCl$_3$); 0.84 (1H, dd, *J* 15.1 and 8.8, $SiC\underline{H}_aH_b$), 0.96 (1H, dd, *J* 15.1 and 4.7, $SiCH_a\underline{H}_b$), 1.00-1.08 (21H, m, overlapping signals 3 × CH and 6 × CH_3 ^{i}Pr), 1.48-1.59 (1H, m, C-4/3 THF), 1.82-1.97 (3H, m, C-4/3 THF), 2.31-2.38 (1H, m, $C\underline{H}CH{=}CH_2$), 2.41 (1H, d, *J* 3.0, OH), 3.31 (1H, app dt, *J* 7.3 and 3.2, $C\underline{H}OH$), 3.73-3.84 (3H, m, overlapping signals C-5 and C-2), 4.98 (1H, dd, *J* 17.3 and 2.0, $CH{=}CH_{cis}\underline{H}_{trans}$), 5.02 (1H, dd, *J* 10.2 and 1.9, $CH{=}C\underline{H}_{cis}H_{trans}$), 5.82 (1H, app dt, *J* 17.3 and 9.8, $C\underline{H}{=}CH_{cis}H_{trans}$); δ_C (100.6 MHz; CDCl$_3$) 11.6 (3 × CH_2, Si^{i}Pr$_3$), 12.5 ($SiCH_2$), 19.1 (6 × CH_3, Si^{i}Pr$_3$), 26.4 (CH_2, THF), 27.9 (CH_2, THF), 42.6 ($SiCH_2\underline{C}H$), 68.0 (CH_2, THF), 78.8 ($H\underline{C}OH$), 80.7 (CH THF), 115.5 ($CH{=}\underline{C}H_2$), 140.7 ($\underline{C}H{=}CH_2$); LRMS (EI$^+$, *m/z*): 269 ([M−^{i}Pr]$^+$, 16%), 157 (31), 131 (100), 103 (75), 75 (55), 71 (46); HRMS (CI$^+$, *m/z*) 330.2827 [M+NH$_4$]$^+$, $C_{18}H_{40}O_2NSi$ requires 330.2823.

Minor diastereoisomer (0.01 g, 0.03 mmol, 5%); R_f 0.32 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3450 (br), 2941(C-H), 2867 (C-H), 2362, 1465 (O-H bend), 1245 (Si-C), 1059 (C-O), 1000, 883; δ_H (400 MHz; CDCl$_3$); 0.67 (1H, dd, *J* 14.9 and 11.2, $SiC\underline{H}_aH_b$), 0.99-1.04 (22H, m, overlapping signals $SiCH_a\underline{H}_b$ and Si^{i}Pr$_3$) 1.75-1.94 (4H, m, overlapping signals C-3 and C-4 THF), 2.24 (1H, d, *J* 8.2, OH), 2.41 (1H, dddd, *J* 11.2 9.4 6.1 and 2.4, $C\underline{H}CH{=}CH_2$), 3.21 (1H, ddd, *J* 8.2 6.1 and 3.2, $\underline{H}COH$), 3.74-3.86 (1H, m, C-5 THF), 4.01 (1H, td, *J* 7.0 and 3.2, CH C-2 THF), 5.04 (1H, dd, *J* 10.2 and 1.9, $CH{=}C\underline{H}_{cis}H_{trans}$), 5.09 (1H, dd, *J* 17.2 and1.9, $CH{=}CH_{cis}\underline{H}_{trans}$), 5.69 (1H, app dt, *J* 17.2 10.2 and 9.4, $C\underline{H}{=}CH_{cis}H_{trans}$); δ_C (100.6 MHz; CDCl$_3$) 10.5 (CH_2, $SiCH_2CH$), 11.6 (3 × CH Si^{i}Pr$_3$), 19.1 (CH_3), 19.1 (CH_3), 26.4 (CH_2, THF), 29.3 (CH_2, THF), 44.9 ($SiCH_2C\underline{H}$), 68.9 (CH_2, C-5 THF), 77.8 ($C\underline{H}OH$), 78.4 (CH, C-2 THF), 116.0 ($CH{=}\underline{C}H_2$), 141.8 ($\underline{C}H{=}CH_2$); LRMS (EI$^+$, *m/z*): 269 ([M−^{i}Pr]$^+$, 16%), 157 (31), 131 (100), 103 (75), 75 (55), 71 (46); HRMS (CI$^+$, *m/z*) 330.2825 [M+NH$_4$]$^+$, $C_{18}H_{40}O_2NSi$ requires 330.2823.

5-benzyl-3-vinyloctahydro-2,2'-bifuran

To a solution of phenylacetaldehyde (0.07 g, 0.6 mmol) in DCM (2 mL) was added in a single portion indium trichloride (0.045 g, 0.2 mmol) and the resulting mixture was stirred for 1 h at room temperature. After this time a solution of 1-(tetrahydrofuran-2-yl)-2-((triisopropylsilyl)methyl)but-3-en-1-ol (0.035 g, 0.11 mmol) in DCM (1 mL) was added and the reaction mixture stirred at room temperature for 16 h. The reaction was quenched by the addition of H_2O (5 mL) and the organic layer separated. The aqueous layer was extracted with DCM (3 × 10 mL) and the combined organic layers were washed with brine (10 mL), separated, dried (MgSO4), filtered and concentrated *in vacuo* to give the impure product as a colourless oil (0.10 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] followed by flash column chromatography [silica gel, gradient elution 100% DCM – 5% diethyl ether : DCM] afforded the desired product containing trace impurities (0.015 g, 0.05 mmol, 40%) as a colourless oil; R_f 0.30 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3063, 2974, 2940, 2865, 1641, 1603, 1497, 1454, 1067, 1028, 947, 912; δ_H (600 MHz; $CDCl_3$); 1.65-1.72 (2H, m, overlapping signals C-3 and C7), 1.79-186 (1H, m, C-2), 1.91-1.97 (2H, m, overlapping signals C-2 and C-3), 2.02 (1H, ddd, *J* 12.2 7.7 and 6.4, C-7), 2.76 (1H, dd, *J* 13.4 and 7.6, C-11 CH_2Ph), 2.82-2.88 (1H, m, C-6), 3.11 (1H, dd, *J* 13.4 and 5.6, C-11 CH_2Ph), 3.77-3.81 (2H, m, overlapping signals C-5 and C-1), 3.84-3.87 (1H, m, C-4), 3.92 (1H, dt, *J* 8.1 and 6.7, C-1), 4.14 (1H, dddd, *J* 8.6 7.6 6.4 and 5.6, CH C-8), 4.98-5.03 (2H, m, $CH{=}C\underline{H}_2$), 5.83 (1H, app dt, *J* 17.0 and 9.8 $C\underline{H}{=}CH_2$); δ_C (100.6 MHz; $CDCl_3$) 26.3 (CH_2, C-2), 28.2 (CH_2, C-3), 38.3 (CH_2, C-7), 42.5 (CH_2, C-11), 47.0 (CH, C-6), 68.8 (CH_2, C-1), 79.0 (CH, C-4), 80.4 (CH, C-8), 84.2 (CH, C-5), 115.7 (CH_2, C-10), 126.3 (CH, *p*-CH Ar), 128.4 (2 × CH, *o*-CH Ar), 129.4 (2 × CH, *m*-CH Ar), 138.6 (CH, C-9), 139.0 (*ipso*-C Ar); LRMS (EI$^+$, *m/z*): 258 (M$^+$, 3%), 167 ([M$^+$-Bn], 6), 123 (71), 117 (68), 104 (24), 91 (Bn, 100), 71 (THF, 34); HRMS (EI$^+$, *m/z*) 258.1614 [M]$^+$, $C_{17}H_{22}O_2$ requires 258.1614.

(±)-2-((*tert*-Butyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (Table 5 entry 6)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of *tert*-butyl(cyclopropylmethyl)diphenylsilane (0.18 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.29 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : cyclohexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.17 g, 0.40 mmol, 66%, *dr* (*trans* : *cis*) 1 : 2.1) as a colourless oil; R_f 0.41 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2930 (C-H), 2857 (C-H), 1691 (C=O), 1448 (C-H), 1228 (Si-C), 1104 (C-O); *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 1.04 (9H, s, $Si\underline{C}(CH_3)_3$), 1.17-1.32 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.40-1.47 (1H, m, $CH_a\underline{H}_b$, C-3 THF), 1.58 (1H, dd, *J* 14.5 and 9.8, $SiC\underline{H}_aH_b$), 2.02 (1H, dd, 14.5 and 4.1 $SiCH_a\underline{H}_b$), 2.03-2.08 (2H, m, CH_2 C-4 THF), 4.14 (1H, app tt, 9.5 and 4.8, CH C-2 THF), 5.07 (1H, dd, *J* 8.4 and 5.5, CH C-5 THF), 7.29-

7.70 (13H, m, Ar), 7.94-7.96 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 17.9 ($SiCH_2$), 18.2 ($Si\underline{C}(CH_3)_3$), 29.8 (CH_2, C-4 THF), 33.0 (CH_2, C-3 THF), 79.4 (CH, C-5 THF), 79.6 (CH, C-2 THF), 127.6 (2 × *o*-CH, Ar), 127.7 (2 × *o*-CH, Ar), 128.6 (2 × *m*-CH, -C(=O)Ph), 128.9 (2 × *o*-CH, -C(=O)Ph), 129.3 (2 × *p*-CH, Ar), 133.2 (*p*-CH, -C(=O)Ph), 134.1 (C, Ar), 134.7 (C, Ar), 135.4 (*ipso*-C, -C(=O)Ph), 136.2 (2 × *m*-CH, Ar), 136.3 (2 × *m*-CH, Ar), 198.4 (C=O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 1.05 (9H, s, Si $C(CH_3)_3$), 1.17-1.32 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.46 (1H, dd, *J* 14.4 and 9.2, $SiC\underline{H}_aH_b$), 1.51-1.56 (1H, m, $CH_a\underline{H}_b$, C-3 THF), 1.95 (1H, dd, *J* 14.4 and 5.0, $SiCH_a\underline{H}_b$), 1.95-2.00 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 2.16 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.20 (1H, app tt, 8.9 and 5.2, CH C-2 THF), 5.19 (1H, dd, *J* 8.0 and 7.0, CH C-5 THF), 7.29-7.70 (13H, m, Ar), 7.86-7.88 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; $CDCl_3$) 18.1 ($SiCH_2$), 18.2 ($Si\underline{C}(CH_3)_3$), 29.4 (CH_2, C-4 THF), 34.0 (CH_2, C-3 THF), 78.6 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.6 (2 × *o*-CH, Ar), 127.7 (2 × *o*-CH, Ar), 128.5 (2 × *m*-CH, -C(=O)Ph), 128.9 (2 × *o*-CH, -C(=O)Ph), 129.2 (2 × *p*-CH, Ar), 133.1 (*p*-CH, -C(=O)Ph), 134.2 (C, Ar), 134.8 (C, Ar), 135.3 (*ipso*-C, -C(=O)Ph), 136.2 (2 × *m*-CH, Ar), 136.3 (2 × *m*-CH, Ar), 199.2 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, ($[M-{}^tBu]^+$ 18%), 329 (87), 183 (42), 135 (100), 105 (72), 77 (33); HRMS (CI^+, *m/z*) 446.2512 $[M+NH_4]^+$, $C_{28}H_{36}O_2NSi$ requires 446.2510. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the C-5 protons of the THF ring, 5.07 *cis* and 5.19 *trans*.

(±)-2-((*tert*-Butyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (Table 5 entry 7)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of *tert*-butyl(cyclopropylmethyl)diphenylsilane (0.18 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 1 h the reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.24 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ethyl : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.18 g, 0.43 mmol, 72%, *dr* (*trans* : *cis*) 1 : 1.1) as a colourless oil. Data is in agreement with that previously recorded.

(±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (Table 5 entry 8)

Following the general procedure C, (cyclopropylmethyl)dimethylphenylsilane (0.12 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at −78 °C furnished the impure product (0.27 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.10 g, 0.32 mmol, 53%, *dr* (*trans* : *cis*) 1 : 1.6) as a colourless oil; R_f 0.22 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3070, 2957 (C-H), 2886 (C-H), 1692 (C=O), 1451 (C-H), 1429, 1230 (Si-C), 1115 (C-O); *cis* diastereoisomer: δ_H (400 MHz; CDCl$_3$); 0.30 (3H, s, SiCH$_3$), 0.32 (3H, s, SiCH$_3$), 1.21 (1H, dd, *J* 14.2 and 8.5, SiC$\underline{H}_a$H$_b$), 1.42-1.51 (2H, m, overlapping signals SiH$_a\underline{H}_b$ and C$\underline{H}_a$H$_b$ C-3 THF), 1.92-2.02 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.09-2.33 (2H, m, CH$_2$ C-4 THF), 4.15 (1H, app tt, *J* 8.7 and 5.8, CH C-2 THF), 5.13 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.33-7.59 (8H, m, Ar), 8.01-8.04 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; CDCl$_3$) −2.3 (SiCH$_3$), −2.0 (SiCH$_3$), 23.6 (SiCH$_2$), 29.4 (CH$_2$, C-4 THF), 33.6 (CH$_2$, C-3 THF), 78.5 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh), 128.5 (2 × *m*-CH, -C(=O)Ph), 129.0 (2 × *o*-CH, -C(=O)Ph), 129.1 (*p*-CH, SiPh), 133.2 (*p*-CH, -C(=O)Ph), 133.7 (2 × *o*-CH, SiPh), 135.5 (*ipso*-C, -C(=O)Ph), 139.0 (C, SiPh), 198.4 (C=O); *trans* diastereoisomer: δ_H (400 MHz; CDCl$_3$); 0.32 (3H, s, SiCH$_3$), 0.33 (3H, s, SiCH$_3$), 1.12 (1H, dd, *J* 14.2 and 8.1, SiC$\underline{H}_a$H$_b$), 1.42 (1H, dd, *J* 14.2 and 6.2, SiH$_a\underline{H}_b$), 1.39-1.52 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.98 (1H, dddd, *J* 12.1 8.1 5.5 and 3.6, CH$_a\underline{H}_b$ C-3 THF), 2.13 (1H, app dtd, *J* 12.7 8.5 and 6.6, C$\underline{H}_a$H$_b$ C-4 THF), 2.25 (1H, app dtd, *J* 12.7 8.4 and 3.6, CH$_a\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.4 and 5.9, CH C-2 THF), 5.27 (1H, dd, *J* 8.2 and 6.6, CH C-5 THF), 7.32-7.36 (3H, m, overlapping signals 2 × *o*-CH and *p*-CH Ar), 7.45 (2H, t, *J* 7.6, 2 × *m*-CH Ar), 7.49-7.52 (2H, m, 2 × *m*-CH Ar), 7.56 (1H, app tt, *J* 7.4 and 1.4, *p*-CH Ar), 7.96-7.99 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; CDCl$_3$) −2.4 (SiCH$_3$), −2.0 (SiCH$_3$), 23.5 (SiCH$_2$), 29.3 (CH$_2$, C-4 THF), 34.4 (CH$_2$, C-3 THF), 78.6 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.9 (2 × *m*-CH, Ar), 128.6 (2 × *m*-CH, -C(=O)Ph), 129.0 (2 × *o*-CH, -C(=O)Ph), 129.0 (*p*-CH, Ar), 133.3 (*p*-CH, -C(=O)Ph), 133.7 (2 × *o*-CH, Ar), 135.3 (*ipso*-C, -C(=O)Ph), 139.1 (C, Ar), 199.4 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 309 ([M−CH$_3$]$^+$, 2%), 267 (5), 239 (10), 219 (16), 135 (100), 105 (21), 77 (15); HRMS (CI$^+$, *m/z*) 342.1878 [M+NH$_4$]$^+$, $C_{20}H_{28}O_2NSi$ requires 342.1884. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.13 *cis* and 5.27 *trans*.

(±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (Table 5 entry 9)

Following the general procedure C, (cyclopropylmethyl)dimethylphenylsilane (0.12 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at 0 °C furnished the impure product (0.26 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.03 g, 0.11 mmol, 18%) as a colourless oil; R_f 0.41 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3070, 2957 (C-H), 2886 (C-H), 1692 (C=O), 1451 (C-H), 1429, 1230 (Si-C), 1115 (C-O); δ_H (400 MHz; $CDCl_3$); 0.32 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.12 (1H, dd, *J* 14.2 and 8.1, $SiC\underline{H}_aH_b$), 1.42 (1H, dd, *J* 14.2 and 6.2, $SiH_a\underline{H}_b$), 1.39-1.52 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.98 (1H, dddd, *J* 12.1 8.1 5.5 and 3.6, $CH_a\underline{H}_b$ C-3 THF), 2.13 (1H, app dtd, *J* 12.7 8.5 and 6.6, $C\underline{H}_aH_b$ C-4 THF), 2.25 (1H, app dtd, *J* 12.7 8.4 and 3.6, $CH_a\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.4 and 5.9, CH C-2 THF), 5.27 (1H, dd, *J* 8.2 and 6.6, CH C-5 THF), 7.32-7.36 (3H, m, overlapping signals 2 × *o*-CH and *p*-CH Ar), 7.45 (2H, t, *J* 7.6, 2 × *m*-CH Ar), 7.49-7.52 (2H, m, 2 × *m*-CH Ar), 7.56 (1H, tt, *J* 7.4 and 1.4, *p*-CH Ar), 7.96-7.99 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −2.0 ($SiCH_3$), 23.5 ($SiCH_2$), 29.3 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 78.6 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh), 128.6 (2 × *m*-CH, -C(=O)Ph), 129.0 (2 × *o*-CH, -C(=O)Ph), 129.0 (*p*-CH, SiPh), 133.3 (*p*-CH, -C(=O)Ph), 133.7 (2 × *o*-CH, SiPh), 135.3 (*ipso*-C, -C(=O)Ph), 139.1 (C, SiPh), 199.4 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 309 ($[M-CH_3]^+$, 2%), 267 (5), 239 (10), 219 (16), 135 (100), 105 (21), 77 (15); HRMS (CI^+, *m/z*) 342.1888 $[M+NH_4]^+$, $C_{20}H_{28}O_2NSi$ requires 342.1884.

(±)-Ethyl-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carboxylate (Table 5 entry 10)

To a stirred solution of freshly distilled ethyl glyoxalate (0.23 g, 2.25 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.29 g, 1.50 mmol) in anhydrous DCM (15 mL) at −78 °C and under an atmosphere of argon was added dropwise, a solution of tin tetrachloride (0.39 g, 1.50 mmol) in anhydrous DCM (8 mL). (The tin tetrachloride solution was prepared by adding a commercial 1 Mol solution of tin tetrachloride (3 mL) to anhydrous DCM (5 mL)). The resulting mixture was allowed to warm to 0 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.47 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.23 g, 0.79 mmol, 53%) as a colourless oil; R_f 0.46 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957 (C-H), 1749 (C-O), 1732 (C-O), 1427, 1180, 1091, 821 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.33 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$), 1.08 (1H, dd, 14.2 and 8.7, $SiC\underline{H}_aH_b$), 1.26 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$), 1.29-1.38 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.39 (1H, dd, *J* 14.2 and 5.7 $SiCH_a\underline{H}_b$), 1.90-1.97 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 2.25-2.31 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.14-4.26 (3H, m, overlapping signals $OC\underline{H}_2CH_3$ and CH C-2 THF), 4.46 (1H, dd, *J* 8.4 and 6.1, CH C-5 THF), 7.33-7.37 (3H, m, Ph), 7.50-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −2.0 ($SiCH_3$), 14.3 ($OCH_2\underline{C}H_3$), 23.4 ($SiCH_2$), 30.7 (CH_2, C-4 THF), 33.8 (CH_2, C-3 THF), 60.8 ($O\underline{C}H_2CH_3$), 76.1 (CH, C-5 THF), 78.8 (CH, C-2 THF), 127.9 (2 × *m*-CH, Ph), 129.1 (*p*-CH, Ph), 133.7 (2 × *o*-CH, Ph), 139.1 (C, Ph) 174.1(C=O); LRMS (EI^+, *m/z*): M^+ not visible, 277 ($[M{-}Me]^+$, 11%), 215 (13), 165 (12), 135 (100), 105 (13), 75 (18); HRMS (CI^+, *m/z*) 310.1824 $[M+NH_4]^+$, $C_{16}H_{28}O_3NSi$ requires 310.1833.

(±)-2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-nitrophenyl)methanone (Table 5 entry 11)

To a stirred solution of freshly distilled 4-nitrophenyl glyoxal (0.16 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a dark yellow oil (0.27 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.05 g, 0.14 mmol, 25%, *dr* (*trans* : *cis*) 1 : 2.6) as a colourless oil; R_f 0.35 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2955, 2879, 1699 (C=O), 1524 (C-N), 1344 (C-N), 1219 (Si-C), 1112 (C-O), 825 (Si-C);

cis diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.26 (3H, m, SiMe), 0.28 (3H, s, SiMe), 1.10 (1H, dd, *J* 14.3 and 7.7, $SiC\underline{H}_aH_b$), 1.33 (1H, dd, *J* 14.3 and 6.5, $SiCH_a\underline{H}_b$), 1.39-1.52 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.94-2.05 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.10-2.19 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 2.36 (1H, app tdd, *J* 8.4, 4.6 and 3.5, $CH_a\underline{H}_b$ C-4 THF), 4.14 (1H, m, CH C-2 THF), 5.00 (1H, dd, *J* 8.6 and 4.7, CH C-5 THF), 7.30-7.34 (3H, m, Ph), 7.47-7.50 (2H, m, Ph), 8.15-8.28 (4H, m, $C_6\underline{H}_4NO_2$); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −2.1 ($SiCH_3$), 23.7 ($SiCH_2$), 28.5 (CH_2, C-4 THF), 33.8 (CH_2, C-3 THF), 80.0 (CH, C-2 THF), 80.5 (CH, C-5 THF), 123.7 (2 × *o*-CH, C_6H_4-NO_2) 127.9 (2 × *m*-CH, Ph), 129.2 (*p*-CH, Ph), 130.5 (2 × *m*-CH, C_6H_4-NO_2) 133.6 (2 × *o*-CH Ph), 138.8 (C, Ph), 140.3 (C, C_6H_4-NO_2), 150.4 (C, C_6H_4-NO_2), 197.2 (CO);

trans diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.29 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 1.12 (1H, dd, *J* 14.4 and 7.4, $SiC\underline{H}_aH_b$), 1.36 (1H, dd, *J* 14.4 and 6.9, $SiCH_a\underline{H}_b$), 1.39-1.52 (1H, m, $C\underline{H}_aH_b$ C-3

THF), 2.01 (1H, m, $\text{CH}_a\underline{\text{H}}_b$ C-3 THF), 2.20-2.27 (2H, m, CH_2 C-4 THF), 4.09 (1H, app dtd, *J* 8.4, 7.1 and 5.7, CH C-2 THF), 5.13 (1H, app t, *J* 7.2, CH C-5 THF), 7.31-7.36 (3H, m, Ar), 7.47-7.49 (2H, m, Ar), 8.10-8.28 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −2.1 ($SiCH_3$), 23.4 ($SiCH_2$), 28.3 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 78.9 (CH, C-2 THF), 79.9 (CH, C-5 THF), 123.7 (2 × *o*-CH, C_6H_4-NO_2) 127.9 (2 × *m*-CH, Ph), 129.2 (*p*-CH, Ph), 130.3 (2 × *m*-CH, C_6H_4-NO_2) 133.6 (2 × *o*-CH Ph), 138.8 (C, Ph), 140.3 (C, C_6H_4-NO_2), 150.4 (C, C_6H_4-NO_2), 198.1 (CO); LRMS (EI^+, *m/z*): M^+ not visible, ($[M{-}Me]^+$ 1%), 312 (8), 285 (8), 219 (14), 135 (100); HRMS (CI^+, *m/z*) 387.1741 $[M+NH_4]^+$, $C_{20}H_{27}N_2O_4Si$ requires 387.1735.

Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the C-5 protons of the THF ring, 5.13 (ppm) and 5.00 (ppm) *trans* and *cis* respectively.

(±)-2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-nitrophenyl)methanone (Table 5 entry 12)

To a stirred solution of freshly distilled 4-nitrophenyl glyoxal (0.16 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.31 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 8. mg, 0.02 mmol, 3%, *dr* (*trans* : *cis*) 1 : 0.2) as a colourless oil. Data is in agreement with that previously recorded.

(±)-2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-bromophenyl)methanone (Table 5 entry 13)

To a stirred solution of freshly distilled 4-bromophenyl glyoxal (0.19 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (6.5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a dark yellow oil (0.29

g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.12 g, 0.29 mmol, 55%, *dr* (*trans* : *cis*) 1 : 1.8) as a colourless oil; R_f 0.50 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3089, 2955, 2879, 1690 (C=O), 1584, 1112, 1069, 835 (Si-C), 727;

cis diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.29 (3H, m, SiMe), 0.31 (3H, s, SiMe), 1.15 (1H, dd, *J* 14.3 and 8.1, SiC$\underline{H}_a$H$_b$), 1.40 (1H, dd, *J* 14.3 and 6.2, SiCH$_a\underline{H}_b$), 1.41-1.48 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.92-2.00 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.09-2.33 (2H, m, CH$_2$ C-4 THF), 4.09-4.17 (1H, m, CH C-2 THF), 5.00 (1H, dd, *J* 8.7 and 4.9, CH C-5 THF), 7.31-7.39 (3H, m, SiPh), 7.49-7.52 (2H, m, SiPh), 7.57-7.60 (2H, m, Ar), 7.88-7.90 (2H, m, Ar); δ_C (100.6 MHz; CDCl$_3$) −2.3 (SiCH$_3$), −2.0 (SiCH$_3$), 23.6 (SiCH$_2$), 28.7 (CH$_2$, C-4 THF), 33.7 (CH$_2$, C-3 THF), 79.6 (CH, C-2 THF), 80.0 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh) 128.3 (*ipso*-C, C$_6$H$_4$Br), 129.1 (*p*-CH, SiPh), 130.8 (2 × *m*-CH, C$_6$H$_4$Br), 131.8 (2 × *o*-CH, C$_6$H$_4$Br), 133.6 (2 × *o*-CH, SiPh), 134.3 (*p*-C, C$_6$H$_4$Br), 138.9 (C, SiPh), 197.4 (CO);

trans diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.32 (3H, s, SiCH$_3$), 0.32 (3H, s, SiCH$_3$), 1.12 (1H, dd, *J* 14.4 and 7.8, SiC$\underline{H}_a$H$_b$), 1.39 (1H, dd, *J* 14.4 and 6.6, SiCH$_a\underline{H}_b$), 1.48 (1H, app dq, *J* 12.1 and 8.8, C$\underline{H}_a$H$_b$ C-3 THF), 1.99 (1H, dddd, *J* 12.1, 8.3, 1.3 and 1.0, CH$_a\underline{H}_b$ C-3 THF), 2.20-2.28 (2H, m, CH$_2$ C-4 THF), 4.14 (1H, app ddd, *J* 14.4, 7.9 and 6.6, CH C-2 THF), 5.16 (1H, dd, *J* 8.0 and 6.6, CH C-5 THF), 7.31-7.39 (3H, m, SiPh), 7.49-7.52 (2H, m, SiPh), 7.57-7.60 (2H, m, Ar), 7.83-7.87 (2H, m, Ar); δ_C (100.6 MHz; CDCl$_3$) −2.3 (SiCH$_3$), −2.0 (SiCH$_3$), 23.4 (SiCH$_2$), 28.7 (CH$_2$, C-4 THF), 34.4 (CH$_2$, C-3 THF), 78.6 (CH, C-2 THF), 79.3 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh) 128.4 (*ipso*-C, C$_6$H$_4$Br), 129.1 (*p*-CH, SiPh), 130.6 (2 × *m*-CH, C$_6$H$_4$Br), 131.9 (2 × *o*-CH, C$_6$H$_4$Br), 133.6 (2 × *o*-CH, SiPh), 134.1 (*p*-C, C$_6$H$_4$Br), 139.0 (C, SiPh), 198.3 (CO); LRMS (EI$^+$, *m/z*): M$^+$ not visible, ([M−Me]$^+$ 2%), 347 (4), 319 (7), 239 (11), 219 (62), 183 (12), 155 (9), 135 (100), 105 (11), 75 (30); HRMS (CI$^+$, *m/z*) 420.0994 [M+NH$_4$]$^+$, C$_{20}$H$_{27}$NO$_2$BrSi requires 420.0989.

Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.16 (ppm) and 5.00 (ppm) *trans* and *cis* respectively.

(±)-2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-bromophenyl)methanone (Table 5 entry 14)

To a stirred solution of freshly distilled 4-bromophenyl glyoxal (0.19 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (6.5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.24 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the *trans* diastereoisomers of the desired product (81 mg, 0.20 mmol, 34%) as a colourless oil. Data is in agreement with that previously recorded.

(±)-(2-((Methyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (Table 5 Entry 15)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)diphenylmethylsilane (0.15 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.5 mmol) in anhydrous DCM (2 mL). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.34 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.09 g, 0.24 mmol, 40%, *dr* (*trans* : *cis*) 0.49 : 1) as a colourless oil; R_f 0.27 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3068 2960, 1688, 1427, 1228, 1110, 873; *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.59 (3H, s, SiMe), 1.40-1.51 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.52 (1H, dd, *J* 14.4 and 8.2, Si$\underline{H}_a$H$_b$), 1.79 (1H, dd, *J* 14.4 and 5.9, SiH$_a\underline{H}_b$), 1.85-1.96 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.09-2.28 (2H, m, CH_2 C-4 THF), 4.18 (1H, app tt, *J* 8.7 and 5.7, CH C-2 THF), 5.11 (1H, dd, *J* 8.7 and 5.0, CH C-5 THF), 7.30-7.58 (13H, m, Ar), 8.00 (2H, app d, *J* 8.3, 2 × o-CH Ar); δ_C (100.6 MHz; $CDCl_3$) −3.3 (SiMe), 22.1 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 33.7 (CH_2, C-3 THF), 79.3 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.0 (4 × *m*-CH, Ar), 128.6 (2 × *m*-CH, Ar), 129.1 (2 × *o*-CH, Ar), 129.3 (2 × *p*-CH, Ar), 133.2 (*p*-CH, Ar), 134.5 (2 × *o*-CH, Ar), 134.6 (2 × *o*-CH, Ar), 135.6 (C, Ar), 137.0 (C, Ar), 199.2 (C=O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.62 (3H, s, SiMe), 1.40-1.51 (2H, m, overlapping signals SiC$\underline{H}_a$H$_b$ and C$\underline{H}_a$H$_b$, C-3 THF), 1.75 (1H, dd, *J* 14.4 and 6.3, SiH$_a\underline{H}_b$), 1.85-1.96 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.09-2.28 (2H, m, CH_2 C-4 THF), 4.25 (1H, app tt, *J* 8.0 and 5.8, CH C-2 THF), 5.23 (1H, dd, *J* 8.2 and 6.6, CH C-5 THF), 7.30-7.58 (13H, m, Ar), 7.94 (2H, app d, *J* 7.4, 2 × *o*-CH Ph) δ_C (100.6 MHz; $CDCl_3$) −3.4 (SiMe), 22.0 ($SiCH_2$), 29.1 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 78.4 (CH, C-2

THF), 79.3 (CH, C-5 THF), 128.0 (4 × *m*-CH, Ar), 128.6 (2 × *m*-CH, Ar), 129.0 (2 × *o*-CH, Ar), 129.3 (2 × *p*-CH, Ar), 133.2 (*p*-CH, Ar), 134.6 (2 × *o*-CH, Ar), 134.7 (2 × *o*-CH, Ar), 135.4 (C, Ar), 137.1 (C, Ar), 198.3 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 309 ([M−Ph]$^+$, 4%), 281 (11), 197 (100), 137 (19), 105 (21), 77 (13); HRMS (ESP, *m/z*) 404.2031 [M+NH$_4$]$^+$, $C_{25}H_{30}O_2NSi$ requires 404.2040. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.11 *cis* and 5.23 *trans*.

(±)-(2-((Methyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (Table 5 entry 16)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)triethylsilane (0.10 g, 0.60 mmol) in anhydrous DCM (5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.26 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 89.7 mg, 0.23 mmol, 38%, *dr* (*trans* : *cis*) 1 : 0.41) as a colourless oil. Data is in agreement with that previously recorded.

(±)-Phenyl(2-((triethylsilyl)methyl)tetrahydrofuran-5-yl)methanone (Table 5 entry 17)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)triethylsilane (0.10 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.16 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded:

Product 1: the desired product as a mixture of *cis* and *trans* diastereoisomers (combined yield 26.0 mg, 0.09 mmol, 14%, *dr* (*trans* : *cis*) 0.88 : 1) as a colourless oil; R_f 0.45 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2909 (C-H), 2951, 2874, 1690 (C=O), 1449, 1228 (Si-C), 1180 (C-O), 1092, 1002; *cis* isomer: δ_H (400 MHz; $CDCl_3$) 0.53 (6H, q, *J* 7.9, 3 × CH_2), 0.91 (9H, t, *J* 7.9, 3 × CH_3), 0.95 (1H, dd, *J* 14.3 and 8.7, $SiC\underline{H}_aH_b$), 1.20 (1H, dd, *J* 14.3 and 6.0, $SiCH_a\underline{H}_b$), 1.49 (1H, dq, *J* 12.0 and 9.2, $C\underline{H}_aH_b$ C-3 THF), 2.05 (1H, dddd, *J* 12.2 7.7 5.3 and 3.5, $CH_a\underline{H}_b$ C-3 THF), 2.17-2.33 (2H, m, overlapping signals $C\underline{H}_2$ C-4 THF), 4.17 (1H app tt, *J* 8.9 and 5.7,CH C-2 THF), 5.13 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.43-7.47 (2H, m, 2 × *m*-CH, Ph), 7.50-7.57 (1H, m, *p*-CH, Ph), 8.00-8.03 (2H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.2 ($SiCH_2$), 29.5 (CH_2, C-4 THF), 33.9 (CH_2, C-3 THF), 79.8 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.1 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.6 (C, Ph), 198.5 (C=O); *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.54 (6H, q, *J* 7.8, 3 × CH_2), 0.88 (1H, dd, *J* 14.1 and 8.4, $SiC\underline{H}_aH_b$), 0.93 (9H, t, *J* 7.9, 3 × CH_3), 1.18 (1H, dd, *J* 14.1 and 6.1, $SiCH_a\underline{H}_b$), 1.53 (1H, dq, *J* 11.6 and 8.7, $C\underline{H}_aH_b$ C-3 THF), 2.06-2.13 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.41-2.22 (1H, m, $C\underline{H}_aH_b$ C-4 THF) 2.28-2.36 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.5 and 5.7, CH C-2 THF), 5.29 (1H, dd, *J* 8.2 and 6.4, CH C-5 THF), 7.45 (2H, app t, *J* 7.5, *m*-CH, Ph), 7.53-7.57 (1H, m, *p*-CH, Ph), 7.98-8.00 (2H, m, *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.1 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 78.8 (CH, C-2 THF), 79.2 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C. Ph), 199.5 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 275 ($[M-Et]^+$, 36%), 233 (63), 199 (22), 163 (15), 115 (100), 105 (48), 77 (46), 59 (45); HRMS (ESP, *m/z*) 305.1924 $[M+H]^+$, $C_{18}H_{29}O_2Si$ requires 305.1931. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the C-5 protons of the THF ring, 5.13 *cis* and 5.29 *trans*.

Product 2: the desired product as the single *cis* diastereoisomer (13.0 mg, 0.04 mmol, 7%) as a colourless oil; R_f 0.45 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2910 (C-H), 2952, 2874, 1690 (C=O), 1450, 1226 (Si-C), 1175 (C-O), 1090, 1001; δ_H (400 MHz; $CDCl_3$) 0.53 (6H, q, *J* 7.9, 3 × CH_2), 0.91 (9H, t, *J* 7.9, 3 × CH_3), 0.95 (1H, dd, *J* 14.3 and 8.7, $SiC\underline{H}_aH_b$), 1.20 (1H, dd, *J* 14.3 and 6.0, $SiCH_a\underline{H}_b$), 1.49 (1H, dq, *J* 12.0 and 9.2, $C\underline{H}_aH_b$ C-3 THF), 2.05 (1H, dddd, *J* 12.2 7.7 5.3 and 3.5, $CH_a\underline{H}_b$ C-3 THF), 2.17-2.33 (2H, m, overlapping signals $C\underline{H}_2$ C-4 THF), 4.17 (1H, app tt, *J* 8.9 and 5.7, CH C-2 THF), 5.13 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.43-7.47 (2H, m, 2 × *m*-CH, Ph), 7.50-7.57 (1H, m, *p*-CH, Ph), 8.00-8.03 (2H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.2 ($SiCH_2$), 29.5 (CH_2, C-4 THF), 33.9 (CH_2, C-3 THF), 79.8 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.1 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.6 (C, Ph), 198.5 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 275 ($[M-Et]^+$, 7%), 233 (66), 199 (24), 163 (15), 115 (100), 105 (50), 77 (46), 59 (45); HRMS (ESP, *m/z*) 305.1935 $[M+H]^+$, $C_{18}H_{29}O_2Si$ requires 305.1931.

(±)-Phenyl(2-((triethylsilyl)methyl)tetrahydrofuran-5-yl)methanone (Table 5 entry 18)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)triethylsilane (0.10 g, 0.60 mmol) in anhydrous DCM (5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.16 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.10 g, 0.32 mmol, 53%, *dr* (*trans* : *cis*) 1 : 0.1) as a colourless oil; *trans* isomer: R_f 0.45 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2952, 2909 (C-H), 2874, 1690 (C=O), 1449, 1229, 1180, 1016, 877; δ_H (400 MHz; $CDCl_3$) 0.54 (6H, q, *J* 7.8, 3 × CH_2), 0.88 (1H, dd, *J* 14.1 and 8.4, $SiC\underline{H}_aH_b$), 0.93 (9H, t, *J* 7.9, 3 × CH_3), 1.18 (1H, dd, *J* 14.1 and 6.1, $SiCH_a\underline{H}_b$), 1.53 (1H, dq, *J* 11.6 and 8.7, $C\underline{H}_aH_b$ C-3 THF), 2.06-2.13 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.41-2.22 (1H, m, $C\underline{H}_aH_b$ C-4 THF) 2.28-2.36 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.5 and 5.7, CH C-2 THF), 5.29 (1H, dd, *J* 8.2 and 6.4,CH C-5 THF), 7.45 (2H, app t, *J* 7.5, *m*-CH Ph), 7.53-7.57 (1H, m, *p*-CH Ph), 7.98-8.00 (2H, m, *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.1 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 78.8 (CH, C-2 THF), 79.2 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 275 ([M−Et]$^+$, 11%), 233 (75), 199 (29), 163 (16), 115 (100), 105 (38), 87 (76), 77 (36), 59 (36); HRMS (ESP, *m/z*) 305.1925 [M+H]$^+$, $C_{18}H_{29}O_2Si$ requires 305.1931.

(±)-Phenyl(2-((tri-*n*-butylsilyl)methyl)tetrahydrofuran-5-yl)methanone (Table 5 entry 19)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of (cyclopropylmethyl)tri-*n*-butylsilane (0.15 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.25 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.09 g, 0.26 mmol, 43%, *dr* (*trans* : *cis*) 1.35 : 1) as a colourless oil; R_f 0.63 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2920 (C-H), 1691 (C=O), 1449 (C-H), 1228 (Si-C), 1180 (C-O), 1080 (C-O); *trans* diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.48-0.53 (6H, m, Si(CH$_2$)$_3$), 0.83-0.97 (10H, m, overlapping signals SiC$\underline{H}_a$H$_b$ and 3 × CH$_3$), 1.14-1.34 (13H, m, overlapping signals SiCH$_a\underline{H}_b$ and 6 × CH$_2$), 1.42-1.56 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 2.01-2.12 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.14-2.35 (2H, m, CH$_2$ C-4 THF), 4.11-4.20 (1H, m, CH C-2 THF), 5.27 (1H, dd, *J* 8.2 and 6.5, CH C-5 THF), 7.42-7.45 (2H, m, 2 × *m*-CH, Ph), 7.51-7.56 (1H, m, *p*-CH, Ph), 7.98-8.02 (1H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; CDCl$_3$) 12.7 (Si(CH$_2$)$_3$), 13.9 (3 × CH$_3$), 20.1 (SiCH$_2$), 26.2 (3 × CH$_2$ Bu), 26.9 (3 × CH$_2$ Bu), 29.2 (CH$_2$, THF), 34.5 (CH$_2$, THF), 78.8 (CH, C-2 THF), 79.1 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 128.9 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.3 (CO); *cis* diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.48-0.53 (6H, m, Si(CH$_2$)$_3$), 0.83-0.97 (11H, m, overlapping signals SiCH$_2$ and 3 × CH$_3$), 1.14-1.34 (12H, m, 6 × CH$_2$), 1.42-1.56 (1H, m,C$\underline{H}_a$H$_b$ C-3 THF), 2.01-2.12 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.14-2.35 (2H, m, CH$_2$ C-4 THF), 4.11-4.20 (1H, m, CH C-2 THF), 5.12 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.42-7.45 (2H, m, 2 × *m*-CH, Ph), 7.51-7.56 (1H, m, *p*-CH, Ph), 7.98-8.02 (1H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; CDCl$_3$) 12.7 (Si(CH$_2$)$_3$), 13.9 (3 × CH$_3$), 20.2 (SiCH$_2$), 26.2 (3 × CH$_2$ Bu), 26.9 (3 × CH$_2$ Bu), 29.3 (CH$_2$, THF), 33.8 (CH$_2$, THF), 79.7 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.5 (2 × *m*-CH, Ph), 129.1 (2 × *o*-CH, Ph), 133.1 (*p*-CH, Ph), 135.5 (C, Ph), 198.2 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, ([M−^{n}Bu]$^+$ 36%), 289 (100), 199 (9), 171 (68), 143 (26), 105 (32), 77 (20); HRMS (CI$^+$, *m/z*) 389.2870 [M+H]$^+$, $C_{24}H_{41}O_2Si$ requires 389.2870. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.27 (ppm) and 5.12 (ppm) *trans* and *cis* respectively.

(±)-Phenyl(2-((tri-*n*-butylsilyl)methyl)tetrahydrofuran-5-yl)methanone (Table 5 entry 20)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.9 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of (cyclopropylmethyl)tri-*n*-butylsilane (0.15 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 1 h the reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched by the addition of H$_2$O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried (MgSO$_4$), filtered and concentrated *in vacuo* to give the impure product (0.29 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : cyclohexane] afforded an inseparable mixture of diastereoisomers of the desired product (combined yield 0.08 g, 0.19 mmol, 31%, *dr* (*trans* : *cis*) 11 : 1) as a colourless oil. Data is in agreement with that previously recorded.

(±)-Ethyl 3-(2-((tert-butyldiphenylsilyl)methyl)tetrahydrofuran-3-yl)-3-phenylacrylate (16a)

A 60% dispersion of sodium hydride in mineral oil (0.08 g, 2.00 mmol) was washed with petroleum ether (3 × 2 mL), dried under reduced pressure and placed under an atmosphere of argon. Diethyl ether (3 mL) was added and to the resulting suspension was added dropwise over 1 min a solution of triethyl phosphonoacetate (0.38 g, 0.34 mL, 1.70 mmol) in diethyl ether (3 mL) at −5 °C. The solution was allowed to warm to room temperature, stirred for a further 15 min followed by the dropwise addition of a solution of (5-((tert-butyldiphenylsilyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (0.73 g, 1.70 mmol, 1 : 2.1 mixture of *trans*/*cis* diastereoisomers) in diethyl ether (3 mL). The resulting yellow solution was stirred for 15 h at 25 °C and monitored by TLC. The reaction was quenched with water (10 mL) and the organic layer separated. The aqueous layer further extracted with diethyl ether (3 × 10 mL). The etherate fractions were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a cloudy colourless oil (0.92 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded two products both as inseparable mixtures of diastereoisomers of the desired compound (combined yield 0.74 g, 1.38 mmol, 87%, product ratio 1.6 : 1) as a colourless oils;

Product 1: (0.45 g, 0.90 mmol, 53%, *dr* 3 : 1), Colourless oil; R_f 0.38 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2931, 2856, 1712 (C=O), 1625, 1427, 1268, 1172 (C-O), 1105, 1027, 877, 820; *Major diastereoisomer:* δ_H (400 MHz; $CDCl_3$); 0.93-1.09 (10H, m, overlapping signals 3 × CH_3 and C$\underline{H}_a$H$_b$ C-3 THF), 1.17-1.60 (1H, m, overlapping signals CH$_a\underline{H}_b$ C-3 THF),1.26 (1H, dd, *J* 14.5 and 9.9, SiC$\underline{H}_a$H$_b$), 1.31 (3H, t, *J* 7.1 OCH$_2$C$\underline{H}_3$), 1.70 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 1.83 (1H, dd, *J* 14.4 and 4.1, SiCH$_a\underline{H}_b$), 2.17 (1H, app dq, *J* 12.7 and 8.5, CH$_a\underline{H}_b$ C-4 THF), 3.96-4.03 (1H, m, CH C-2 THF), 4.21 (2H, q, *J* 7.1, OC$\underline{H}_2$CH$_3$), 5.66 (1H, app t, *J* 7.7, CH, C-5 THF), 5.90 (1H, d, *J* 0.8, C=CH), 7.58-7.67 (4H, m, Ar), 7.31-7.49 (11H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.3 (OCH$_2\underline{C}$H$_3$), 17.6 (SiCH$_2$), 18.3 (3 × C, ^{t}Bu), 27.8 (3 × CH$_3$, ^{t}Bu), 32.3 (CH$_2$, C-4 THF), 33.5 (CH$_2$, C-3 THF), 60.2 (O$\underline{C}$H$_2$CH$_3$), 75.6 (CH, C-5 THF), 78.4 (CH, C-2 THF), 119.6 ($\underline{C}$H=C), 127.5 (CH, Ar), 127.6 (CH, Ar), 127.7 (CH, Ar), 128.2 (CH, Ar), 128.8 (CH, Ar), 129.2 (CH, Ar), 129.2 (CH, Ar), 134.0 (C, Ar), 134.8 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 139.2 (C, Ar), 160.4 ($\underline{C}$=CH), 165.9 (C=O); *Minor diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 1.04 (9H, s, 3 × CH$_3$), 1.17-1.60 (4H, m, overlapping signals CH$_2$ C-3 THF and C$\underline{H}_a$H$_b$ C-4 THF and SiC$\underline{H}_a$H$_b$), 1.32 (3H, t, *J* 7.1, OCH$_2$C$\underline{H}_3$), 1.87 (1H, dd, *J* 14.4 and 4.1, SiCH$_a\underline{H}_b$), 2.30 (1H, app dtd, *J* 12.5 7.2 and 1.9, CH$_a\underline{H}_b$ C-4 THF), 3.81-3.88 (1H, m, CH C-2 THF), 4.20 (2H, q, *J* 7.1, OC$\underline{H}_2$CH$_3$), 5.81 (1H, d, *J* 1.0, C=CH), 5.91 (1H, app t, *J*

7.7, CH C-5 THF), 7.31-7.49 (11H, m, Ar), 7.58-7.67 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.3 ($OCH_2\underline{C}H_3$), 18.1 ($SiCH_2$), 18.3 (3 × C, ^{t}Bu), 27.8 (3 × CH_3, ^{t}Bu), 33.1 (CH_2, C-4 THF), 34.6 (CH_2, C-3 THF), 60.2 ($O\underline{C}H_2CH_3$), 75.8 (CH, C-5 THF), 78.4 (CH, C-2 THF), 119.3 ($\underline{C}H$=C), 127.6 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 128.0 (CH, Ar), 128.7 (CH, Ar), 129.1 (CH, Ar), 129.2 (CH, Ar), 134.0 (C, Ar), 134.8 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 139.1 (C, Ar), 161.9 (C=CH), 165.9 (C=O); LRMS (EI^+, *m/z*): 498 ($[M]^{+}$, 3%), 441(100), 199 (42), 181 (18), 135 (39), 105 (12); HRMS (ESP^+, *m/z*) 499.2656 $[M+H]^+$, $C_{32}H_{39}O_3Si$ requires 499.2663.

Product 2: (0.29 g, 0.58 mmol, 34%, *dr* 1.7 : 1), Colourless oil; R_f 0.29 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2931, 2858, 1722 (C=O), 1648, 1427, 1223, 1155 (C-O), 1103, 1050, 819; *Major diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 1.02-1.18 (13H, m, overlapping signals 3 × CH_3, $OCH_2C\underline{H}_3$ and $C\underline{H}_aH_b$ C-3 THF), 1.17-1.40 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 1.47-1.55 (1H, m, $SiC\underline{H}_aH_b$), 1.57-1.78 (2H, m, $C\underline{H}_aH_b$ C-4 THF), 2.00 (1H, dd, *J* 14.4 and 4.4, $SiCH_a\underline{H}_b$), 3.97-4.10 (3H, m, overlapping signals $OC\underline{H}_2CH_3$ and CH C-2 THF), 4.49 (1H, dd, *J* 6.0 and 1.5, CH C-5 THF), 6.27 (1H, d, *J* 1.5, C=CH),7.10-7.17 (2H, m, Ar), 7.30-7.46 (9H, m, Ar), 7.66-7.74 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.0 ($OCH_2\underline{C}H_3$), 18.0 ($SiCH_2$), 18.5 (3 × C, ^{t}Bu), 27.9 (3 × CH_3, ^{t}Bu), 31.5 (CH_2, C-4 THF), 32.7 (CH_2, C-3 THF), 59.8 ($O\underline{C}H_2CH_3$), 78.6 (CH, C-2 THF), 81.0 (CH, C-5 THF), 116.0 (C=$\underline{C}$H), 127.6 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 128.7 (CH, Ar), 127.8 (CH, Ar), 129.3 (CH, Ar), 129.3 (CH, Ar), 134.0 (C, Ar), 134.6 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 138.0 (C, Ar), 159.3 (C=CH), 166.4 (C=O); *Minor diastereoisomer:* 1.02-1.18 (12H, m, overlapping signals 3 × CH_3 and $OCH_2C\underline{H}_3$), 1.17-1.40 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.47-1.55 (3H, m, overlapping signals $C\underline{H}_aH_b$ C-4 THF, $CH_a\underline{H}_b$ C-3 THF and $SiC\underline{H}_aH_b$), 1.83-1.89 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 1.93 (1H, dd, *J* 14.5 and 4.7, $SiCH_a\underline{H}_b$), 3.97-4.10 (2H, m, $OC\underline{H}_2CH_3$ overlapping signals with other diastereomer), 4.22 (1H, app tt, *J* 9.1 and 4.6, CH C-2 THF), 4.69 (1H, app tt, *J* 7.8 and 1.4, CH C-5 THF), 6.11 (1H, d, *J* 1.5, C=CH), 7.10-7.17 (2H, m, Ar), 7.30-7.46 (9H, m, Ar), 7.66-7.74 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.0 ($OCH_2\underline{C}H_3$), 18.2 ($SiCH_2$), 18.5 (3 × C, ^{t}Bu), 27.9 (6 × CH_3, ^{t}Bu), 32.5 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 59.8 ($O\underline{C}H_2CH_3$), 78.2 (CH, C-2 THF), 81.1 (CH, C-5 THF), 114.9 (C=CH), 127.5 (CH, Ar), 127.6 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 127.9 (CH, Ar), 129.1 (CH, Ar), 129.2 (CH, Ar), 134.0 (C, Ar), 134.8 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 137.8 (C, Ar), 159.6 ($\underline{C}$=CH), 166.3 (C=O); LRMS (EI^+, *m/z*): 498 ($[M]^{+}$, 3%), 441(100), 199 (42), 181 (18), 135 (39), 105 (12); HRMS (ESP^+, *m/z*) 516.2918 $[M+NH]^+$, $C_{32}H_{42}O_3NSi$ requires 516.2928.

(±)-Ethyl 3-(2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)-3-phenylacrylate (16b)

A 60% dispersion of sodium hydride in mineral oil (0.02 g, 0.50 mmol) was washed with *n*-hexane (2 × 1 mL), dried under reduced pressure and placed under an atmosphere of argon. Diethyl ether (1 mL) was added and the suspension cooled to 0 °C followed by the dropwise addition of triethyl phosphonoacetate (0.10 g, 0.08 mL, 0.45 mmol). The solution was allowed to warm to room temperature, stirred for a further 15 min followed by the dropwise addition of a solution of (±-5-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (0.13 g, 0.40 mmol, only *trans* diastereoisomer) in diethyl ether (1.5 mL). The resulting yellow solution was stirred for 15 h at 25 °C and monitored by TLC. After this time, the reaction was quenched with water (10 mL) and the organic layer separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a colourless oil (0.18 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded two diastereoisomers of the title compound (combined yield 0.15 g, 0.38 mmol, 96%) as colourless oils:

Major diastereoisomer: (0.08 g, 0.20 mmol, 51%); R_f 0.29 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957 (C-H), 1724 (C=O), 16.26 (C=C), 1220 (Si-C), 1154 (C-O), 1095 (C-O), 823 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.36 (3H, s, $SiCH_3$), 0.38 (3H, s, $SiCH_3$), 1.08 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$), 1.12 (1H, dd, *J* 14.2 and 7.8, $SiC\underline{H}_aH_b$), 1.37 (1H, dd, *J* 14.2 and 6.6, $SiCH_a\underline{H}_b$), 1.37-1.46 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.59-1.69 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 1.90-2.00 (2H, m, overlapping signals C-3 and C-4 THF), 4.00 (2H, qd, *J* 7.1 and 2.3, $OC\underline{H}_2CH_3$), 4.19 (1H, dtd, *J* 7.8 6.6 and 1.3, CH C-2 THF), 4.72 (1H, ddd, *J* 8.1, 6.9 and 1.4, CH C-5 THF), 6.18 (1H, d, *J* 1.5, $C{=}C(H)CO_2Et$), 7.13-7.17 (2H, m, Ar), 7.29-7.40 (6H, m, Ar), 7.53-7.58 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −1.9 ($SiCH_3$), 14.1 ($OCH_2\underline{C}H_3$), 24.0 ($SiCH_2$), 32.0 (CH_2, C-4 THF), 34.9 (CH_2, C-3 THF), 59.9 ($O\underline{C}H_2CH_3$), 78.3 (CH, C-2 THF), 81.3 (CH, C-5 THF), 115.0 ($C{=}\underline{C}(H)CO_2Et$), 127.6 (2 × *o*-CH, Ar), 127.8 (*p*-CH, Ar), 127.9 (2 × *m*-CH, Ar), 128.0 (2 × *m*-CH, Ar), 129.1 (*p*-CH, Ar), 133.7 (2 × *o*-CH, Ar), 137.9 (C, Ar), 139.1 (C, Ar), 159.8 ($\underline{C}{=}C(H)CO_2Et$), 166.5 ($C{=}C(H)\underline{C}O_2Et$); LRMS (EI$^+$, *m/z*): 394 (M$^+$, 6%), 349 ([M−OEt]$^+$, 4), 307 (6), 275 (5), 175 (11), 135 (100) 77 (5); HRMS (ESP, *m/z*) 412.2302 $[M+NH_4]^+$, $C_{24}H_{34}O_3NSi$ requires 412.2302.

Minor diastereoisomer: (0.07 g, 0.18 mmol, 45%); R_f 0.49 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957 (C-H), 1711 (C=O), 1626 (C=C), 1267 (Si-C), 1169 (C-O), 1027 (C-O), 823 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.24 (3H, s, $SiCH_3$), 0.26 (3H, s, $SiCH_3$), 1.05 (1H, dd, *J* 14.3 and 7.7, $SiC\underline{H}_aH_b$), 1.26 (1H, dd, *J* 14.3 and 6.5, $SiCH_a\underline{H}_b$), 1.30 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$), 1.44 (1H, dddd, *J* 11.6 10.9 8.9 and7.6, $C\underline{H}_aH_b$ C-3 THF), 1.70 (1H, dddd, *J* 12.3 10.9 9.1 and 7.5, $C\underline{H}_aH_b$ C-4 THF), 1.84 (1H, dddd, 11.6 7.5 5.3 and 2.0, $CH_a\underline{H}_b$ C-3 THF), 2.38 (1H, dtd, *J* 12.3 7.2 and 2.0, $CH_a\underline{H}_b$ C-4 THF), 3.80 (1H, dddd, *J* 8.9 7.7 6.5 and 5.4, CH C-2 THF), 4.18 (2H, q, *J* 7.1, $OC\underline{H}_2CH_3$), 5.86 (1H, dd, *J* 9.1 and 7.0, CH C-5 THF), 7.27-7.38 (8H, m, Ar), 7.45-7.47 (2H, m, *o*-CH SiPh); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −1.9 ($SiCH_3$), 14.4 ($OCH_2\underline{C}H_3$), 23.9 ($SiCH_2$),

33.0 (CH_2, C-4 THF), 35.3(CH_2, C-3 THF), 60.3 ($O\underline{C}H_2CH_3$), 76.3 (CH, C-5 THF), 78.1 (CH, C-2 THF), 119.4 ($C{=}\underline{C}(H)CO_2Et$), 127.8 (2 × *m*-CH, Ar), 127.8 (2 × *m*-CH, Ar), 128.1 (*p*-CH, Ar), 128.8 (2 × *o*-CH, Ar), 129.0 (*p*-CH, Ar), 133.7 (2 × *o*-CH, Ar), 139.3 (C Ar), 139.3 (C Ar), 161.9 ($\underline{C}{=}C(H)CO_2Et$), 166.1 ($C{=}C(H)\underline{C}O_2Et$); LRMS ($EI^+$, *m/z*): 394 ($M^+$, 6%), 349 ($[M{-}OEt]^+$, 4), 307 (6), 275 (5), 175 (11), 135 (100) 77 (5); HRMS (ESP, *m/z*) 395.2036 $[M+H]^+$, $C_{24}H_{31}O_3Si$ requires 395.2037.

Methyl 3-(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)acrylate (19)

To a stirred solution of (±)-ethyl 2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carboxylate (0.38 g, 1.30 mmol) in anhydrous DCM (18 mL) under an atmosphere of nitrogen was added a 1M solution of DIBAL-H (2.6 mL, 2.6 mmol) in toluene at -78 °C. The resulting solution was stirred at -78 C for 1 h and monitored by TLC. The reaction was quenched by adding sat. aq. NH_4Cl (10 mL) and allowed to warm to room temperature. Rochelle's salts (10 mL, sat. aq.) were added and the reaction stirred for 30 min at room temperature. The mixture was diluted with DCM (20 mL) and the organic phase separated. The aqueous phase was extracted with DCM (2 × 20 mL) and the combined organic phase was washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated under reduced pressure to give 2-(dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carbaldehyde as a colourless oil (0.25 g, 1.01 mmol, 78%); R_f 0.16 [20% diethyl ether : hexane]; δ_H (400 MHz; $CDCl_3$) 0.34 (s, $SiCH_3$), 0.36 (s, $SiCH_3$), 1.11 (1H, dd, *J* 14.2 and 8.1, $SiC\underline{H_a}H_b$), 1.21-1.46 (3H, m, $SiCH_a\underline{H_b}$ and CH_2 C-3 THF), 1.79-2.21 (2H, m, CH_2 C-4 THF), 4.04-4.11 (1H, m, CH C-2 THF), 4.25-4.30 (1H, m, CH C-5 THF), 7.33-7.38 (3H, m, Ar), 7.52-7.56 (2H, m, Ar), 9.61 (1H, d, *J* 1.7, CHO); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 23.4 ($SiCH_2$), 27.6 (CH_2, C-4 THF), 34.0 (CH_2, C-3 THF), 79.2 (CH, C-2 THF), 82.0 (CH, C-5 THF), 128.0 (2 × *m*-CH, SiPh), 129.2 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 138.8 (C, SiPh), 203.5 (CO); LRMS (EI^+, *m/z*): M^+ not visible, 233 ($[M{-}Me]^+$ 1%), 219 (19), 191 (9), 135 (100), 105 (11), 75 (15). The impure product was used immediately in the next reaction without further purification:

A 60% dispersion of sodium hydride in mineral oil (0.024 g, 1.00 mmol) was washed with *n*-hexane (2 × 1 mL), dried under reduced pressure and placed under an atmosphere of argon. Diethyl ether (3 mL) was added followed by the dropwise addition of a solution of trimethyl phosphonoacetate (0.20 g, 0.16 mL, 1.10 mmol) in anhydrous diethyl ether (5 mL). The solution was stirred at room temperature for further 15 min followed by the dropwise addition of a solution of 2-(dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carbaldehyde (0.25 g, 1.01 mmol, only *trans* diastereoisomer) in anhydrous diethyl ether (4 mL). The resulting yellow solution was stirred for 16 h at 25 °C and monitored by TLC. After this time, the reaction was quenched with water (10 mL) and the organic layer separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a yellow oil (0.26 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 15% diethyl ether : hexane] afforded the *cis* and *trans* diastereoisomers of the title compound (combined yield 0.164 g, 0.54 mmol, 53%) as colourless oils:

Trans diastereoisomer: (0.13 g, 0.43 mmol, 44%); R_f 0.35 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3069, 2957, 1722 (C=O), 1659 (C=C), 1261, 1164 (C-O), 1112 (C-O), 819 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.33 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$), 1.08 (1H, dd, *J* 14.2 and 7.9, $SiC\underline{H}_aH_b$), 1.32 (1H, dd, *J* 14.2 and 6.5, $SiCH_a\underline{H}_b$), 1.39-1.49 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.59-1.68 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.93-2.00 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.16 (1H, dtd, *J* 12.1 7.6 and 3.4, $CH_a\underline{H}_b$ C-4 THF), 3.73 (3H, s, OCH_3), 4.08-4.15 (1H, m, CH C-2 THF), 4.57 (1H, app tdd, *J* 7.2 4.9 and 1.4, CH C-5 THF), 5.99 (1H, dd, *J* 15.6 and 1.4, $HC=C(\underline{H})CO_2Me$), 6.89 (1H, dd, *J* 15.6 and 4.9, $\underline{H}C=C(H)CO_2Me$), 7.34-7.36 (3H, m, SiPh), 7.51-7.54 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −1.9 ($SiCH_3$), 23.9 ($SiCH_2$), 32.5 (CH_2, C-4 THF), 34.8 (CH_2, C-3 THF), 51.6 (OCH_3), 76.7 (CH, C-5 THF), 77.7 (CH, C-2 THF), 119.2 ($HC=\underline{C}(H)CO_2Me$), 127.9 (2 × *m*-CH, SiPh), 129.1 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.1 (C, SiPh), 149.6 ($H\underline{C}=C(H)CO_2Me$), 167.2 ($HC=C(H)\underline{C}O_2Me$); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 289 ([M-Me]$^+$, 22%), 227 (26), 185 (32), 151 (37), 135 (100), 121 (17); HRMS (ESP, *m/z*) 327.1381 [M+Na]$^+$, $C_{17}H_{24}O_3Si$ requires 327.1387.

Cis diastereoisomer: (0.034 g, 0.11 mmol, 11%); R_f 0.48 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3069, 2952, 1720 (C=O), 1646 (C=C), 1176 (C-O), 1112, 1025 (C-O), 818 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.32 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.09 (1H, dd, *J* 14.3 and 8.6, $SiC\underline{H}_aH_b$), 1.34 (1H, dd, *J* 14.3 and 6.0, $SiCH_a\underline{H}_b$), 1.37-159 (2H, m, overlapping signals $C\underline{H}_aH_b$ C-3 THF and $C\underline{H}_aH_b$ C-4 THF), 1.90-1.97 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.37 (1H, dtd, *J* 12.2 7.3 and 2.4, $CH_a\underline{H}_b$ C-4 THF), 3.70 (3H, s, OCH_3), 4.01 (1H, tt, *J* 8.5 and 5.7, CH C-2 THF), 5.39 (1H, app q, *J* 7.4, CH C-5 THF), 5.73 (1H, dd, *J* 11.6 and 1.3, $HC=C(\underline{H})CO_2Me$), 6.27 (1H, dd, *J* 11.6 and 7.4, $\underline{H}C=C(H)CO_2Me$), 7.34-7.36 (3H, m, SiPh), 7.51-7.54 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −1.9 ($SiCH_3$), 23.7 ($SiCH_2$), 33.2 (CH_2, C-4 THF), 34.9 (CH_2, C-3 THF), 51.4 (OCH_3), 74.9 (CH, C-5 THF), 77.6 (CH, C-2 THF), 118.3 ($HC=\underline{C}(H)CO_2Me$), 127.9 (2 × *m*-CH, SiPh), 129.1 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.2 (C, SiPh), 152.9 ($H\underline{C}=C(H)CO_2Me$), 166.5 ($HC=C(H)\underline{C}O_2Me$); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 289 ([M-Me]$^+$, 22%), 227 (26), 185 (32), 151 (37), 135 (100), 121 (17); HRMS (ESP, *m/z*) 327.1382 [M+Na]$^+$, $C_{17}H_{24}O_3Si$ requires 327.1387.

(±)-1-Phenyl-1-(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)but-3-en-1-ol (20)

To a stirred solution of phenyl(5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)methanone (0.18 g, 0.52 mmol) in THF (3.5 mL) at 0 °C was added a solution of allylmagnesium chloride (2 M solution in THF, 0.32 mL, 0.64 mmol). The mixture was stirred at 0 °C for 1 h then warmed to room temperature and stirred for a further 14 h. The mixture was cooled to 0 °C, quenched with 10% *w*/*v* aqueous ammonium chloride solution (10 mL), warmed to room temperature and partitioned between water and diethyl ether. The organic phase was separated and the aqueous phase extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.22 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded two diastereoisomers of the title compound (combined yield 0.17 g, 0.44 mmol, 85%) as colourless oils:

Major diastereoisomer: (0.12 g, 0.31 mmol, 60%); R_f 0.54 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3556 (O-H), 2941, 2864, 1640 (C=C), 1463, 1446, 1183, 1066, 881; δ_H (400 MHz; $CDCl_3$) 0.85 (1H, dd, *J* 14.4 and 6.3, SiC$\underline{H}_a$H$_b$), 0.94-1.02 (22H, m, overlapping signals $^i\underline{Pr}_3$SiCH$_a\underline{H}_b$), 1.41-1.51 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.78-1.88 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 1.90-1.99 (2H, m, overlapping signals CH$_a\underline{H}_b$ C-3 and CH$_a\underline{H}_b$ C-4 THF), 2.46 (1H, s, OH), 2.54 (1H, dd, *J* 13.9 and 8.0, C$\underline{H}_a$H$_b$CH=CH$_2$), 2.81 (1H, dd, *J* 13.9 and 6.5 CH$_a\underline{H}_b$CH=CH$_2$), 3.96-4.03 (1H, m, CH C-2 THF), 4.24 (1H, dd, *J* 8.9 and 6.0, CH C-5 THF), 5.03 (1H, dd, *J* 10.2 and 1.0, CH=CH$_{trans}\underline{H}_{cis}$), 5.08 (1H, br d, *J* 17.2, CH=C$\underline{H}_{trans}$H$_{cis}$), 5.55 (1H, dddd, *J* 17.2 10.1 7.8 and 6.6, C$\underline{H}$=CH$_{trans}$H$_{cis}$), 7.23 (1H, br t, *J* 7.0, *p*-CH Ph), 7.32 (2H, br t, *J* 7.5, 2 × *m*-CH Ph), 7.48 (2H, br d, *J* 8.0, 2 × *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^{i}Pr$_3$), 17.5 (SiCH$_2$), 18.9 (3 × CH$_3$ Si^{i}Pr$_3$), 18.9 (3 × CH$_3$ Si^{i}Pr$_3$), 27.6 (CH$_2$, C-4 THF), 36.3 (CH$_2$, C-3 THF), 43.3 ($\underline{C}$H$_2$CH=CH$_2$), 76.9 (COH), 78.3 (CH, C-2 THF), 84.4 (CH, C-5 THF), 118.9 (CH=C$\underline{H}_2$), 126.3 (2 × *o*-CH, Ph), 126.7 (*p*-CH, Ph), 127.8 (2 × *m*-CH, Ph), 133.5 (C$\underline{H}$=CH$_2$), 143.9 (C, Ph); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 345 ([M−^{i}Pr]$^+$, 27%), 303 (25), 261 (13), 241 (31), 157 (100), 131 (80), 115 (58), 105 (63), 103 (70), 87 (27), 75 (43); HRMS (ESP, *m/z*) 406.3131 [M+NH$_4$]$^+$, $C_{24}H_{44}O_2NSi$ requires 406.3136.

Minor diastereoisomer: (0.05 g, 0.13 mmol, 25%); R_f 0.68 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3560 (O-H), 2941, 2864, 1640 (C=C), 1463, 1447, 1179, 1066, 881; δ_H (400 MHz; $CDCl_3$) 0.93 (1H, dd, *J* 14.4 and 6.3, SiC$\underline{H}_a$H$_b$), 1.05-1.13 (22H, m, overlapping signals $^i\underline{Pr}_3$SiCH$_a\underline{H}_b$), 1.35-1.48 (2H, m, C-3/4 THF), 1.63-1.73 (2H, m, C-3/4 THF), 1.93-2.03 (1H, m, C-3/4 THF), 2.41 (1H, s, OH), 2.69 (1H, dd, *J* 14.3 and 6.6, C$\underline{H}_a$H$_b$CH=CH$_2$), 2.81 (1H, dd, *J* 14.3 and 7.8 CH$_a\underline{H}_b$CH=CH$_2$), 4.21-4.28 (2H, m, overlapping signals CH C-2 THF and CH C-5 THF), 4.95-5.04 (2H, m, overlapping signals CH=C$\underline{H}_{trans}\underline{H}_{cis}$), 5.58 (1H, dddd, *J* 17.0 10.2 7.8 and 6.6, C$\underline{H}$=CH$_{trans}$H$_{cis}$), 7.22 (1H, br t, *J* 7.2, *p*-CH Ph), 7.32 (2H, br dd, *J* 8.1 and 7.2, 2 × *m*-CH Ph), 7.38

(2H, br d, *J* 8.1, 2 × *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH Si^iPr_3), 17.6 ($SiCH_2$), 19.0 (6 × CH_3 Si^iPr_3), 27.7 (CH_2, THF), 36.4 (CH_2, THF), 45.8 ($\underline{C}H_2CH=CH_2$), 76.7 (COH), 79.8 (CH, C-2 THF), 84.4 (CH, C-5 THF), 118.1 ($CH=C\underline{H_2}$), 125.3 (2 × *o*-CH, Ph), 126.6 (*p*-CH, Ph), 128.1 (2 × *m*-CH, Ph), 134.1 ($C\underline{H}=CH_2$), 142.8 (C, Ph); LRMS (EI^+, *m/z*): M^+ not visible, 345 ($[M-{}^iPr]^+$, 20%), 303 (28), 261 (35), 241 (26), 157 (100), 131 (89), 115 (78), 105 (85), 103 (91), 75 (68); HRMS (ESP, *m/z*) 406.3130 $[M+NH_4]^+$, $C_{24}H_{44}O_2NSi$ requires 406.3136.

(±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanol (21a)

The following procedure was carried out on a range of scales from 0.2 mmol to 2 mmol: To a stirred solution of 2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (0.13 g, 0.40 mmol) in HPLC grade methanol (3.0 mL) at 0 °C was added in one portion $NaBH_4$ (0.02 g, 0.52 mmol). The mixture was stirred at 0 °C until effervescence had ceased then warmed to room temperature and stirred for a further 2 h. The reaction was quenched by the addition of acetic acid (10 drops), concentrated to approximately one quarter of the volume under reduced pressure and partitioned between dichloromethane (10 mL) and water (10 mL). The organic phase was separated and the aqueous phase extracted with dichloromenthane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude product (0.11 g) as a cloudy colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 30% diethyl ether : hexane] afforded title compound as an inseparable mixture of the two diastereoisomers (combined yield 0.11 g, 0.34 mmol, 85%, *dr* 2.5 : 1) as colourless oils; R_f 0.36 [30% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3440 (O-H), 2955, 2864, 1452, 1248, 1194, 1026, 833; *Major Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.38 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$), 1.13 (1H, dd, *J* 14.2 and 7.6, $SiC\underline{H_a}H_b$), 1.12 (1H, dd, *J* 14.2 and 6.6, $SiCH_a\underline{H_b}$), 1.37-1.66 (2H, m, $C\underline{H_a}H_b$ C-3 and $C\underline{H_a}H_b$ C-4 THF), 1.73 (1H, dddd, *J* 12.5, 8.2, 7.3 and 2.9, $CH_a\underline{H_b}$ C-4 THF), 1.81-2.02 (1H, m, $CH_a\underline{H_b}$ C-3 THF), 3.03 (1H, d, *J* 2.2, OH), 4.06 (1H, q, *J* 7.4, CH C-5 THF), 4.12-4.20 (1H, m, CH C-2 THF), 4.39 (1H, dd, *J* 7,7 and 2.2, $\underline{H}COH$), 7.25-7.42 (8H, m, Ar), 7.54-7.59 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −2.0 ($SiCH_3$), 23.7 ($SiCH_2$), 28.6 (CH_2, C-4 THF), 35.2 (CH_2, C-3 THF), 77.3 (COH), 77.5 (CH, C-2 THF), 82.7 (CH, C-5 THF), 127.2 (CH, Ar), 127.9 (CH, Ar), 127.9 (CH, Ar), 128.4 (CH, Ar), 129.1 (CH, Ar), 133.6 (CH, Ar), 139.1 (C, Ar), 140.5(C, Ar); *Minor Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.35 (3H, s, $SiCH_3$), 0.36 (3H, s, $SiCH_3$), 1.10 (1H, dd, *J* 14.2 and 8.2, $SiC\underline{H_a}H_b$), 1.36 (1H, dd, *J* 14.2 and 6.3, $SiCH_a\underline{H_b}$), 1.37-1.66 (2H, m, $C\underline{H_a}H_b$ C-3 and $C\underline{H_a}H_b$ C-4 THF), 1.81-2.02 (2H, m, $CH_a\underline{H_b}$ C-3 and $CH_a\underline{H_b}$ C-4 THF), 2.62 (1H, d, *J* 2.5, OH), 4.12-4.20 (2H, m, CH C-2 THF and CH C-5 THF), 4.91(1H, br t, *J* 3.1, $\underline{H}COH$), 7.25-7.42 (8H, m, Ar), 7.54-7.59 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), -2.0 ($SiCH_3$), 24.2 ($SiCH_2$), 25.7 (CH_2, C-4 THF), 35.0 (CH_2, C-3 THF), 74.2

(COH), 78.5 (CH, C-2 THF), 82.0 (CH, C-5 THF),126.1 (CH, Ar), 127.3 (CH, Ar), 128.0 (CH, Ar), 128.2 (CH, Ar), 129.0 (CH, Ar), 133.6 (CH, Ar), 139.1 (C, Ar), 140.5(C, Ar); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 219 ([M−BnOH]$^+$, 12%), 135 (100), 107 (7), 75 (13); HRMS (ESP, *m/z*) 344.2039 [M+NH$_4$]$^+$, $C_{20}H_{30}O_2NSi$ requires 344.2040. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the $\underline{H}$COH proton at 4.39 (major diastereoisomer) and 4.91 ppm (minor diastereoisomer).

(±)-Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanol (21b)

To a stirred solution of phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanone (0.40 g, 1.16 mmol) in HPLC grade methanol (7.0 mL) at 0 °C was added in one portion NaBH$_4$ (0.11 g, 2.90 mmol). The mixture was stirred at 0 °C until effervescence had ceased then warmed to room temperature and stirred for a further 15 h. The reaction was quenched by the addition of acetic acid (0.1 mL), concentrated to approximately one quarter of the volume under reduced pressure and partitioned between dichloromethane (10 mL) and water (10 mL). The organic phase was separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO$_4$), filtered and concentrated *in vacuo* to give the crude product (0.33 g) as a cloudy colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded title compound as an inseparable mixture of the two diastereoisomers (combined yield 0.31 g, 0.89 mmol, 77 %, dr 2.6 : 1) as a colourless oil; R_f 0.29 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3426 (O-H), 2940, 2864, 1462, 1195, 1027, 881; *Major Diastereoisomer:* δ_H (400 MHz; CDCl$_3$) 0.94 (1H, dd, *J* 14.5 and 6.8, SiC$\underline{H}_a$H$_b$), 1.03-1.12 (21H, m, overlapping signals Si$^i\underline{Pr}_3$), 1.12 (1H, dd, *J* 14.5 and 7.4, SiCH$_a\underline{H}_b$), 1.42-1.79 (3H, m, CH$_2$ C-3 and C$\underline{H}_a$H$_b$C-4 THF), 2.03-2.15 (1H, m, CH$_a\underline{H}_b$ C-4 THF), 3.06 (1H, d, *J* 1.6, OH), 4.08 (1H, q, *J* 7.4, C-5 THF), 4.19-4.29 (1H, m, overlapping signals C-2 THF), 4.42 (1H, dd, *J* 7.9 and 1.6, $\underline{H}$COH), 7.24-7.39 (5H, m, Ph); δ_C (100.6 MHz; CDCl$_3$) 11.5 (3 × CH Si^{i}Pr$_3$), 17.7 (SiCH$_2$), 19.0 (6 × CH$_3$ Si^{i}Pr$_3$), 28.8 (CH$_2$, C-4 THF), 36.1 (CH$_2$, C-3 THF), 77.5 (COH), 77.6 (CH, C-2 THF), 83.0 (CH, C-5 THF), 127.2 (2 × *o*-CH, Ph), 128.0 (*p*-CH, Ph), 128.4 (2 × *m*-CH, Ph), 140.4 (C, Ph); *Minor Diastereoisomer:* δ_H (400 MHz; CDCl$_3$) 0.92 (1H, dd, *J* 14.4 and 7.9, SiC$\underline{H}_a$H$_b$), 1.03-1.12 (22H, m, overlapping signals $^i\underline{Pr}_3$SiCH$_a\underline{H}_b$), 1.42-179 (2H, m, overlapping signals C$\underline{H}_a$H$_b$ C-3 and C$\underline{H}_a$H$_b$ C-4 THF), 1.89 (1H, dddd, *J* 12.2, 10.8, 9.1 and 7.6, CH$_a\underline{H}_b$ C-3 THF), 2.03-2.15 (1H, m, CH$_a\underline{H}_b$ C-4 THF), 2.59 (1H, d, *J* 2.5, OH), 4.19-4.29 (2H, m, overlapping signals C-5 and C-2 THF), 4.91 (1H, dd appearing as br t, *J* 2.5, $\underline{H}$COH), 7.24-7.39 (5H, m, Ph); δ_C (100.6 MHz; CDCl$_3$) 11.4 (3 × CH Si^{i}Pr$_3$), 17.1 (CH$_2$, ^{i}Pr$_3$SiCH$_2$), 19.0 (6 × CH$_3$ Si^{i}Pr$_3$), 26.0 (CH$_2$, C-4 THF), 35.7 (CH$_2$, C-3 THF), 74.3 (COH), 78.7 (CH, C-2 THF), 82.2 (CH, C-5 THF), 126.1 (2 × *o*-CH, Ph), 127.4 (*p*-CH, Ph), 128.3 (2 × *m*-CH, Ph), 140.5 (C, Ph); LRMS

(EI$^+$, *m/z*): M$^+$ not visible, 305 ([M−^{i}Pr]$^+$, 9%), 287 (3), 263 (6), 241 (24), 157 (100), 131 (68), 103 (86), 75 (50); HRMS (ESP, *m/z*) 366.2822 [M+NH$_4$]$^+$, $C_{21}H_{40}O_2NSi$ requires 366.2823. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the HCOH proton at 4.42 (major diastereoisomer) and 4.91 ppm (minor diastereoisomer).

((2-(benzyloxy(phenyl)methyl)tetrahydrofuran-5-yl)methyl)dimethyl(phenyl)silane (22)

A 60% dispersion of sodium hydride in mineral oil (12.0 mg, 0.50 mmol) was washed with *n*-hexane (2 × 1 mL), dried under reduced pressure and placed under an atmosphere of argon. To the resulting suspension dissolved in THF (1.5 mL) was added, dropwise, benzyl bromide (0.06 g, 0.04 mL, 0.35 mmol) and a solution of (2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanol **21a** (0.13 g, 0.38 mmol) in THF (1 mL) at room temperature. The resulting solution was stirred for 15 h at 30 °C and monitored by TLC. After this time, the reaction was partitioned between water (10 mL) and DCM (10 mL) and the organic layer separated. The aqueous layer was extracted with DCM (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a colourless oil (0.26 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the title compound as an inseparable mixture of 4 diastereoisomers (combined yield 0.13 g, 0.31 mmol, 89%) as a colourless oil; R_f 0.76 [20% diethyl ether : hexane]; LRMS (EI$^+$, *m/z*): 416 ([M]$^+$, 1%), 241 (9), 219 (10), 197 (12), 135 (100), 91 (72). Full characterisation of the product was not possible because of the number of diastereoisomers present. The material was used in the next step without further purification.

(±)-(5-(Benzyloxy(phenyl)methyl)tetrahydrofuran-2-yl)methanol (28)

(5-(Benzyloxy(phenyl)methyl)tetrahydrofuran-2-yl)methanol was prepared according to the procedure reported by Fleming *et al.*[38] To a stirred solution of ((5-(benzyloxy(phenyl)methyl)tetrahydrofuran-2-yl)methyl)dimethyl(phenyl)silane (0.12 g, 0.31 mmol) in peracetic acid (30% *wt* sol. in acetic acid, 3 mL) was added in one portion mercury (II) acetate (0.11 g, 0.35 mmol). The reaction was stirred for 2 h then washed with water (10 mL), sat. NaS_2O_3 (10 mL), sat. $NaHCO_3$ (10 mL) The aqueous layer was extracted with DCM (3 × 10 mL) and the organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a white solid (0.19 g). Purification by flash column chromatography [silica gel, gradient elution 50% hexane : diethyl ether – 100% diethyl ether] isolated a single diastereoisomer of the title compound (0.03 g, 0.10 mmol, 32%) as a colourless viscous oil; R_f 0.14 [80% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3439 (O-H), 3062, 3030, 2870, 1495, 1454, 1062 (C-O); δ_H (400 MHz; $CDCl_3$) 1.55-1.67 (3H, m, overlapping signals

CH_2 C-4 and $C\underline{H}_aH_b$ C-3 THF), 1.73-1.82 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.16 (1H, br s, OH), 3.43 (1H, app dd, *J* 11.1 and 5.1, $C\underline{H}_aH_bOH$), 3.66 (1H, app br d, *J* 11.7, $CH_a\underline{H}_bOH$), 4.04-4.10 (1H, m, CH C-2 THF), 4.24-4.31 (2H, m, overlapping signals CH C-5 THF and $\underline{H}COBn$), 4.34 (1H, d, *J* 12.1 $PhC\underline{H}_aH_bO$), 4.56 (1H, d, *J* 12.1, $PhCH_a\underline{H}_bO$), 7.24-7.39 (10H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 27.3 (CH_2, C-3 THF), 28.9 (CH_2, C-4 THF), 65.0 (CH_2OH), 70.6 ($Ph\underline{C}H_2O$), 80.1 (CH, C-2 THF), 82.5 (CH, C-5 THF), 84.0 ($\underline{H}COBn$), 127.6 (p-CH, Ar), 127.9 (2 × o-CH, Ar), 128.0 (2 × *o*-CH, Ar), 128.2 (*p*-CH, Ar), 128.4 (2 × *m*-CH, Ar), 128.5 (2 × *m*-CH, Ar), 138.5 (C, Ar), 139.0 (C, Ar); LRMS (EI^+, *m/z*): 298 ($[M]^+$, 1%), 197 (26), 101 (23), 91 (100), 57 (28); HRMS (ESP, *m/z*) 316.1902 $[M+NH_4]^+$, $C_{19}H_{26}O_3N$ requires 316.1907.

(±)-Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methyl acetate (23)

To a stirred solution of phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanol (0.05 g, 0.14 mmol) in DCM (5 mL) was added acetic anhydride (20.0 μL, 0.21 mmol) and in one portion DMAP (4.00 mg, 0.03 mmol, 20 mol%). The reaction mixture was stirred at room temperature and monitored by TLC. After 15 h the reaction was quenched with a saturated solution of $NaHCO_3$ (3 mL). The organic phase was separated and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude product (0.03 g) as a colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded title compound as an inseparable mixture of the two diastereoisomers (combined yield 31.0 mg, 0.08 mmol, 57%, *dr* 2.4 : 1) as colourless oils; R_f 0.58 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2940, 2864, 1742 (C=O), 1462, 1368, 1232, 1022, 882; *Major Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.91 (1H, dd, *J* 14.5 and 6.7, $SiC\underline{H}_aH_b$), 0.99-1.10 (22H, m, overlapping signals $\underline{^iPr_3}SiCH_a\underline{H}_b$), 1.38-1.48 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.50-1.59 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.67-1.74 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 1.93-2.05 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.07 (3H, s, CO_2CH_3), 4.11-4.18 (1H, m, CH C-2 THF), 4.29-4.35 (1H, m, CH C-5 THF), 5.61 (1H, d, *J* 7.9, HCO), 7.27-7.36 (5H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^iPr_3), 17.0 ($SiCH_2$), 19.0 (6 × CH_3 Si^iPr_3), 21.4 (CH_3, CO_2CH_3), 29.3 (CH_2, C-4 THF), 35.8 (CH_2, C-3 THF), 77.5 (CH, C-2 THF), 78.4 (HCO), 79.8 (CH, C-5 THF), 127.7 (CH, Ar), 128.2 (CH, Ar), 128.5 (CH, Ar), 137.9 (C, Ar), 170.4 (C, CO_2CH_3); *Minor Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.85 (1H, dd, *J* 14.4 and 7.4, $SiC\underline{H_a}H_b$), 0.99-1.10 (22H, m, overlapping signals $\underline{^iPr_3}SiCH_a\underline{H}_b$), 1.38-1.48 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.79-1.88 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.93-2.05 (2H, m, $CH_a\underline{H}_b$ C-3 and $CH_a\underline{H}_b$ C-4 THF), 2.10 (3H, s, CO_2CH_3), 3.97 (1H, dtd, *J* 9.0 7.1 and 5.1, CH C-2 THF), 4.29-4.35 (1H, m, CH C-5 THF), 5.76 (1H, d, *J* 6.6, HCO), 7.27-7.36 (5H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^iPr_3), 17.0 ($SiCH_2$), 19.0 (6 × CH_3 Si^iPr_3), 21.4 ($CO_2\underline{C}H_3$), 28.4 (CH_2, C-4 THF), 35.6 (CH_2, C-3 THF), 77.6

(HCO), 78.1 (CH, C-2 THF), 80.0 (CH, C-5 THF), 127.5 (CH, Ar), 128.0 (CH, Ar), 128.2 (CH, Ar), 137.8 (C, Ar), 170.4 (C, CO_2CH_3); LRMS (EI^+, *m/z*): M^+ not visible, 331 ($[M-CO_2Me]^+$, 2%), 241 (18), 173 (100), 157 (71), 115 (25), 75 (19); HRMS (ESP, *m/z*) 391.2665 $[M+H]^+$, $C_{20}H_{39}O_3Si$ requires 391.2663. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the $\underline{H}CO$ proton at 5.61(major diastereoisomer) and 5.76 ppm (minor diastereoisomer).

(±)-Phenyl-(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methyl 4-nitrobenzoate (24)

To a stirred solution of 4-nitrobenzoic acid (1.00 g, 6.00 mmol) in DCM (10 mL) at room temperature was added oxalyl chloride (1.50 g, 1.05 mL, 12.0 mmol) and DMF (5 drops). The reaction was stirred for 3 h at room temperature and the volatiles removed under reduced pressure to give a crystalline solid. The residue was taken up in DCM (10 mL) to give a 0.6 M solution of 4-nitrobenzoyl chloride in DCM which was used immediately in the next reaction.

To a stirred solution of phenyl(5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)methanol (0.31 g, 0.89 mmol) in DCM (2 mL) was added a solution of freshly prepared 4-nitrobenzoyl chloride in DCM (0.6 M, 1.70 mL, 1.00 mmol). To the resulting yellow/orange solution was added dropwise triethylamine (0.20 g, 0.30 mL, 2.00 mmol) and DMAP (1 crystal). After 24 h the reaction had become a red/brown colour and was partitioned between water (10 mL) and DCM (10 mL). The organic phase was separated, washed with a 10% *w*/*v* aqueous sodium hydrogen carbonate solution (10 mL) and the aqueous phase extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a brown gum. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded title compound as an inseparable mixture of diastereoisomers (combined yield 0.29 g, 0.64 mmol, 72%, *dr* 3 : 1) as colourless viscous oils; R_f 0.44 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2941, 2864, 1727 (C=O), 1529 (N=O), 1463, 1346 (N=O), 1270, 1101, 882; *Major Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.84-1.08 (23H, m, overlapping signals $^{i}\underline{Pr}_3SiC\underline{H}_2$), 1.45-1.55 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.60-1.67 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.80 (1H, dtd, *J* 12.6 7.5 and 2.3, $CH_a\underline{H}_b$ C-4 THF), 2.02-2.13 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 4.20 (1H, tt, *J* 8.4 and 5.5, CH C-2 THF), 4.46-4.53 (1H, m, CH C-5 THF), 5.89 (1H, d, *J* 8.0, HCO), 7.31-7.46 (5H, m, Ar), 8.23-8.32 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH $Si^{i}Pr_3$), 17.0 ($SiCH_2$), 19.0 (6 × CH_3 $Si^{i}Pr_3$), 29.4 (CH_2, C-4 THF), 36.3 (CH_2, C-3 THF), 77.7 (CH, C-2 THF), 80.0 (CH, C-5 THF), 80.1 (HCO), 123.5 (CH, Ar), 127.7 (CH, Ar), 128.5 (CH, Ar), 128.7 (CH, Ar), 131.0 (CH, Ar), 136.2 (C, Ar), 137.2 (C, Ar), 150.6 (C, Ar), 164.0 (C=O); *Minor Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.84-1.08 (23H, m, overlapping signals $^{i}\underline{Pr}_3SiC\underline{H}_2$), 1.45-1.55 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.87-1.97 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 2.02-2.13 (1H, m, $CH_a\underline{H}_b$ C-3 and $CH_a\underline{H}_b$ C-4 THF), 3.97-4.20 (1H, m, CH C-2 THF), 4.46-4.53 (1H, m, CH

C-5 THF), 6.04 (1H, d, *J* 4.4, HCO), 7.31-7.46 (5H, m, Ar), 8.23-8.32 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^iPr_3), 17.1 ($SiCH_2$), 19.0 (6 × CH_3 Si^iPr_3), 28.5 (CH_2, C-4 THF), 35.9 (CH_2, C-3 THF), 78.4 (CH, C-2 THF), 79.2 (HCO), 80.0 (CH, C-5 THF), 123.7 (CH, Ar), 127.5 (CH, Ar), 128.4 (CH, Ar), 128.8 (CH, Ar), 130.9 (CH, Ar), 136.0 (C, Ar), 137.0 (C, Ar), 150.7 (C, Ar), 163.9 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 280 (100), 241 (5), 157 (46), 150 (30), 115 (14), 91 (11); HRMS (ESP, *m/z*) 498.2664 $[M+H]^+$, $C_{28}H_{40}O_5NSi$ requires 498.2670. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the $\underline{H}CO$ proton at 5.89 (major diastereoisomer) and 6.04 ppm (minor diastereoisomer).

O-(2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methyl-*S*-methyl carbonodithioate

O-(2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methyl-*S*-methyl carbonodithioate was prepared according to the procedure reported by Calter *et al.*[47] To a stirred solution of (2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanol (0.41 g, 1.30 mmol) in THF (25 mL) at 0 °C was added carbon disulphide (5.41 mL, 90.0 mmol) and diiodomethane (5.30 mL, 85.0 mmol). The mixture was stirred at 0 °C for 30 min followed by the addition of sodium hydride (60% suspension in mineral oil, 0.10 g, 2.50 mmol). The reaction was stirred for 1 h at 0 °C and then quenched by the addition of crushed ice (30 g) and allowed to warm to room temperature. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a yellow oil (0.59 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the title compound as inseparable mixture of diastereoisomers (combined yield 0.37 g, 0.85 mmol, 69%, *dr* 2.5 : 1) as a colourless oil; R_f 0.75 and 0.70 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2954, 2864, 1427, 1209, 1112, 1049, 819; *Major Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.39 (3H, s, $SiCH_3$), 0.41 (3H, s, $SiCH_3$), 1.14 (1H, dd, *J* 14.4 and 6.9, $SiC\underline{H}_aH_b$), 1.33 (1H, dd, *J* 14.4 and 7.4, $SiCH_a\underline{H}_b$), 1.39-1.49 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.60-1.70 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.78-1.86 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 1.89-2.07 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.59 (3H, s, SCH_3), 4.15 (1H, dtd, *J* 8.9 7.1, 5.2, CH C-2 THF), 4.55 (1H, q, *J* 7.2, C-5 THF), 6.51 (1H, d, *J* 7.1, HCOC), 7.32-7.44 (8H, m, Ar), 7.59-7.61 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 19.0 (SMe), 23.5 ($SiCH_2$), 29.0 (CH_2, C-4 THF), 35.2 (CH_2, C-3 THF), 77.7 (CH, C-2 THF), 79.7 (CH, C-5 THF), 86.7 ($H\underline{C}OC$), 127.9 (CH, Ar), 128.1 (CH, Ar), 128.5 (2 overlapping CH, Ar), 129.0 (CH, Ar), 133.8 (CH, Ar), 136.7 (CH, Ar), 139.2 (C, Ar), 214.9 ($O\underline{C}S_2Me$); *Minor Diastereoisomer:* δ_H (400 MHz; $CDCl_3$) 0.34 (3H, s, $SiCH_3$), 0.35 (3H, s, $SiCH_3$), 1.09 (1H, dd, *J* 14.5 and 6.8, $SiC\underline{H}_aH_b$), 1.29 (1H, dd, *J* 14.5 and 7.0,

$SiCH_a\underline{H}_b$), 1.39-1.49 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.89-2.07 (3H, m, $CH_a\underline{H}_b$ C-3 and CH_2 C-4 THF), 2.59 (1H, s, SCH_3), 4.02-4.09 (1H, m, CH C-2 THF), 4.49 (1H, td, *J* 7.1 and 4.7, CH C-5 THF), 6.61 (1H, d, *J* 4.7, $\underline{H}COC$), 7.32-7.44 (8H, m, Ar), 7.54-7.57 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −2.3 ($SiCH_3$), 19.1 (SMe), 23.7 ($SiCH_2$), 28.1 (CH_2, C-4 THF), 35.0 (CH_2, C-3 THF), 78.1 (CH, C-2 THF), 80.0 (CH, C-5 THF), 86.1 (COH), 127.6 (CH, Ar), 127.8 (CH, Ar), 128.2 (CH, Ar), 128.4 (CH, Ar), 129.0 (CH, Ar), 133.7 (CH, Ar), 139.2 (C, Ar), 214.9 ($O\underline{C}S_2Me$), one aromatic carbon not visible; HRMS (ESP, *m/z*) 434.1635 $[M+NH_4]^+$, $C_{22}H_{32}O_2NSSi$ requires 434.1638. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the $\underline{H}COH$ proton at 6.51 (major diastereoisomer) and 6.61 ppm (minor diastereoisomer).

(±)-((5-Benzyltetrahydrofuran-2-yl)methyl)dimethyl(phenyl)silane (25)

A stirred solution of *O*-(5-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-2-yl)(phenyl)methyl-*S*-methyl carbonodithioate (0.20 g, 0.48 mmol) and tri-*n*-butyltin hydride (0.67 mL, 2.50 mmol) in toluene (5.5 mL) was degassed with nitrogen. To the reaction mixture at reflux temperature was added portionwise AIBN (3 × 0.005 g, 0.05 mmol, 10 mol%), after 3 h the reaction was cooled and concentrated *in vacuo* to yield the impure product as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the title compound as a single diastereoisomer (0.13 g, 0.40 mmol, 84%) as a colourless oil (Found: C, 77.1; H, 8.4. $C_{20}H_{26}OSi$ requires C, 77.4; H, 8.4%); R_f 0.4 [10% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957, 1247, 1112, 1074, 835, 819; δ_H (600 MHz; $CDCl_3$) 0.31 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.09 (1H, dd, *J* 14.2 and 8.1, $SiC\underline{H}_aH_b$), 1.32 (1H, dd, *J* 14.2 and 6.3, $SiCH_a\underline{H}_b$), 1.35-1.41 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.52-1.58 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.90-1.96 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-4 and $CH_a\underline{H}_b$ C-3 THF), 2.67 (1H, dd, *J* 13.5 and 6.8, $PhC\underline{H}_aH_b$), 2.91 (1H, dd, *J* 13.5 and 6.2, $PhCH_a\underline{H}_b$), 4.11 (1H, app tt, *J* 8.2 and 5.8, CH C-2 THF), 4.55 (1H, app dq, *J* 7.9 and 6.4, CH C-5 THF), 7.19-7.21 (3H, m, Ar), 7.26-7.31 (2H, m, Ar), 7.33-7.37 (3H, m, Ar), 7.52-54 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −1.9 ($SiCH_3$), 24.2 ($SiCH_2$), 32.2 (CH_2, C-4 THF), 35.0 (CH_2, C-3 THF), 42.5 ($PhCH_2$), 76.7 (CH, C-2 THF), 78.9 (CH, C-5 THF), 126.2 (CH, Ar), 127.9 (CH, Ar), 128.3 (CH, Ar), 129.0 (CH, Ar), 129.4 (CH, Ar), 133.8 (CH, Ar), 139.2 (C, Ar), 139.4 (C, Ar); LRMS (EI^+, *m/z*): M^+ not visible, 295 ($[M-Me]^+$, 2%), 233 (4), 219 (19), 135 (100), 105 (6), 91 (20), 75 (20); HRMS (ESP, *m/z*) 328.2093 $[M+NH_4]^+$, $C_{20}H_{30}ONSi$ requires 328.2091.

(±)-(2-Methyl-5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (26)

A 60% dispersion of sodium hydride in mineral oil (0.03 g, 0.83 mmol) was washed with *n*-hexane (2 × 2 mL), dried under reduced pressure and placed under an atmosphere of argon. The residue was suspended in THF (1.5 mL) followed by the dropwise addition of a solution of phenyl(5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)methanone (0.19 g, 0.55 mmol) in THF (1 mL). After effervescence had ceased and the reaction had become yellow, diiodomethane (0.12 g, 0.05 mL, 0.83 mmol) was added and the reaction stirred for 2 h at room temperature and monitored by TLC. The reaction was quenched with 0.1 M HCl (10 mL), neutralised with saturated aqueous sodium hydrogen carbonate solution (10 mL) and the organic layer separated. The aqueous layer was extracted with DCM (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a pale yellow oil (0.16 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded an inseparable diastereoisomeric mixture of compound (combined yield 0.15 g, 0.42 mmol, 76%, *dr* 1.5 : 1) as a colourless oil; R_f 0.53 [10% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2941, 2864, 1681, 1462, 1091, 882; *Major Diastereoisomer:* δ_H (600 MHz; $CDCl_3$) 0.97 (1H, dd, *J* 14.6 and 7.2, SiC$\underline{H}_a$H$_b$), 1.92-1.12 (22H, m, overlapping signals $\underline{^iPr_3}$SiCH$_a\underline{H}_b$), 1.43 (1H, ddt, *J* 12.1 10.2 and 8.3, C$\underline{H}_a$H$_b$ C-4 THF), 1.55 (3H, s, Me) 1.79 (1H, ddd, *J* 12.8 10.2 and 7.5, C$\underline{H}_a$H$_b$ C-3 THF), 2.06 (1H, dddd, *J* 12.1 7.6 5.4 and 3.1, CH$_a\underline{H}_b$ C-4 THF), 2.82 (1H, ddd, *J* 12.8 8.1 and 3.1, CH$_a\underline{H}_b$ C-3 THF), 4.36 (1H, dddd, *J* 8.9 7.2 6.8 and 5.4, CH C-5 THF), 7.37-7.40 (2H, m, *m*-CH Ph), 7.47-7.51 (1H, m, *p*-CH Ph), 8.19 (2H, dd, *J* 8.4 and 1.3, *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.3 (3 × CH Si^{i}Pr$_3$), 17.4 ($SiCH_2$), 18.9 (6 × CH_3 Si^{i}Pr$_3$), 26.4 (CH_3), 35.2 (CH_2, C-4 THF), 37.1 (CH_2, C-3 THF), 78.8 (CH, C-5 THF), 88.9 (CH, C-2 THF), 127.9 (2 × *m*-CH, Ph), 130.6 (2 × *o*-CH, Ph), 132.4 (*p*-CH, Ph), 135.4 (C, Ph), 203.0 (C=O); *Minor Diastereoisomer:* δ_H (600 MHz; $CDCl_3$) 1.92-1.12 (22H, m, overlapping signals $\underline{^iPr_3}$SiCH$_a\underline{H}_b$), 1.14 (1H, dd, *J* 14.5 and 7.0, SiCH$_a\underline{H}_b$) 1.59-1.60 (1H, m, C-4 THF), 1.61 (3H, s, Me) 1.83 (1H, ddd, *J* 12.7 9.1 and 5.0, C$\underline{H}_a$H$_b$ C-3 THF), 1.98-2.03 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 2.67 (1H, dt, *J* 12.7 and 8.1, CH$_a\underline{H}_b$ C-3 THF), 3.94 (1H, m, C-5 THF), 7.37-7.40 (2H, m, *m*-CH, Ph), 7.47-7.51 (1H, m, *p*-CH, Ph), 8.17 (2H, dd, *J* 8.4 and 1.2, *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^{i}Pr$_3$), 17.8 ($SiCH_2$), 18.9 (6 × CH_3 Si^{i}Pr$_3$), 27.0 (CH_3), 34.7 (CH_2, C-4 THF), 36.2 (CH_2, C-3 THF), 78.4 (CH, C-5 THF), 88.9 (CH, C-2 THF), 128.0 (2 × *m*-CH, Ph), 130.1 (2 × *o*-CH, Ph), 132.5 (*p*-CH, Ph), 135.2 (C, Ph), 204.9 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 317 ([M−^{i}Pr]$^+$, 70%), 255 (100), 157 (59), 115 (65), 105 (67), 91 (27), 77 (32); HRMS (ESP, *m/z*) 361.2554 [M+NH$_4$]$^+$, $C_{22}H_{37}O_2Si$ requires 361.2557. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 4.36 (major diastereoisomer) and 3.94 ppm (minor diastereoisomer).

(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4'-methoxybiphenyl-4-yl)methanone (27)

To a stirred mixture of 4-methyloxyphenyl boronic acid (0.034 g, 0.22 mmol), potassium carbonate (0.041 g, 0.30 mmol), (±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-bromophenyl)methanone (0.060 g, 0.15 mmol, *trans* diastereoisomer) in dioxane/water (10 : 1, 1.5 mL) was added and bis(triphenylphosphine)palladium dichloride (0.021 g, 0.03 mmol). The resulting mixture was degassed with nitrogen, heated at 90 °C and monitored by TLC. After 24 h the reaction was diluted with diethyl ether and filtered through a pad of silica washing with diethyl ether (2 × 10 mL). The filtrate was concentrated *in vacuo* to give the impure product as a brown oil (0.14 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as a white solid (0.053 g, 0.12 mmol, 82%, *dr* (*trans* : *cis*) 1 : 0.08); R_f 0.17 [20% diethyl ether : hexane]; mp 179-183 °C (hexane); ν_{max}(film)/cm^{-1} 2953, 1687 (C=O), 1599, 1248, 1180, 1112, 820 (Si-C), 726; *trans* diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.35 (6H, s, Si(CH$_3$)$_2$), 1.14 (1H, dd, *J* 14.2 and 8.1, $\mathrm{SiC\underline{H}_aH_b}$), 1.44 (1H, dd, *J* 14.2 and 6.2, $\mathrm{SiCH_a\underline{H}_b}$), 1.49 (1H, app dq, *J* 11.8 and 8.7, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 1.97-2.04 (1H, m, $\mathrm{CH_a\underline{H}_b}$ C-3 THF), 2.13-2.23 (1H, m, $\mathrm{C\underline{H}_aH_b}$ C-4 THF), 2.26-2.34 (1H, m, $\mathrm{CH_a\underline{H}_b}$ C-4 THF), 3.87 (3H, s, OMe), 4.18-4.26 (1H, m, CH C-2 THF), 5.28 (1H, dd, *J* 8.0 and 6.8, CH C-5 THF), 7.00 (2H, app d, *J* 8.6, Ar), 7.33-7.36 (3H, m, Ar), 7.51-7.65 (2H, m, Ar), 7.58 (2H, app d, *J* 8.6, Ar), 7.63 (2H, app d, *J* 8.3, Ar), 8.03 (2H, app d, *J* 8.3, Ar); δ_C (100.6 MHz; CDCl$_3$) −2.3 (SiCH$_3$), −2.0 (SiCH$_3$), 23.5 (SiCH$_2$), 29.3 (CH$_2$, C-4 THF), 34.4 (CH$_2$, C-3 THF), 55.5 (OCH$_3$), 78.6 (CH, C-2 THF), 79.3 (CH, C-5 THF), 114.5 (2 × CH, Ar), 126.7 (2 × CH, Ar), 127.9 (2 × CH, Ar), 128.5 (2 × CH, Ar), 129.1 (CH, Ar), 129.6 (2 × CH, Ar), 132.4 (C, Ar), 133.4 (C, Ar), 133.7 (2 × CH, Ar), 139.0 (C, Ar), 145.5 (C, Ar), 160.1 (C, Ar), 198.3 (CO); LRMS (EI$^+$, *m/z*): 430 ([M]$^+$ 7%), 345 (14), 219 (13), 211 (21), 135 (100), 75 (15); HRMS (CI$^+$, *m/z*) 453.1845 [M+Na]$^+$, $C_{27}H_{30}O_3NaSi$ requires 453.1856. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.28 (ppm) and 5.13 (ppm) *trans* and *cis* respectively.

1-Dimethyl(phenyl)silyl-3-dimethy(phenyl)silylpropene (32)

a) by metallation: 1-Dimethyl(phenyl)silyl-3-dimethy(phenyl)silylpropene was prepared according to the procedure reported by Fleming *et al.* Dimethylphenylsilylpropene (3.52 g, 20.0 mmol) was added dropwise to a stirred mixture of freshly distilled *N*,*N*,*N*,*N*-tetramethylethylenediamine (3.50 mL, 23.0 mmol) and *n*-butyllithium (9.0 mL of a 2.5 M solution in hexane, 22.5 mmol) at −5 °C and the mixture kept at −5 ºC for 3.5 h. Chlorodimethylphenylsilane (3.39 mL, 21.0 mmol) was added dropwise and the mixture was kept at −5 ºC for 1 h (colour changed from orange to yellow), then poured into 1 M HCl (20 mL) and extracted with petroleum spirit (40-60 ºC). The extract was washed with 1 M HCl (20 mL), water (20 mL), dried (MgSO$_4$), filtered and concentrated *in vacuo* to yield the impure product as a pale yellow/brown oil (6.02 g). Purification by flash column chromatography [silica gel, hexane] afforded the desired product (5.35 g, 17.0 mmol, 86%) as a colourless oil; R_f 0.36 [petroleum spirit 40-60 ºC]; ν_{max}(film)/cm^{-1} 3069, 2956, 1603 (C=C), 1486, 1247, 1139, 809; δ_H (400 MHz; $CDCl_3$) 0.29 (6H, s, 2 × CH_3), 0.29 (6H, s, 2 × CH_3), 1.92 (2H, d, *J* 7.8, $C\underline{H}_2CH{=}CH$), 5.57 (1H, d, *J* 18.4, $CH_2CH{=}C\underline{H}$), 6.09 (1H, dt, *J* 18.4 and 7.8, $CH_2C\underline{H}{=}CH$), 7.33-7.40 (6H, m, Ar), 7.47-7.51 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.2 (2 × CH_3), −2.1 (2 × CH_3), 27.9 ($\underline{C}H_2CH{=}CH$), 126.6 ($CH_2CH{=}\underline{C}H$), 127.8 (2 × *m*-CH, Ar), 127.9 (2 × *m*-CH, Ar), 128.9 (*p*-CH, Ar), 129.2 (*p*-CH, Ar), 133.8 (2 × *o*-CH, Ar), 134.0 (2 × *o*-CH, Ar), 138.6 (C, Ar), 139.7 (C, Ar), 145.4 ($CH_2\underline{C}H{=}CH$); LRMS (EI$^+$, *m/z*): 310 (M$^+$, 1%), 295 (2), 197 (17), 160 (32), 135 (100), 105 (10); HRMS (ESP, *m/z*) 311.1651 [M+H]$^+$, $C_{19}H_{27}Si_2$ requires 311.1646.

b) by metathesis: To a stirred mixture of allyldimthylphenylsilane (0.56 g, 3.20 mmol) and vinyldimethylphenylsilane (2.60 g, 16.0 mmol) in argon degassed DCM (10 mL) was added rapidly a solution of (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium (0.10 g, 0.16 mmol, 10 mol%) in DCM (1 mL). The reaction immediately changed colour from green to brown and was heated at 35 °C and monitored by TLC. After 24 h the reaction was concentrated to approximately one quarter of the volume under reduced pressure and filtered through a pad of silica gel eluting with DCM (2 × 100 mL). The filtrate was concentrated *in vacuo* to yield the impure product as a pale green/brown residue (2.24 g). Purification by flash column chromatography [silica gel, hexane] afforded the desired product (0.27 g, 0.87 mmol, 27%, *dr* 17:1 *trans*:*cis*) as a colourless oil; R_f 0.34 [petroleum spirit 40-60 ºC]; *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.29 (6H, s, 2 × CH_3), 0.29 (6H, s, 2 × CH_3), 1.92 (2H, d, *J* 7.8, $C\underline{H}_2CH{=}CH$), 5.57 (1H, d, *J* 18.4, $CH_2CH{=}C\underline{H}$), 6.09 (1H, dt, *J* 18.4 and 7.8, $CH_2C\underline{H}{=}CH$), 7.33-7.40 (6H, m, Ar), 7.47-7.51 (4H, m, Ar); *cis* isomer: 0.31 (6H, s, 2 × CH_3), 0.30 (6H, s, 2 × CH_3), 1.85 (2H, dd, *J* 8.5 and 1.3, $C\underline{H}_2CH{=}CH$), 5.53 (1H, dt, *J* 13.9, $CH_2CH{=}C\underline{H}$), 6.46 (1H, dt, *J* 13.9 and 8.5, $CH_2C\underline{H}{=}CH$), 7.34-7.39 (6H, m, Ar), 7.47-7.58 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.2 (2 × CH_3), −2.1 (2 × CH_3), 27.9 ($\underline{C}H_2CH{=}CH$), 126.6 ($CH_2CH{=}\underline{C}H$), 127.8 (2 × *m*-CH, Ar), 127.9 (2 × *m*-CH, Ar), 128.9 (*p*-CH, Ar), 129.2 (*p*-CH, Ar), 133.8 (2 × *o*-CH, Ar), 134.0 (2 × *o*-CH, Ar), 138.6 (C, Ar), 139.7 (C, Ar), 145.4 ($CH_2\underline{C}H{=}CH$). All other characterisation data the same as above, the ratio of diastereoisomers calculated by analysis of the ^{1}H NMR integrals for the $SiCHC\underline{H}CH$ proton at 6.09 ppm (*trans* diastereoisomer) and 6.46 ppm (*cis* diastereoisomer).

(±)-((2-(Dimethyl(phenyl)silyl)cyclopropyl)methyl)dimethyl(phenyl)silane (29)

To a stirred suspension of zinc powder (4.29 g, 65.0 mmol) and copper chloride (6.43 g, 65.0 mmol) in anhydrous diethyl ether (100 mL) which had been heated at reflux temperature for 30 min and allowed to cool to room temperature was added 1-dimethyl(phenyl)silyl-3-dimethy(phenyl)silylpropene (4.03 g, 13.0 mmol) and diiodomethane (6.96 g, 2.09 mL, 26.0 mmol).

The reaction was heated at reflux temperature for 24 h, cooled to room temperature and filtered through celite washing with diethyl ether (50 mL). The filtrate was washed with 1M HCl (2 x 30 mL) followed by 10% *w*/*v* aqueous sodium bicarbonate solution until pH 7. The combined aqueous layers were extracted with diethyl ether (3 × 30 mL) and the combine organic layers were washed with brine (20 mL), 10% *w*/*v* aqueous sodium thiosulphate solution (2 × 20 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a colourless oil (4.05 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica (1 : 3) eluting with petroleum ether (40-60 °C) gave the desired product (2.35 g, 7.20 mmol, 56%) as a colourless oil; R_f 0.32 [petroleum ether (40-60 °C]; ν_{max}(film)/cm^{-1} 3068, 3049, 2955, 2896, 1487, 1247, 1113, 828, 806; δ_H (400 MHz; $CDCl_3$) −0.43 (1H, dt, *J* 9.8 and 6.5, SiCH), 0.15 (3H, s, $SiCH_3$), 0.19 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 0.31 (3H, s, $SiCH_3$), 0.33-0.38 (1H, m, $C\underline{H}_aH_b$ cyclopropyl), 0.46 (1H, td, *J* 7.1 and 3.6, $CH_a\underline{H}_b$ cyclopropyl), 0.63-0.71 (1H, m, $SiCH_2C\underline{H}$), 0.88 (2H, d, *J* 6.8, $SiC\underline{H}_2CH$), 7.34-7.37 (6H, m, Ar), 7.51-7.54 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.6 ($SiCH_3$), −3.3 ($SiCH_3$), −2.6 ($SiCH_3$), −2.5 ($SiCH_3$), 5.7 ($PhMe_2Si\underline{C}H$), 11.1 (CH_2 cyclopropyl), 11.2 ($SiCH_2\underline{C}H$), 22.8 ($Si\underline{C}H_2CH$), 127.8 (2 × *m*-CH, Ar), 127.8 (2 × *m*-CH, Ar), 128.9 (2 × *p*-CH, Ar), 133.7 (2 × *o*-CH, Ar), 133.9 (2 × *o*-CH, Ar), 139.5 (C, Ar), 139.7 (C, Ar); LRMS (EI$^+$, *m/z*): 324 (M$^+$, 23%), 271 (24), 197 (16), 174 (20), 135 (100), 112 (9); HRMS (EI, *m/z*) 324.1725 [M]$^+$, $C_{20}H_{28}Si_2$ requires 324.1724.

(±)-(4-(dimethyl(phenyl)silyl)-5-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (33) and but-3-enyldimethyl(phenyl)silane (35)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of a solution of (±)-((2-(Dimethyl(phenyl)silyl)cyclopropyl)methyl)dimethyl(phenyl)silane (0.19 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 5 h the reaction was quenched by the addition of wet acetone (5 mL) and allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.38 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as single diastereoisomer (7 mg, 0.01 mmol, 2%) as a colourless oil; R_f 0.44 [20% diethyl ether : hexane]; δ_H (600 MHz; $CDCl_3$); 0.22 (3H, s, $SiCH_3$), 0.27 (3H, s, $SiCH_3$), 0.27 (6H, s, 2 × CH_3), 0.89-0.98 (2H, m, $SiCH_2$), 1.37 (1H, ddd, *J* 12.1

10.6 and 8.2, CH C-4 THF), 2.07 (1H, app td, *J* 12.5 and 7.7, $C\underline{H}_aH_b$ C-3 THF), 2.30 (1H, app dt, *J* 12.8 and 7.9, $CH_a\underline{H}_b$ C-3 THF), 3.96 (1H, ddd, *J* 10.5 8.7 and 4.1 CH C-5 THF), 5.08 (1H, app t, *J* 7.7, CH C-2 THF), 7.29-7.55 (13H, m, Ar), 7.93 (2H, app dd, *J* 8.4 and 1.3, 2 × *o*-CH -C(O)Ph); δ_C (100.6 MHz; $CDCl_3$) −4.2 ($SiCH_3$), −4.0 ($SiCH_3$), −2.4 ($SiCH_3$), −1.8 ($SiCH_3$), 23.4 ($SiCH_2$), 32.8 (CH_2, C-3 THF), 36.7 (CH, C-4 THF), 79.7 (CH, C-2 THF), 80.8 (CH, C-5 THF), 127.7 (CH, Ar), 128.0 (CH, Ar), 128.5 (CH, Ar), 129.2 (CH, Ar), 129.4 (CH, Ar), 133. 1 (CH, Ar), 133.8 (CH, Ar), 133.9 (CH, Ar), 135.6 (C, Ar), 137. 5 (C, Ar), 139.9 (C, Ar), 199.6 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 353 ($[M-PhCO]^+$, 2%), 239 (2), 209 (26), 135 (100), 105 (8), 67 (25); HRMS (ESI, *m/z*) 476.2429 $[M+NH_4]^+$, $C_{28}H_{38}O_2NSi_2$ requires 476.2436.

But-3-enyldimethyl(phenyl)silane (35): (0.02 g, 0.12 mmol, 20%) as a colourless oil; R_f 0.35 [hexane]; δ_H (400 MHz; $CDCl_3$); 0.28 (6H, s, $SiMe_2$), 0.84-0.88 (2H, m, $SiCH_2$), 2.04-2.10 (2H, m, $C\underline{H}_2CH=CH_2$), 4.89 (1H, app d, *J* 10.1, $CH_2CH=C\underline{H}_{cis}H_{trans}$), 4.99 (1H, app dd, $CH_2CH=CH_{cis}\underline{H}_{trans}$), 5.88 (1H, ddt, *J* 17.1 10.1 and 6.2, $CH_2C\underline{H}=CH_2$), 7.35-7.37 (3H, m, SiPh), 7.51-7.56 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) -2.9 ($SiMe_2$), 14.9 ($SiCH_2$), 28.1 ($\underline{C}H_2CH=CH_2$), 112.9 ($CH_2CH=\underline{C}H_2$), 127.9 (2 × *m*-CH, SiPh), 129.0 (p-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.4 (*ipso*-C, SiPh), 141.7 ($CH_2\underline{C}H=CH_2$); LRMS (EI^+, *m/z*): 190 ($[M]^+$, 4%), 175 (13), 162 (11), 135 (100), 121 (27), 105 (13). The spectral data is in good agreement with previously reported values.

4-(Dimethyl(phenyl)silyl)but-2-enenitrile (238)

To a stirred solution of dimethylphenylallylsilane (0.56 g, 3.2 mmol) and acyrlonitrile (0.51 g, 0.37 mL, 9.6 mmol) in argon degassed DCM (10 mL) was added a solution of (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)-ruthenium (0.1 g, 0.16 mmol, 5 mol %) in DCM (1 mL) The reaction immediately changed colour from green to black and was heated at 35 °C and monitored by TLC. After 24 h the solvent was removed *in vacuo* to give the impure product (0.72 g). Purification by flash column chromatography [silica gel, gradient elution 100 % petroleum ether (40-60 °C) - 20 % diethylether : petroleum ether (40-60 °C)] afforded an inseparable mixture of the two geometric isomers of the product (combined yield 0.14 g, 2.0 mmol, 64 %, dr. *cis* : *trans* 1 : 0.3) as a colourless oil: R_f 0.33 [10 % diethylether : petroleum ether (40-60 °C)]; *cis* isomer: δ_H (400 MHz; $CDCl_3$) 0.41 (6H, s, $SiMe_2$), 2.24 (2H, dd, *J* 9.0 and 1.0, $SiCH_2$), 5.15 (1H, dt, *J* 10.8 and 1.0, $CH=C\underline{H}CN$), 6.48 (1H, dt, *J* 10.8 and 9.0, $C\underline{H}=CHCN$), 7.37-7.42 (3H, m, Ph), 7.52-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) -3.3 ($SiMe_2$), 24.9 ($SiCH_2$), 96.4 ($CH=\underline{C}HCN$), 116.8 ($CH=CH\underline{C}N$), 128.1 (2 × *m*-CH, Ph), 129.7 (*p*-CH, Ph), 133.6 (2 × *o*-CH, Ph), 136.7 (*ipso*-C, Ph), 152.9 ($\underline{C}H=CHCN$); *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.37 (6H, s, $SiMe_2$), 1.99 (2H, dd, *J* 8.8 and 1.4, $SiCH_2$), 5.08 (1H, dt, *J* 16.1 and 1.4, $CH=C\underline{H}CN$), 6.71 (1H, dt, *J* 16.1 and 8.8, $C\underline{H}=CHCN$), 7.37-7.42 (3H, m, Ph), 7.48-7.50 (2H, m, Ph); δ_C (100.6

MHz; $CDCl_3$) -3.4 ($SiMe_2$), 25.8 ($SiCH_2$), 97.1 (CH=$\underline{C}$HCN), 118.2 (CH=CH$\underline{C}$N), 128.2 (2 × *m*-CH, Ph), 129.8 (*p*-CH, Ph), 133.5 (2 × *o*-CH, Ph), 136.4 (*ipso*-C, Ph), 153.9 ($\underline{C}$H=CHCN). Diastereomeric ratio calculated by analysis of the ^{1}H NMR integrals for the C$\underline{H}$=CHCN protons, 6.48 (*cis* diastereoisomer) and 6.71 ppm (*trans* diastereoisomer).

2-((Dimethyl(phenyl)silyl)methyl)cyclopropanecarbonitrile (30)

Diazoacetonitrile was prepared according to the procedure reported by Witiak *et al.*[48] To a suspension of α-aminoacetonitrile bisulfite (3.68 g, 24.0 mmol) in DCM (28 mL) at 0 °C was cautiously added dropwise an aqueous solution of sodium nitrite (4.96 g, 72.0 mmol) in distilled water (22 mL) at a rate that the temperature of the reaction did not rise above 0 °C. During the addition effervescence was observed to occur. The reaction was allowed to stir for 30 min at 0 °C after which time a green solution and precipitate existed. The organic layer was separated and the aqueous layer further extracted with DCM (20 mL). The combined organic phases were washed with 1% aqueous sodium hydrogen carbonate solution (10 mL), separated, dried ($MgSO_4$), filtered and place under and inert atmosphere. The solution (0.5 M solution of diazoacetonitrile in DCM) was used immediately and without purification as diazacetonitrile has been reported to be highly explosive at high concentrations. To a stirred mixture of allyldimethylphenylsilane (2.47 g, 14.0 mmol) and dirhodium tetraacetate dihydrate (0.17 g, 0.38 mmol) in degassed DCM (2.4 mL) heated at 35 °C was added using a syringe pump (4 mL/h) diethyl 2-diazomalonate (24.0 mL, 12.0 mmol, 0.5 M solution in DCM). The reaction was heated at 35 °C (oil bath) for 6 h, filtered and concentrated *in vacuo* to give the impure product as a red oil (2.65 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded an inseparable mixture of the two geometric isomers the desired (0.73 g, 3.40 mmol, 30%, *dr* 1 : 0.6) as a colourless oil; R_f 0.20 [10% diethyl ether - hexane]; ν_{max}(film)/cm^{-1} 3070 (CH cyclopropyl), 2956, 2897, 2233 (C≡N), 1427, 1427, 1250, 1114, 831; major isomer: δ_H (600 MHz; $CDCl_3$) 0.38 (3H, s, SiMe), 0.39 (3H, s, SiMe), 0.65-0.72 (1H, m C$\underline{H}_a$$H_b$ cyclopropyl), 0.80 (1H, dd, *J* 14.8 and 9.2, SiC$\underline{H}_a$$H_b$), 1.11 (1H, td, *J* 8.4 and 5.1, C$H_a$$\underline{H}_b$ cyclopropyl), 1.16-1.23 (1H, m, CHCN), 1.28 (1H, dd, *J* 14.8 and 5.2, SiC$H_a$$\underline{H}_b$), 1.35-1.41 (1H, m, CH cyclopropyl), 7.36-7.40 (3H, m, Ph), 7.51-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −2.9 (SiMe), −2.8 (SiMe), 4.1 (CH cylopropyl), 15.0 ($\underline{C}$HCN cyclopropyl), 15.4 (CH_2 cyclopropyl), 17.3 ($SiCH_2$), 120.9 (CN), 128.0 (2 × *m*-CH, Ph), 129.4 (*p*-CH, Ph), 133.7 (2 × *o*-CH, Ph), 138.1 (C, Ph); minor isomer: δ_H (600 MHz; $CDCl_3$) 0.36 (3H, s, SiMe), 0.37 (3H, s, SiMe), 0.65-0.72 (2H, m, overlapping signals SiC$\underline{H}_a$$H_b$ and C$\underline{H}_a$$H_b$ cyclopropyl), 0.90-0.93 (1H, m, CH cyclopropyl), 0.96 (1H, dd, *J* 14.8 and 6.4, SiC$H_a$$\underline{H}_b$), 1.16-1.23 (1H, m, C$H_a$$\underline{H}_b$ cyclopropyl), 1.35-1.41 (1H, m, CHCN), 7.36-7.40 (3H, m, Ph), 7.51-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −3.1 (SiMe), −2.9 (SiMe), 4.4 (CH cylopropyl), 15.8 (CH_2 cyclopropyl), 18.1 (CHCN cyclopropyl), 20.4 ($SiCH_2$), 122.0 (CN), 128.1 (2 × *m*-CH, Ph), 129.5 (*p*-CH, Ph), 133.6 (2 × *o*-CH, Ph), 137.9 (C, Ph); LRMS (EI^+, *m/z*): 215 ($[M]^+$, 3%), 200 (6), 135 (100) 105 (10); HRMS (EI, *m/z*) 215.1127 $[M]^+$, $C_{13}H_{17}NSi$ requires 215.1125.

(*E*/*Z*)-3-dimethylphenylsilyl-1-phenyl-1-propene (39)

Preparation of anhydrous cobalt (II) chloride: Cobalt chloride hexahydrate (approx 2 g) was weighed into a 25 mL flask, placed under vacuum (0.05 mmHg) and gently heated with a heat gun. The red solid was observed to “bump” as the water was removed and change to a bright blue solid. The anhydrous cobalt (II) chloride was placed under nitrogen and used immediately.

Preparation of dimethylphenylsilylmethylmagnesium chloride: To a stirred suspension of magnesium turnings (2.26 g, 93.0 mmol) in THF (19 mL) was added dropwise neat 1,2-dibromoethane (0.82 g, 0.40 mL, 4.52 mmol). After effervescence had subsided (chloromethyl)dimethylphenylsilane (3.70 g, 3.60 mL, 20.0 mmol) was added at such a rate to maintain a gentle reflux during the course of the addition. The reaction mixture was allowed to stir for 15 min at room temperature to give a light gray solution of dimethylphenylsilylmethylmagnesium chloride (approx. 1 M in THF).

Preparation of (*E*/*Z*)-3-dimethylphenylsilyl-1-phenyl-1-propene based on the procedure reported by Affo *et al*.[41] To a blue solution of anhydrous cobalt (II) chloride (0.31 g, 2.40 mmol) and β-bromostyrene (2.20 g, 1.55 mL, 12.0 mmol, *E*/*Z* =1: 0.1) in THF (12 mL) was added dropwise a solution of dimethylphenylsilylmagnesium chloride (18.0 mL, 18.0 mmol, 1 M solution in THF) at 0 °C. During the addition the reaction mixture became a brown colour. The ice bath was removed and the reaction allowed to stir at room temperature over 18 h then partitioned between saturated aqueous ammonium chloride solution (30 mL) and ethyl acetate (20 mL). The organic phase was separated and the aqueous phase extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a brown oil (4.25 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 2% diethyl ether : hexane] afforded the desired product (3.08 g, 12.0 mmol, 98%, *trans* : *cis* 1 : 0.1) as a mixture of isomers and as a colourless oil; R_f 0.19 [hexane]; ν_{max}(film)/cm^{-1} 3023, 2955, 1640 (C=C), 1427, 1248, 1113, 813; *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.37 (6H, s, $SiMe_2$), 1.95 (2H, d, *J* 6.8, $SiCH_2$), 6.22-6.32 (2H, m, C$\underline{H}$=C$\underline{H}$), 7.18-7.21 (1H, m, Ar), 7.28-7.32 (4H, m, Ar), 7.39-7.43 (3H, m, Ar), 7.57-7.59 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.2 ($SiMe_2$), 23.2 ($SiCH_2$), 125.7 (CH, Ar), 126.4 (CH, Ar), 127.3 (CH=CH), 128.0 (CH, Ar), 128.6 (CH, Ar), 129.1 (CH=CH), 129.2 (CH, Ar), 133.8 (CH, Ar), 138.5 (C, Ar), 138.7 (C, Ar); *cis* isomer: δ_H (400 MHz; $CDCl_3$) 0.35 (6H, s, $SiMe_2$), 2.11 (2H, dd, *J* 9.0 and 1.1, $SiCH_2$), 5.75 (1H, dt, *J* 11.7 and 9.0, $CH_2C\underline{H}$=CH), 6.39 (1H, d, *J* 11.7, CH_2CH=C$\underline{H}$), 7.19-7.41 (8H, m, Ar), 7.51-7.56 (8H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.0 ($SiMe_2$), 18.8 ($SiCH_2$), 126.3 (CH, Ar), 127.7 (CH=CH), 127.8 (CH, Ar), 128.2 (CH=CH), 128.4 (CH, Ar), 128.7 (CH, Ar), 129.2 (CH, Ar), 133.7 (CH, Ar), 138.2 (C, Ar), 138.7 (C, Ar); LRMS (EI^+, *m/z*): 252 ($[M]^+$, 9%), 135 (100), 115 (9) 105 (15), 91 (6); HRMS (EI, *m/z*) 252.1331 $[M]^+$, $C_{17}H_{20}Si$ requires 252.1331. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the $SiC\underline{H}_2$ protons at 1.95 (*E*-diastereoisomer) and 2.11 ppm (*Z*-diastereoisomer).

(±)-Dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (40)

To a stirred suspension of zinc powder (3.96 g, 60.0 mmol) and copper chloride (5.94 g, 60.0 mmol) in anhydrous diethyl ether (90 mL), which had been heated at reflux temperature for 30 min and allowed to cool to room temperature, was added 3-dimethylphenylsilyl-1-phenyl-1-propene (1.57 g, 6.00 mmol) and diiodomethane (6.43 g, 1.93 mL, 24.0 mmol). The reaction was heated at reflux temperature for 48 h, cooled to room temperature and filtered through celite washing with diethyl ether (3 × 30 mL). The filtrate was washed with 1M HCl (2 x 25 mL) followed by 10% *w*/*v* aqueous sodium bicarbonate solution until pH 7. The combined aqueous layers were extracted with diethyl ether (3 x 30 mL) and the combined organic layers were washed with 10% *w*/*v* aqueous sodium thiosulphate solution (2 × 20 mL), brine (20 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a yellow oil (1.05 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica (1 : 1) eluting with hexane gave the desired product (0.58 g, 2.20 mmol, 36%) as a colourless oil; R_f 0.26 [hexane]; ν_{max}(film)/cm^{-1} 3067 (C-H cyclopropyl), 2999, 2955, 2896, 1605 (Ar-H), 1427, 1248, 1113, 831 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.33 (3H, s, SiMe), 0.34 (3H, s, SiMe), 0.71-0.76 (1H, m, $C\underline{H}_aH_b$ cyclopropyl), 0.86-1.04 (4H, m, overlapping signals $SiC\underline{H}_2$, CH and $CH_a\underline{H}_b$ cyclopropyl), 1.53-1.57 (1H, m, $PhC\underline{H}$ cyclopropyl), 6.77 (2H, d, *J* 7.8, 2 × *o*-CH Ph), 7.10-7.14 (1H, m, *p*-CH Ph), 7.23 (2H, t, *J* 7.8, 2 × *m*-CH Ph), 7.32-7.37 (3H, m, SiPh), 7.51-7.53 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) −2.7 (SiMe), −2.6 (SiMe), 18.5 (CH_2 cyclopropyl), 19.7 (CH cyclopropyl), 21.6 ($SiCH_2$), 25.3 ($PhC\underline{H}$, cyclopropyl), 125.2 (*p*-CH, Ph), 125.5 (2 × *o*-CH, Ph), 127.9 (2 × *m*-CH, SiPh), 128.3 (2 × *m*-CH, Ph), 129.3 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.4 (C, SiPh), 144.0 (C, Ph); LRMS (EI^+, *m/z*): 266 ($[M]^+$, 3%), 238 (7), 188 (11), 135 (100), 105 (9), 91 (8); HRMS (EI^+, *m/z*) 266.1487 $[M]^+$, $C_{18}H_{22}Si$ requires 266.1485.

(±)-(5-((dimethyl(phenyl)silyl)methyl)-3-phenyltetrahydrofuran-2-yl)(phenyl)methanone (41a)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (3 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (3 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of a solution of dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (0.16 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 5 h the reaction was quenched by the addition of wet acetone (5 mL) and allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.25 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] followed by flash column chromatography [silica gel, gradient elution 60% dichloromethane : hexane] afforded the desired product as single diastereoisomer (0.02 g, 0.04 mmol, 7%) as a colourless oil; R_f 0.48 [60% dichloromethane : hexane]; δ_H (600 MHz; $CDCl_3$); 0.28 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 1.24 (1H, dd, *J* 14.3 and 8.0, $SiC\underline{H}_aH_b$), 1.48 (1H, dd, *J* 14.3 and 6.5, $SiH_a\underline{H}_b$), 2.01 (1H, app dt, *J* 12.7 and 8.7, $C\underline{H}_aH_b$ C-4 THF), 2.14 (1H, ddd, *J* 12.6 6.3 and 4.8, $CH_a\underline{H}_b$ C-4 THF), 3.84 (1H, app dt, *J* 8.9 and 5.1, CH C-3 THF), 4.50 (1H, app tt, *J* 7.8 and 6.5, CH C-5 THF), 5.14 (1H, d, *J* 5.5, CH C-2 THF), 7.20-7.41 (10H, m, Ar), 7.50-7.53 (3H, m, Ar), 7.92-7.93 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 24.2 ($SiCH_2$), 42.5 (CH_2 C-4 THF), 47.4 (CH C-3 THF), 79.3 (CH C-5 THF), 86.6 (CH C-2 THF), 126.9 (CH, Ar), 127.6 (CH, Ar), 127.9 (CH, Ar), 128.5 (CH, Ar), 128.9 (CH, Ar), 129.1 (CH, Ar), 129.3 (CH, Ar), 133.3 (CH, Ar), 133.7 (CH, Ar), 135.6 (C, Ar), 139.0 (C, Ar), 142.9 (C, Ar), 197.5 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 295 ($[M-PhCO]^+$, 12%), 277 (4), 239 (5), 135 (100), 105 (13), 91 (10), 77 (15); HRMS (ESI, *m/z*) 418.2195 $[M+NH_4]^+$, $C_{26}H_{32}O_2NSi$ requires 418.2197.

(±)-(5-((dimethyl(phenyl)silyl)methyl)-4-phenyltetrahydrofuran-2-yl)(phenyl)methanone (42) and (±)-(5-((dimethyl(phenyl)silyl)methyl)-3-phenyltetrahydrofuran-2-yl)(phenyl)methanone (41b)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (0.16 g, 0.60 mmol) in anhydrous DCM (6 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.01 g, 0.04 mL, 0.36 mmol) in anhydrous DCM (3 mL). The reaction was stirred at 0 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.257 g) as a yellow oil. Purification by flash column chromatography [silica gel, 50 % dichloromethane : hexane] afforded product **42** (yield 0.024 g, 0.06 mmol, 10 %) as a colourless oil; R_f 0.48 [50 % dichloromethane : hexane]; δ_H (400

MHz; CDCl$_3$) 0.21 (3H, s, SiCH$_3$), 0.28 (3H, s, SiCH$_3$), 1.04-1.06 (2H, m, SiCH$_2$), 2.50 (1H, ddd, *J* 13.0 10.6 and 7.2, C$\underline{\mathrm{H}}_a$H$_b$ C-3 THF), 2.67 (1H, dt, *J* 13.1 and 8.4, CH$_a\underline{\mathrm{H}}_b$ C-3 THF), 2.95 (1H, q, *J* 9.4, CH C-4 THF), 4.00 (1H, ddd, J 9.4 7.3 and 5.9, CH C-5 THF), 5.38 (1H, dd, *J* 8.1 and 7.3, CH C-2 THF), 7.17-7.61 (13H, m, Ar), 8.04 (2H, app dd, *J* 8.1 and 0.9, Ar); δ_C (100.6 MHz; CDCl$_3$) -2.5 (SiCH$_3$), -1.9 (SiCH$_3$), 20.4 (SiCH$_2$), 37.2 (CH$_2$ C-3 THF) 55.3 (CH, C-4 THF), 78.7 (CH, C-2 THF), 84.3 (CH C-5 THF), 127.0 (CH, Ph), 127.7 (CH, Ph), 128.8 (CH, Ph), 129.2 (CH, Ph), 133.4 (CH, Ph), 133.7 (CH, Ph), 135.4 (C, Ph), 139.6 (C, Ph), 140.0 (C, Ph), 198.9 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 323 ([M-Ph]$^+$, 1 %), 296 (10), 239 (4), 135 (60), 117 (100), 105 (40), 91 (10), 77 (21); HRMS (ESP, *m/z*) 418.2196 [M+NH$_4$]$^+$, C$_{26}$H$_{282}$NSi requires 418.2197.

(±)-(5-((dimethyl(phenyl)silyl)methyl)-3-phenyltetrahydrofuran-2-yl)(phenyl)methanone (41b) (0.034 g, 0.09 mmol, 14 %) is a colourless oil; R$_f$ 0.35 [50 % dichloromethane : hexane]; δ_H (600 MHz; CDCl$_3$) 0.31 (3H, s, SiCH$_3$), 0.33 (3H, s, SiCH$_3$), 1.24 (1H, dd, *J* 14.3 and 8.0, SiC$\underline{\mathrm{H}}_a$H$_b$), 1.52 (1H, dd, *J* 14.2 and 6.2, SiCH$_a\underline{\mathrm{H}}_b$), 1.78 (1H, app dt, *J* 12.2 and 10.3, C$\underline{\mathrm{H}}_a$H$_b$ C-4 THF), 2.44 (1H, ddd, *J* 12.3 7.8 and 4.7, CH$_a\underline{\mathrm{H}}_b$ C-4 THF), 3.78 (1H, dt, *J* 10.3 and 7.4, CH C-3 THF), 4.29 (1H, dddd, *J* 10.3 7.7 6.4 and 4.8, CH C-5 THF), 5.19 (1H, d, *J* 6.8, CH C-2 THF), 7.20-7.39 (10H, m, Ar), 7.48-7.52 (3H, m, Ar), 7.30 (2H, app dd, *J* 8.3 and 1.0, Ar); δ_C (100.6 MHz; CDCl$_3$) -2.2 (SiCH$_3$), -2.0 (SiCH$_3$), 23.2 (SiCH$_2$), 45.2 (CH$_2$ C-4 THF) 48.3 (CH, C-4 THF), 79.3 (CH, C-5 THF), 86.1 (CH C-2 THF), 126.9 (CH, Ph), 127.8 (CH, Ph), 127.9 (CH, Ph), 128.4 (CH, Ph), 128.9 (CH, Ph), 129.1 (CH, Ph), 129.3 (CH, Ph), 133.3 (CH, Ph), 133.7 (CH, Ph), 135.4 (C, Ph), 138.9 (C, Ph), 142.6 (C, Ph), 198.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 295 ([M-PhCO]$^+$, 18 %), 277 (4), 239 (5), 135 (100), 105 (19), 91 (8), 77 (14); HRMS (ESI, *m/z*) 418.2190 [M+NH$_4$]$^+$, C$_{26}$H$_{32}$O$_2$NSi requires 418.2197.

(±)-(4-((dimethyl(phenyl)silyl)methyl)-5-phenyltetrahydrofuran-2-yl)(phenyl)methanone (43)

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (0.16 g, 0.60 mmol) in anhydrous DCM (6 mL) at -78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.01 g, 0.04 mL, 0.36 mmol) in anhydrous DCM (3 mL). The reaction was stirred and allowed to warm to 0 °C and monitored by TLC. After 2 h at 0 °C the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried (MgSO$_4$), filtered and concentrated *in vacuo* to give the impure product (0.219 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution, 100 % hexane – 10 % diethyl ether : hexane] followed by preparative TLC [60 % dichloromethane : hexane] afforded product (yield 0.007 g, 0.02 mmol, 3 %) as a colourless oil; R$_f$ 0.19 [60 % dichloromethane :

hexane]; δ_H (400 MHz; $CDCl_3$) 0.21 (3H, s, $SiCH_3$), 0.23 (3H, s, $SiCH_3$), 0.75 (1H, dd, *J* 14.7 and 11.3, $SiC\underline{H}_aH_b$), 0.99 (1H, dd, *J* 14.7 and 2.8, $SiCH_a\underline{H}_b$), 1.85 (1H, ddd, *J* 12.3 10.8 and 8.7, $C\underline{H}_aH_b$ C-3 THF), 2.18 (1H, m, CH C-4 THF), 2.45 (1H, dt, *J* 12.6 and 7.4, $CH_a\underline{H}_b$ C-3 THF), 4.50 (1H, d, *J* 9.1, CH C-5 THF), 5.44 (1H, t, *J* 8.0, CH C-2 THF), 7.25-7.56 (13H, m, Ar), 7.98 (2H, app d, *J* 8.1, Ar); δ_C (100.6 MHz; $CDCl_3$) -2.4 ($SiCH_3$), -2.0 ($SiCH_3$), 16.9 ($SiCH_2$), 38.2 (CH_2 C-3 THF) 44.9 (CH, C-4 THF), 79.9 (CH, C-2 THF), 90.1 (CH, C-5 THF), 127.1 (CH, Ph), 128.0 (CH, Ph), 128.1 (CH, Ph), 128.5 (CH, Ph), 128.7 (CH, Ph), 129.0 (CH, Ph), 129.2 (CH, Ph), 133.4 (CH, Ph), 133.6 (CH, Ph), 135.4 (C, Ph), 138.7 (C, Ph), 140.2 (C, Ph), 199.0 (C=O).

Associated content

Further experimental details, including those of screening and optimisation reactions, together with copies of ^{1}H and ^{13}C NMR spectra.

Author information

Corresponding author:
Email: A.Dobbs@gre.ac.uk

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ELECTRONIC SUPPORTING INFORMATION

Synthesis and Reactions of Donor Cyclopropanes: efficient routes to *cis*- and *trans*-tetrahydrofurans

Jonathan Dunn and Adrian Dobbs

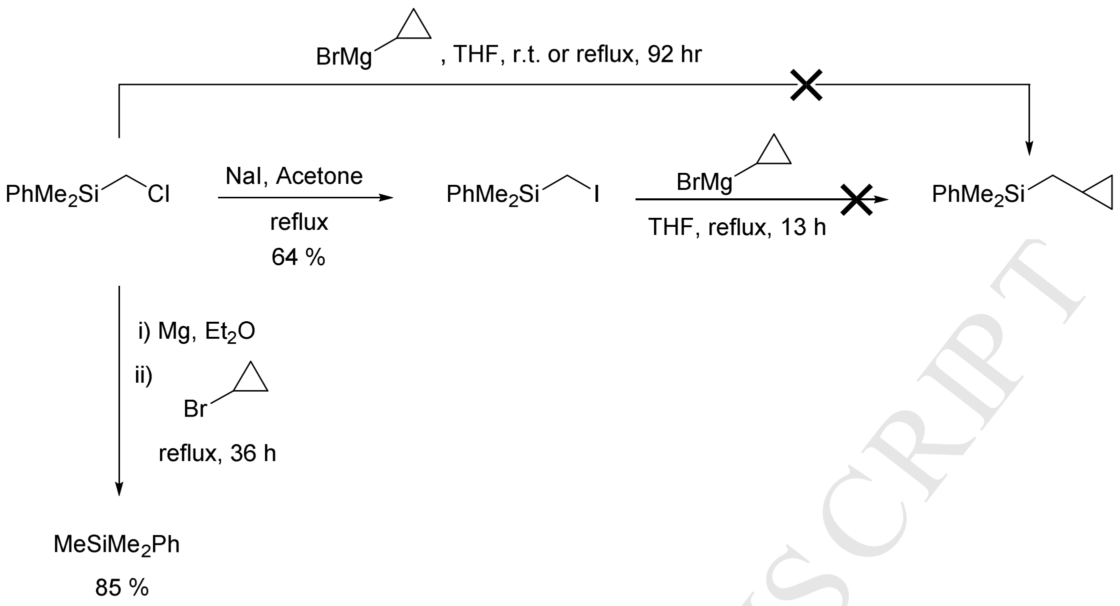
[a]**School of Biological and Chemical Sciences, Queen Mary, University of London, Mile End Road, London E1 4NS, UK.**

[b]**School of Science, University of Greenwich, Central Avenue, Chatham Maritime, KENT ME4 4TB, UK**

Email: A.Dobbs@gre.ac.uk

Contents

Unsuccessful methods for the synthesis of silylmethylcyclopropanes



General Experimental Details

Reaction Conditions

All reactions were carried out under an atmosphere of nitrogen or argon unless otherwise stated, using oven or flame-dried glassware and all transfers were performed using either plastic or glass syringes. Degassed solutions were prepared by rapidly bubbling nitrogen gas through the required solvent for approximately 10 min prior to use. Stirring was by internal magnetic follower and all reactions were monitored by tlc.

Solvents

Petroleum ether or petrol refers to the fraction of petroleum ether boiling between 40 °C and 60 °C, unless otherwise stated. Anhydrous THF, diethyl ether, dichloromethane, toluene and DMF were purified using a MBRAUN MB SPS-800 solvent purification system or as follows: dichloromethane and 1,2-dichloroethane were freshly distilled over calcium hydride; THF was distilled over sodium with benzophenone as an indicator; diethyl ether and toluene were dried over sodium wire and distilled. All other solvents were purified by standard procedures[i] or used as supplied from commercial sources.

Reagents

Commercially available reagents were used as supplied unless otherwise stated. Where appropriate, reagents were purified by distillation or recrystallisation. Ethyl glyoxalate was distilled from commercially available 1:1 ethyl glyoxalate toluene solution according to the procedure reported by Evans *et al*.REF *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA) was purified by distillation over potassium hydroxide under an atmosphere of argon. Mechanically activated magnesium turnings were prepared by vigorous dry stirring with a Teflon-coated stirrer bar for 24 h under an atmosphere of nitrogen as reported in the literature.[75]

Chromatography

Flash column chromatography was carried out using Fluka silica gel 60 (220-240 mesh) (Brockmann 2-3); samples were applied as a concentrated solution in an appropriate solvent. Thin layer chromatography (TLC) was performed on pre-coated aluminium backed plates with either Merck Kieselgel 60 F254 or Merck Aluminium Oxide 60 F254. Visualisation was either by ultraviolet light (λ = 254 nm) or by staining with acidified aqueous potassium permanganate solution followed by heating. Preparative layer chromatography was performed on pre-coated glass backed plates with Merck silica gel 60 F254 (thickness 1000 μm).

Instrumentation

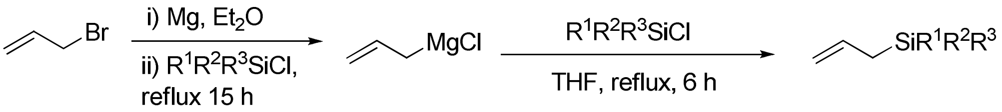
Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Low resolution mass spectra were recorded on an Agilent 6890 Series GC System with a 5973 mass spectrometry detector. High and low resolution mass spectra were recorded on a Thermofisher LTQ Orbitrap XL, Finnigan MAT 95 XP, Thermofisher DSQ-II, Agilent 5975C Inert XL GC/MSD or Micromass Quattro II instrument (EPSRC Mass Spectrometry Service, Swansea). Infrared spectra were recorded using either a Shimadzu FTIR-8300 spectrometer, with samples prepared as thin films between NaCl plates or on KBr disks, or on a Perkin Elmer Spectrum 65 FT-IR spectrometer with universal ATR sampling accessory. FTIR spectra were recorded in the range of 600-4000 cm^{-1} and only selected absorbances (ν_{max}) are reported. Elemental analyses (CHN) were obtained using an Exeter Analytical EA44 analyser from the micro analysis service at University College London. X-ray crystal structures were obtained at QMUL using a KAPPA APEX ii DUO diffractometer with dual Cu and Mo Sources and APEX ii CCD area detector.

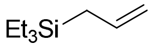
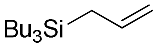
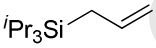
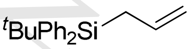
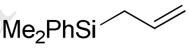
NMR spectra were recorded on one of the following spectrometers: a JEOL JNM-EX270 operating at 270 MHz (^{1}H), 67.8 MHz (^{13}C) and 109.3 MHz (^{31}P); a Bruker AMX-400 operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) fitted with a variable temperature probe controlled by a Bruker B-VT-2000 controller; a Bruker Avance 400 operating at 400 MHz (^{1}H), 100 MHz (^{13}C), 162 MHz (^{31}P) and 149.2 MHz (^{119}Sn); a Bruker Avance III operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) or a Bruker AV600 operating at 600 MHz (^{1}H) and 150 MHz (^{13}C). Chemical shift values (δ_H and δ_C) are reported as values in parts per million (ppm) relative to either tetramethylsilane or the residual protic solvent as the internal standard reference for ^{1}H NMR spectra and from the solvent peaks for ^{13}C NMR using values from the literature.[ii] Coupling constants (*J* values) are quoted to one decimal place with values in hertz and are quoted twice where possible, each being recorded as observed in the spectrum without averaging. Multiplets are reported over the range at which they appear. ^{1}H NMR data is presented in the form δ_H (integration, multiplicity, coupling constants, assignment). The multiplicity of the signal is designated by the following abbreviations: s-singlet, d-doublet, t-triplet, q-quartet, and m-multiplet. The abbreviation br refers to a broad signal and app refers to apparent. ^{13}C NMR spectra are recorded in the form δ_C (assignment) or (multiplicity, coupling constants, assignment) where appropriate.

Characterisation

Full characterisation of a compound within this experimental chapter includes, but is not limited to, IR, ^{1}H NMR, ^{13}C NMR, low-resolution mass spectra and high-resolution mass spectra data. For compounds that have previously been fully characterised in the literature two or more pieces of spectroscopic data are presented. In many cases assignment of ^{1}H and ^{13}C NMR signals are supported by DEPT and two-dimensional COSY and HSQC experiments. Assignment of relative stereochemistry is based on analysis of nOe studies.

Table 1 Synthesis of allylsilanes using a Grignard methodology



Entry	R^1	R^2	R^3	Product	Yield (%)[a]
1	Et	Et	Et	 **153**	90[b]
2	Bu	Bu	Bu	 **155**	88
3	^{i}Pr	^{i}Pr	^{i}Pr	 **156**	81
4	Me	Ph	Ph	 **157**	59[b]
5	^{t}Bu	Ph	Ph	 **158**	92
6	Me	Me	Ph	 **154**	86

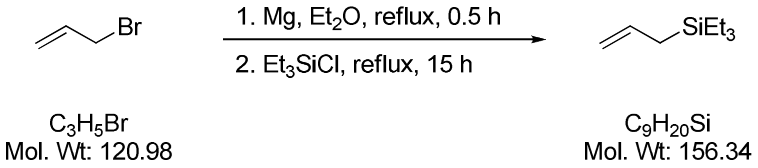
[a] Purified and isolated yields; [b] Grignard reagent was prepared (from the allyl bromide and activated magnesium turnings) prior to the addition of the chlorosilane

General Procedure A - Preparation of allylsilanes

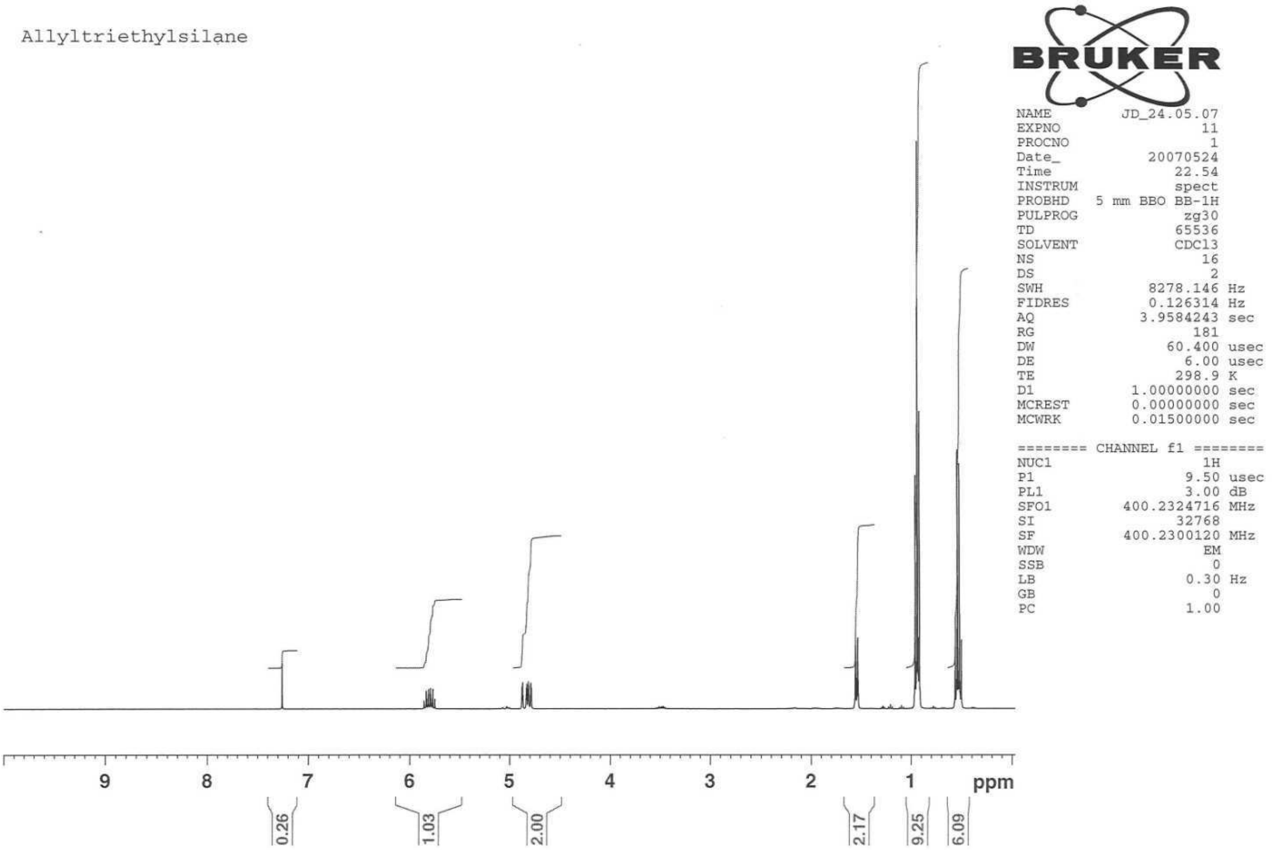
A solution of chlorosilane (1 eq.) in anhydrous THF (0.3 mL/mmol) was added cautiously to a stirred solution of allylmagnesium chloride (1.4 eq., 2 M solution in THF) at room temperature under an atmosphere of argon and the resulting mixture stirred at 55 °C for 15 h. The mixture was cooled to 0 °C, quenched with 10% *w*/*v* aqueous ammonium chloride solution (1.5 mL/mmol), warmed to room temperature and partitioned between water and diethyl ether. The organic phase was separated and the aqueous phase extracted with diethyl ether. The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The products were purified by flash column chromatography.

TABLE 1 ENTRY 1

Allyltriethylsilane



To a stirred suspension of magnesium turnings (1.82 g, 75.0 mmol) in anhydrous diethyl ether (50 mL) under an atmosphere of argon was added several crystals of iodine, upon which the solution turned brown. After 10 min the solution became clear and allylbromide (8.47 g, 6.10 mL, 70.0 mmol) was cautiously added dropwise at a rate sufficient to maintain gentle reflux during the addition. The mixture was stirred for a further 30 min before chlorotriethylsilane (4.06 g, 4.53 mL, 27.0 mmol) was added dropwise at a rate sufficient to maintain gentle reflux. The mixture was heated to reflux temperature for 15 h. After this time, the reaction mixture was cooled to approximately −15 °C and a 10% *w*/*v* aqueous ammonium chloride solution (90 mL) was added dropwise with efficient stirring over a period of 30 min. Two layers developed and the organic phase was separated. The aqueous phase was extracted with diethyl ether (3 × 20 mL) and the combined organic portions were washed with brine (20 mL), separated, dried ($MgSO_4$) and filtered. The diethyl ether and allylbromide were removed by distillation at atmospheric pressure. Purification of the resulting residue by either Kugelrohr distillation or flash column chromatography [silica gel, hexane] gave the desired product (3.78 g, 24.2 mmol, 90%) as a colourless oil; bp 81-83 °C/35 mmHg, (lit.[iii,iv] 37 °C/3 mmHg); R_f 0.75 [hexane]; ν_{max}(film)/cm^{-1} 2953, 2875, 1630 (C=C), 1416, 1237, 1153, 1011, 891; δ_H (400 MHz; $CDCl_3$) 0.54 (6H, q, *J* 8.0, 3 × CH_2), 0.94 (9H, t, *J* 8.0, 3 × CH_3), 1.54 (2H, dt, *J* 8.2 and 1.2, $C\underline{H}_2CH{=}CH_2$), 4.81 (1H, ddt, *J* 10.1 2.2 and 0.9, $CH_2CH{=}C\underline{H}_{cis}H_{trans}$), 4.87 (1H, ddt, *J* 16.9 2.2 and 1.4, $CH_2CH{=}CH_{cis}\underline{H}_{trans}$), 5.81 (1H, ddt, *J* 16.9 10.1 and 8.2, $CH_2C\underline{H}{=}CH_{cis}H_{trans}$); δ_C (100.6 MHz; $CDCl_3$) 3.3 (3 × CH_2), 7.5 (3 × CH_3), 19.6 ($\underline{C}H_2CH{=}CH_2$), 112.6 ($CH_2CH{=}\underline{C}H_2$), 135.6 ($CH_2\underline{C}H{=}CH_2$); LRMS (EI$^+$, *m*/*z*) 156 ([M]$^+$, 4%), 127 (4), 115 (87), 99 (31), 87 (100), 57 (38); HRMS (EI$^+$, *m/z*) 156.1329 [M]$^+$, $C_9H_{20}Si$ requires 156.1329. The data is in good agreement with previously reported values.[v]



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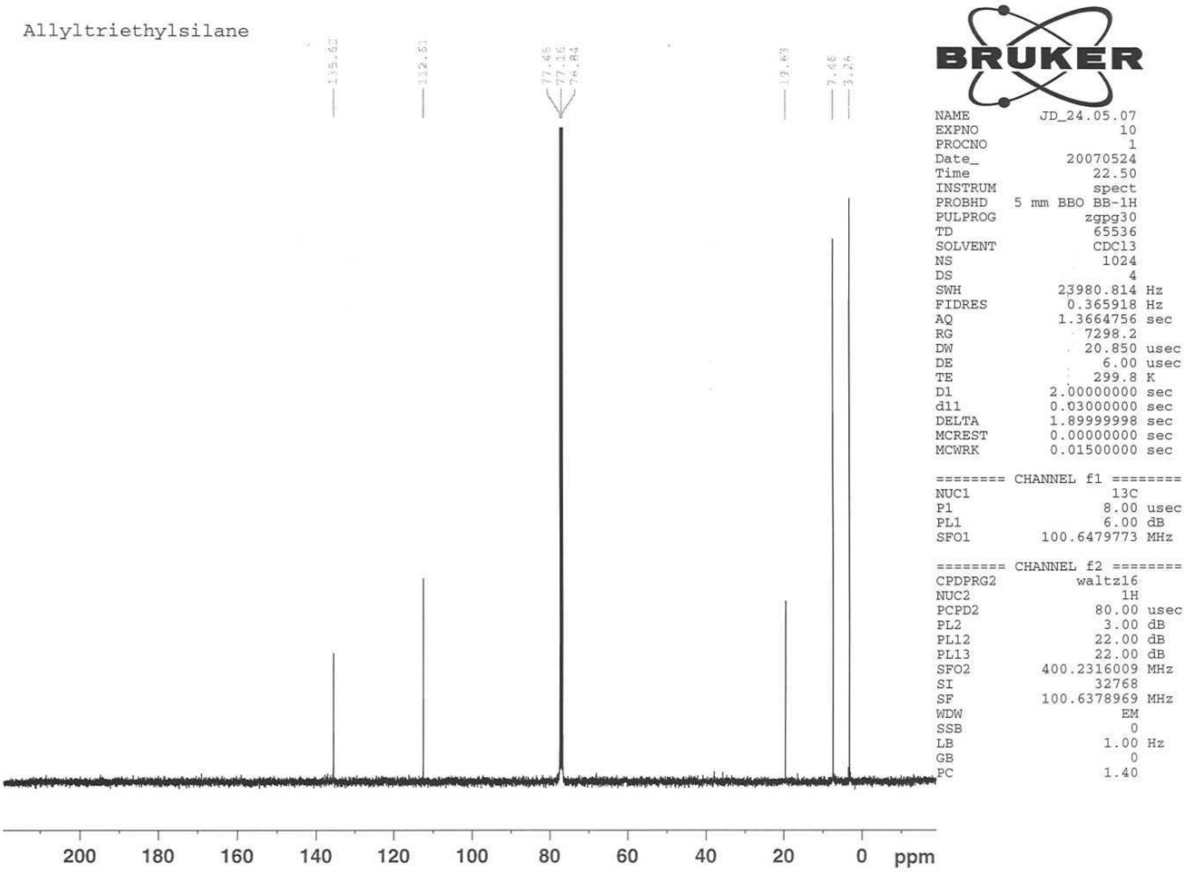
Time                 22.54
INSTRUM              spect
PROBHD     5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                     181
DW                  60.400 usec
DE                    6.00 usec
TE                   298.9 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

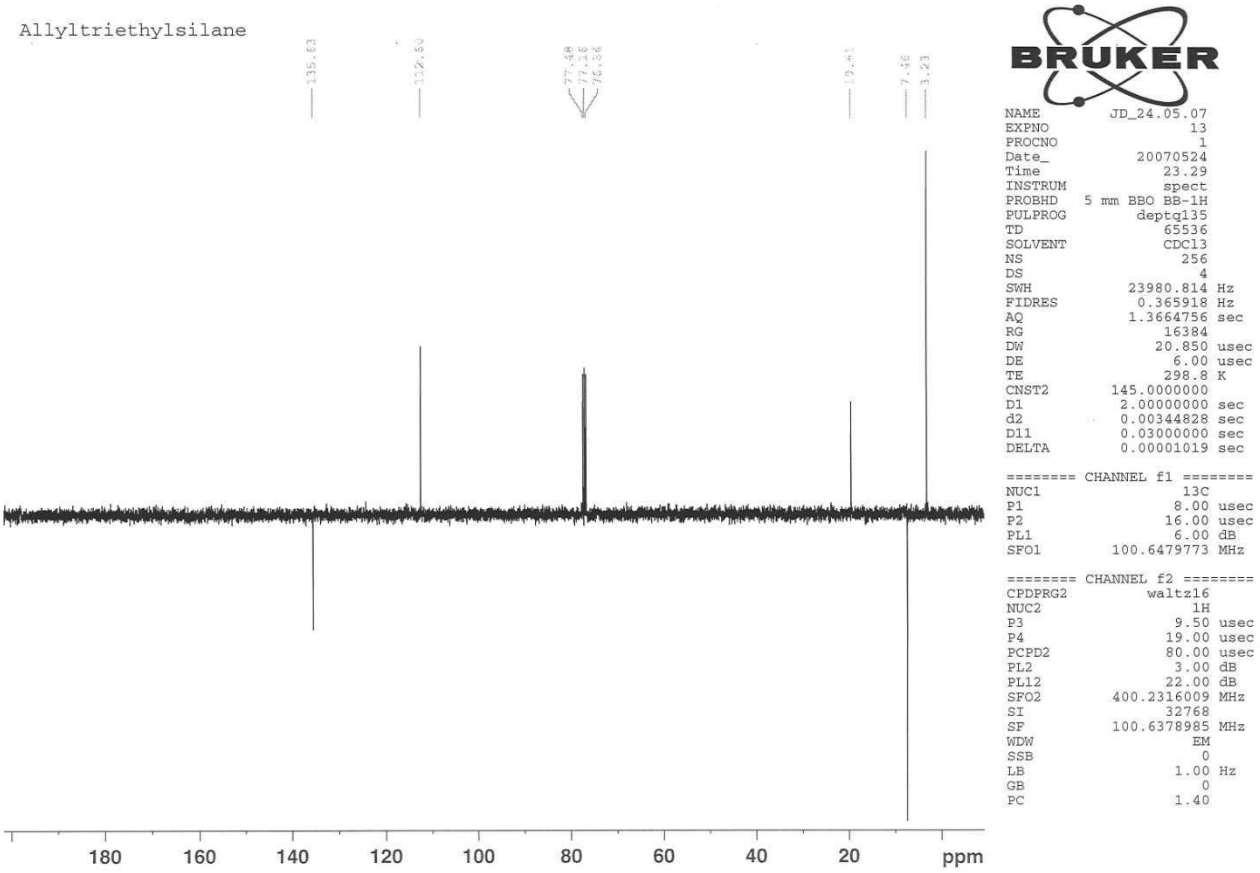
======== CHANNEL f1 ========
NUC1                    1H
P1                    9.50 usec
PL1                   3.00 dB
SFO1           400.2324716 MHz
SI                   32768
SF             400.2300120 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
NAME           JD_24.05.07
EXPNO                   10
PROCNO                   1
Date_             20070524
Time                 22.50
INSTRUM              spect
PROBHD     5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                  7298.2
DW                  20.850 usec
DE                    6.00 usec
TE                   299.8 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6378969 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



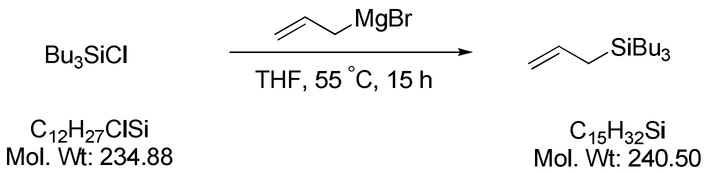
```
NAME         JD_24.05.07
EXPNO                 13
PROCNO                 1
Date_           20070524
Time               23.29
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG        deptq135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 298.8 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
P2                 16.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

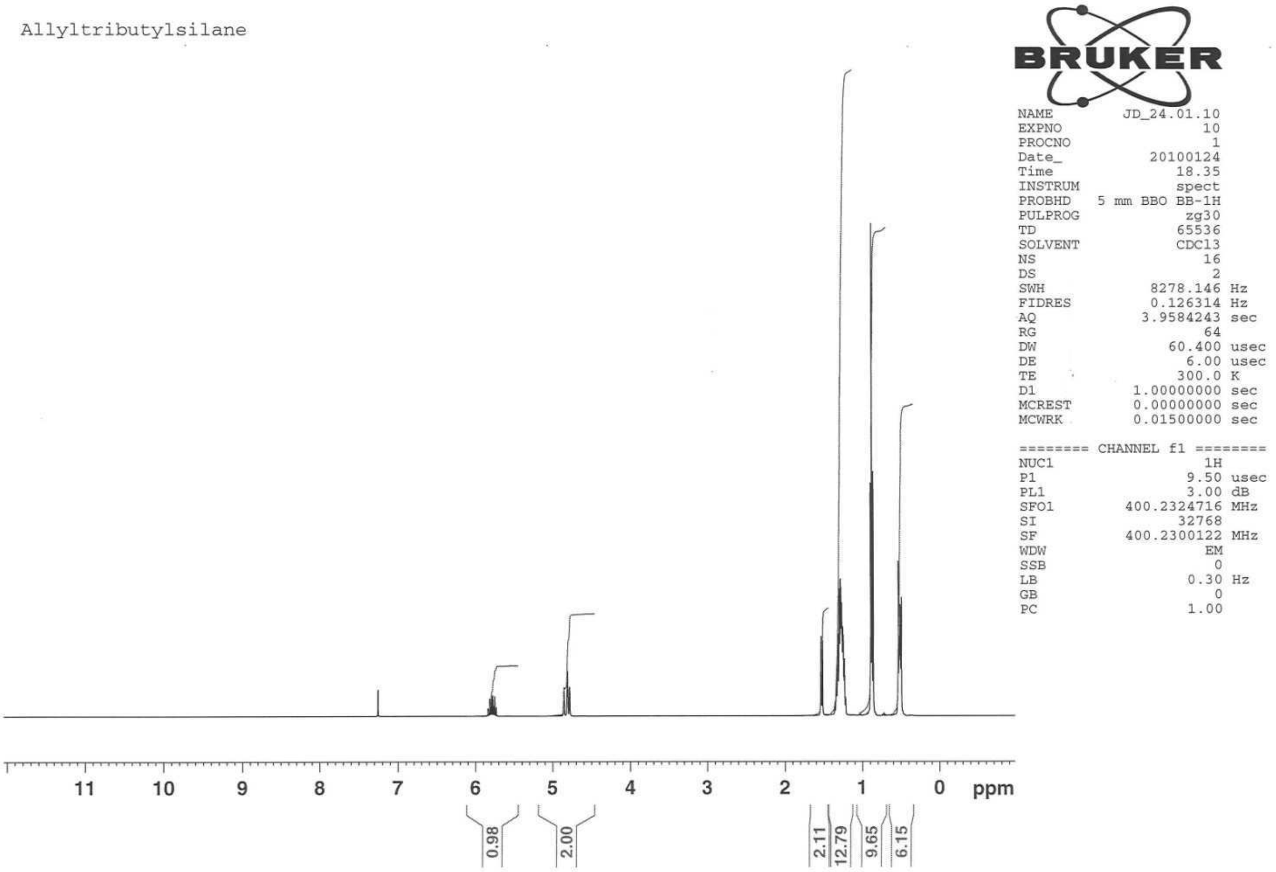
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  9.50 usec
P4                 19.00 usec
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6378985 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

TABLE 1 ENTRY 2

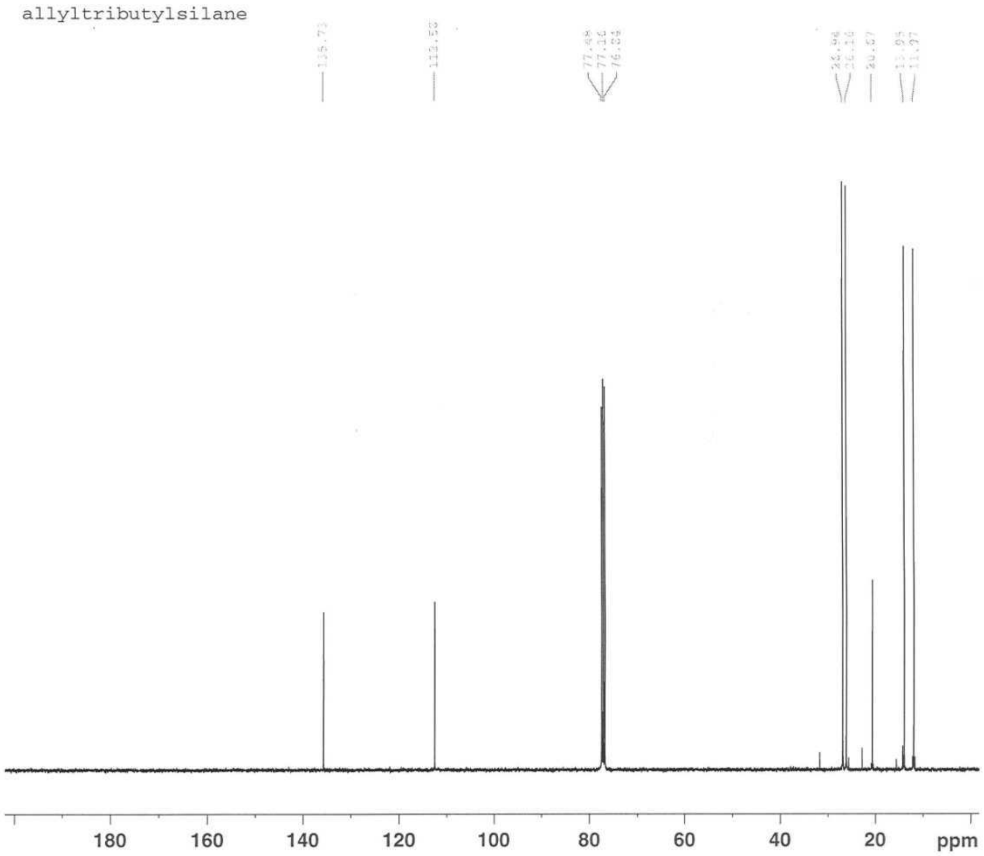
Allyltri-*n*-butylsilane



Following the general procedure A, chlorotri-*n*-butylsilane (4.93 g, 21.0 mmol) furnished the impure product (4.96 g) as a colourless oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (4.45 g, 18.5 mmol, 88%) as a colourless oil; R_f 0.82 [hexane]; ν_{max}(film)/cm^{-1} 2956, 2918, 1630 (C=C), 1195, 890; δ_H (400 MHz; $CDCl_3$) 0.50-0.54 (6H, m, 3 × CH_2 $SiCH_2$), 0.89 (9H, t, *J* 7.0, 3 × CH_3), 1.22-1.37 (12H, m, 6 × CH_2), 1.53 (2H, d, *J* 8.2, $C\underline{H}_2CH=CH_2$), 4.80 (1H, dd, *J* 10.1 and 2.2, $CH=C\underline{H}_{cis}H_{trans}$), 4.84 (1H, dd, *J* 16.9 and 2.2, $CH=CH_{cis}\underline{H}_{trans}$), 5.79 (1H, ddt, *J* 16.9 10.1 and 8.2, $CH_2C\underline{H}=CH_{cis}H_{trans}$); δ_C (100.6 MHz; $CDCl_3$) 12.0 (3 × CH_2, $SiCH_2$), 14.0 (3 × CH_3, Bu), 20.7 ($\underline{C}H_2CH=CH_2$), 26.2 (3 × CH_2, Bu), 26.9 (3 × CH_2, Bu), 112.6 ($CH_2CH=\underline{C}H_2$), 135.7 ($CH_2\underline{C}H=CH_2$); LRMS (EI^+, *m/z*) 199 ($[M-Allyl]^+$, 72%), 143 (100), 127 (28), 101 (18), 87 (15); HRMS (EI^+, *m/z*) 239.2190 $[M]^+$, $C_{15}H_{32}Si$ requires 239.2189.



allyltributylsilane

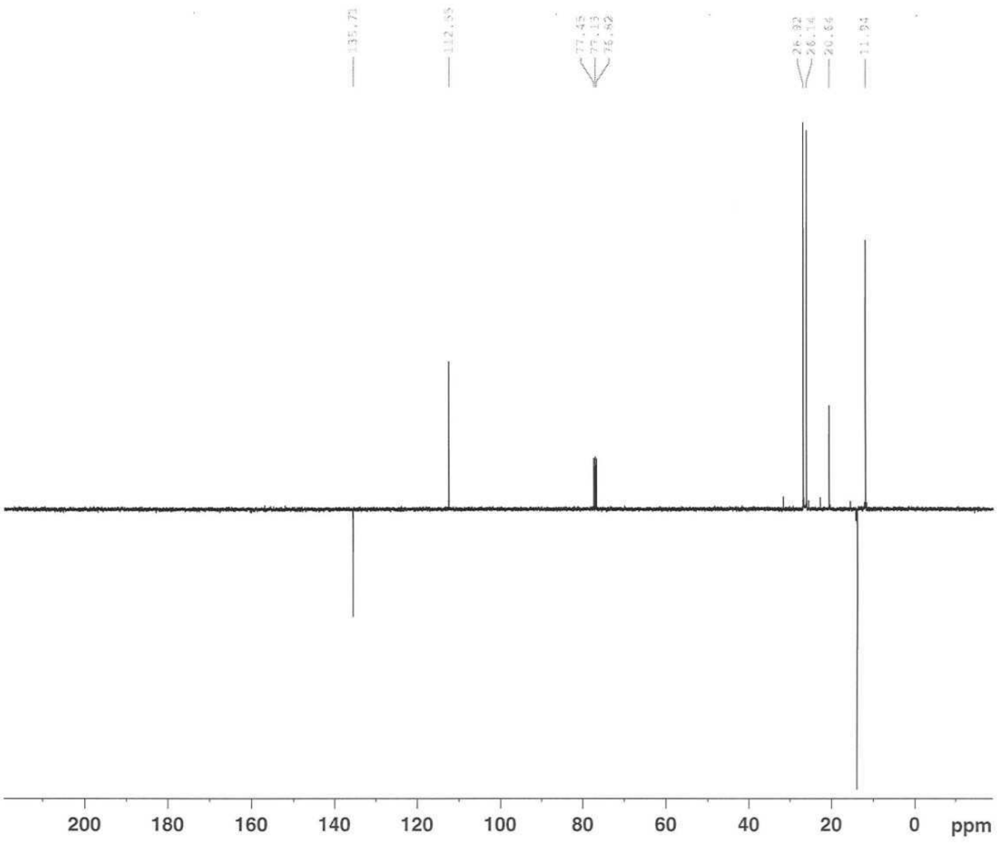


```
NAME          JD_24.01.10
EXPNO                  11
PROCNO                  1
Date_            20100124
Time                19.36
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               18390.4
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379006 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

JD-07-352 C1 F1



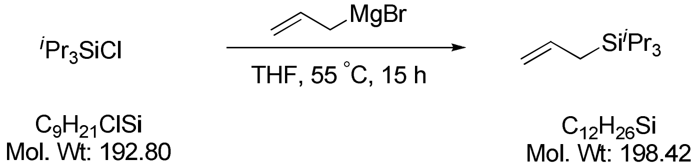
```
NAME          JD_24.01.10
EXPNO                  12
PROCNO                  1
Date_            20100124
Time                19.53
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG         deptq135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
P2                 16.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

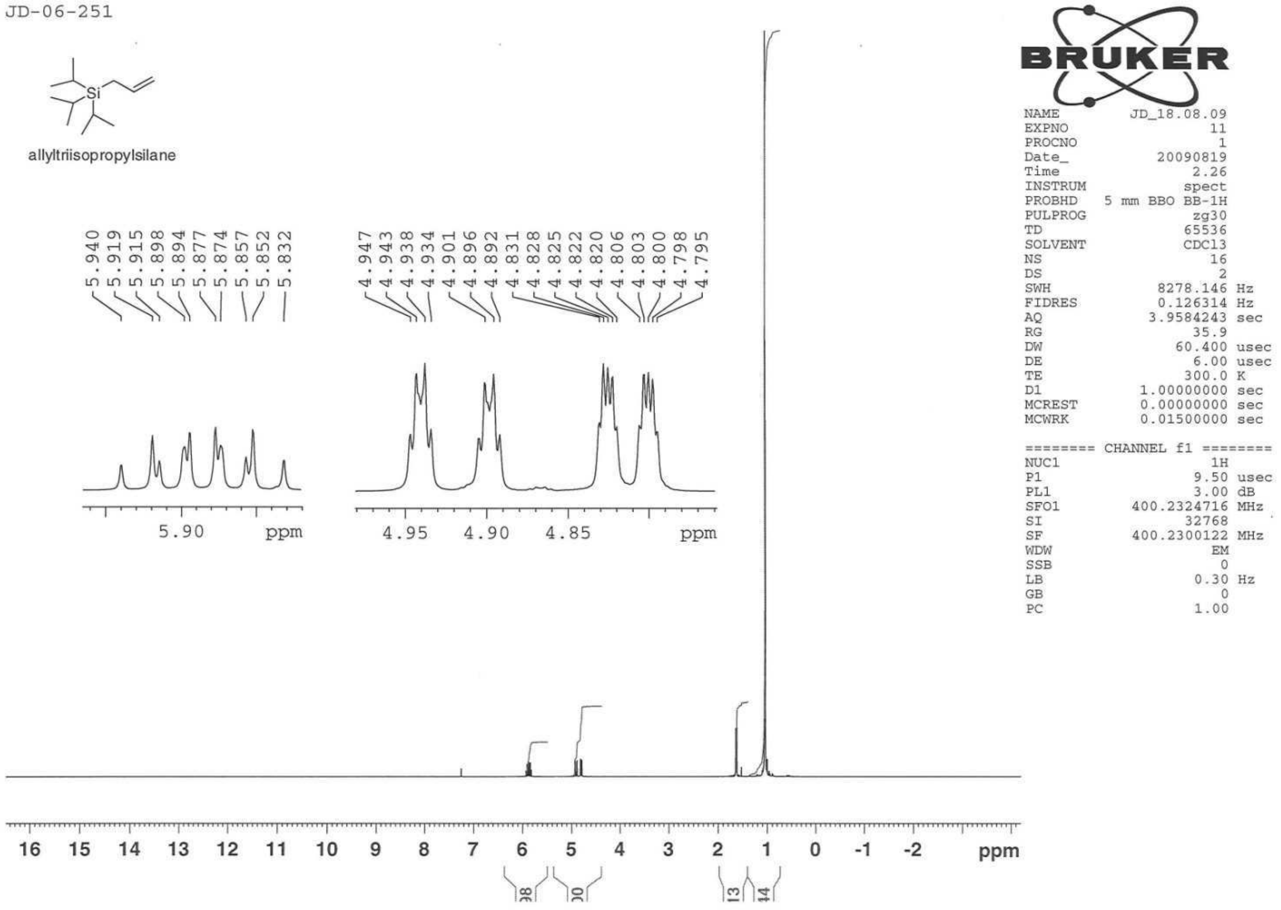
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  9.50 usec
P4                 19.00 usec
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379033 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

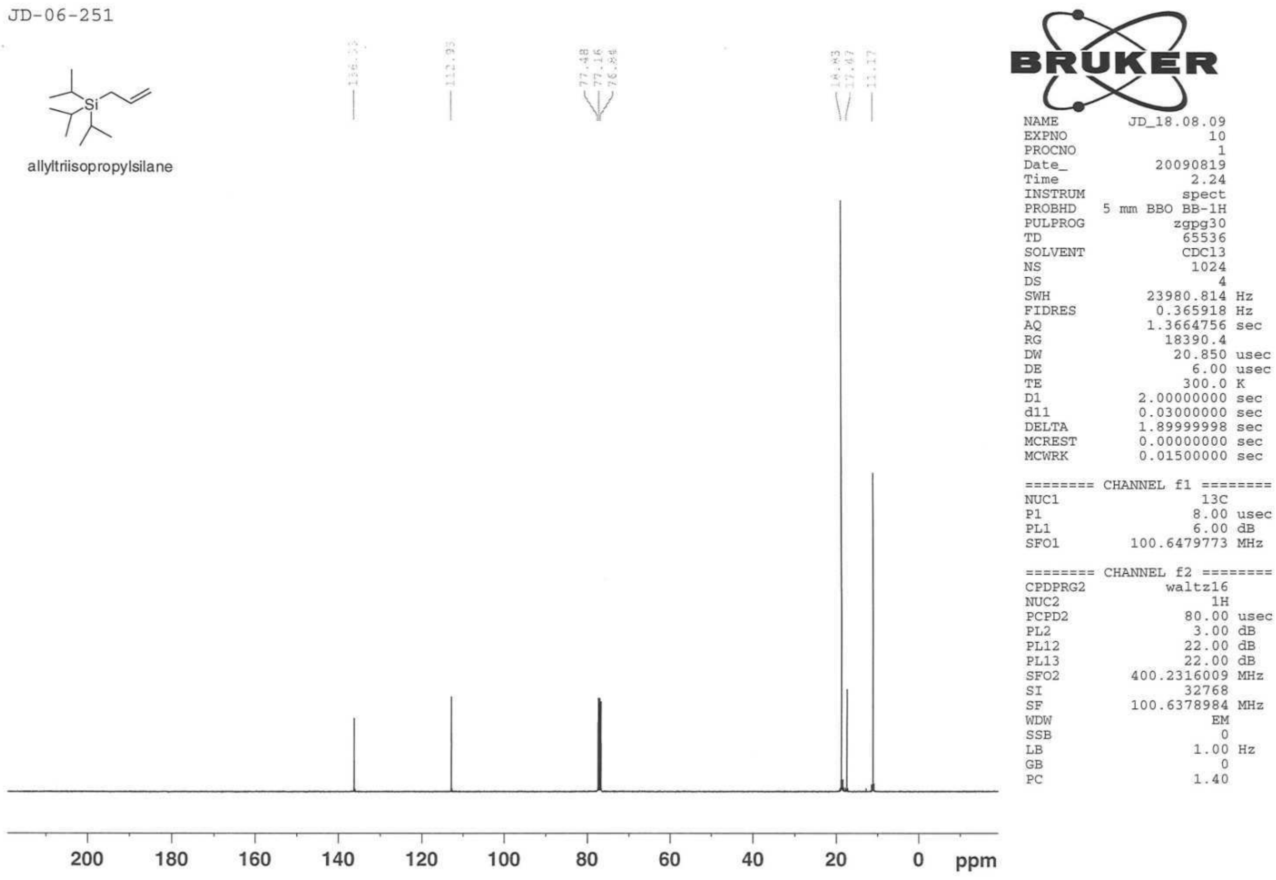
TABLE 1 ENTRY 3

Allyltriisopropylsilane



Following the general procedure A, chlorotriisopropylsilane (6.75, 7.92 mL, 35.0 mmol) furnished the impure product (7.17 g) as a pale yellow oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (6.52 g, 32.8 mmol, 94%) as a colourless oil; R_f 0.79 [hexane]; bp 74-79 °C/0.4 mmHg, (lit.[vi] 45-50 °C/0.2 mmHg); δ_H (400 MHz; CDCl$_3$) 0.97-1.11 (21H, m, overlapping doublet and septet 3 × ^{i}Pr), 1.64 (2H, dt, *J* 8.2 and 1.2, C$\underline{H}_2$CH=CH$_2$), 4.81 (1H, ddt, *J* 10.0 2.2 and 1.2, CH$_2$CH=C$\underline{H}_{cis}$H$_{trans}$), 4.92 (1H, ddt, *J* 16.9 2.2 and 1.2, CH$_2$CH=CH$_{cis}\underline{H}_{trans}$), 5.89 (1H, ddt, *J* 16.9 10.0 and 8.2, CH$_2$C$\underline{H}$=CH$_2$); δ_C (100.6 MHz; CDCl$_3$) 11.2 (3 × CH, ^{i}Pr), 17.5 (SiCH$_2$), 18.8 (6 × CH$_3$), 112.9 (CH$_2$CH=$\underline{C}$H$_2$), 136.3 (CH$_2\underline{C}$H=CH$_2$); LRMS (EI$^+$, *m/z*) 198 ([M]$^+$, 3%), 157 (100), 115 (60), 85 (52). The data is in good agreement with previously reported values.[vii]

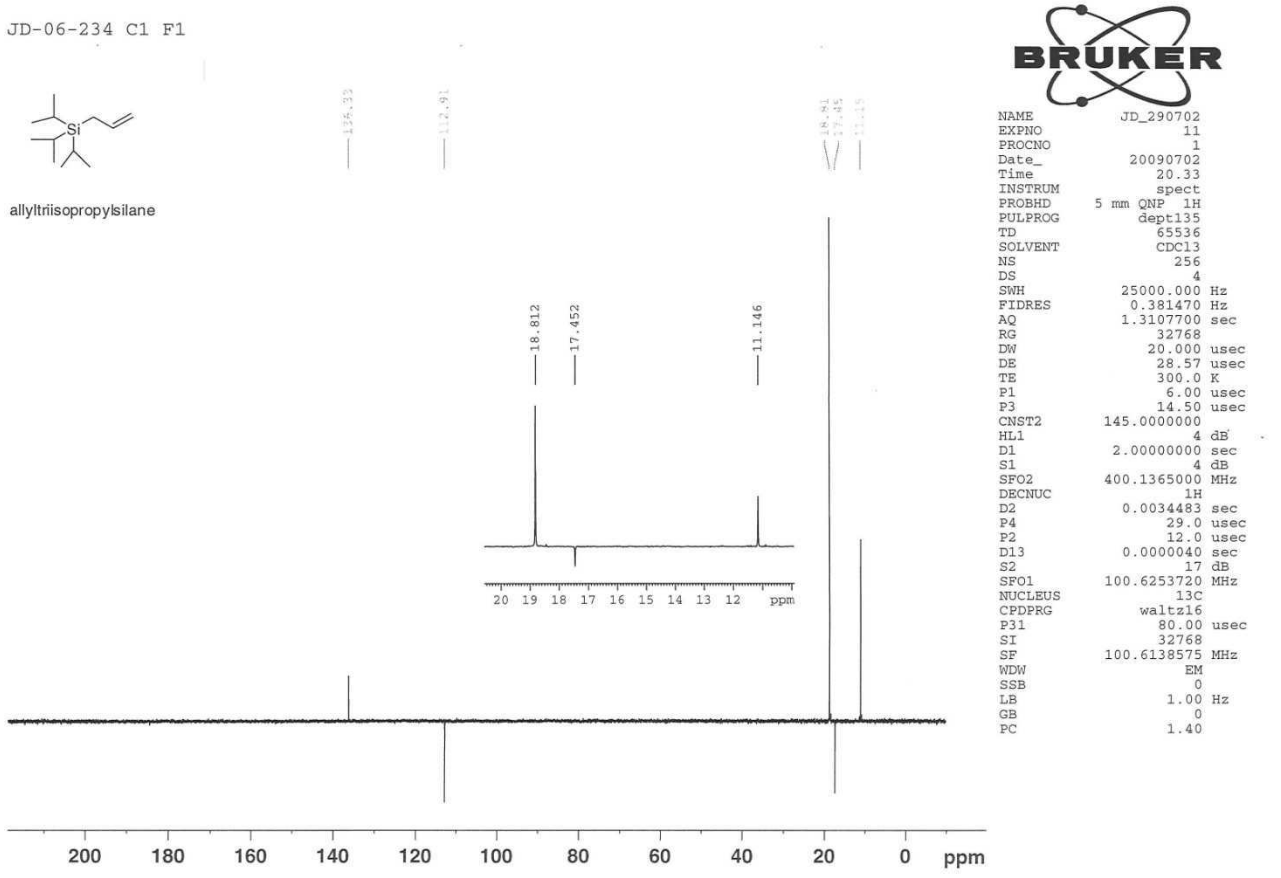




```
NAME           JD_18.08.09
EXPNO                   10
PROCNO                   1
Date_             20090819
Time                  2.24
INSTRUM              spect
PROBHD     5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT              CDCl3
NS                   1024
DS                      4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

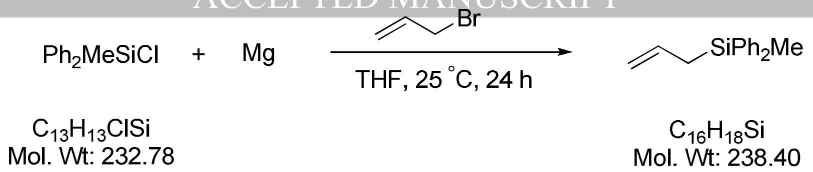
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6378984 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



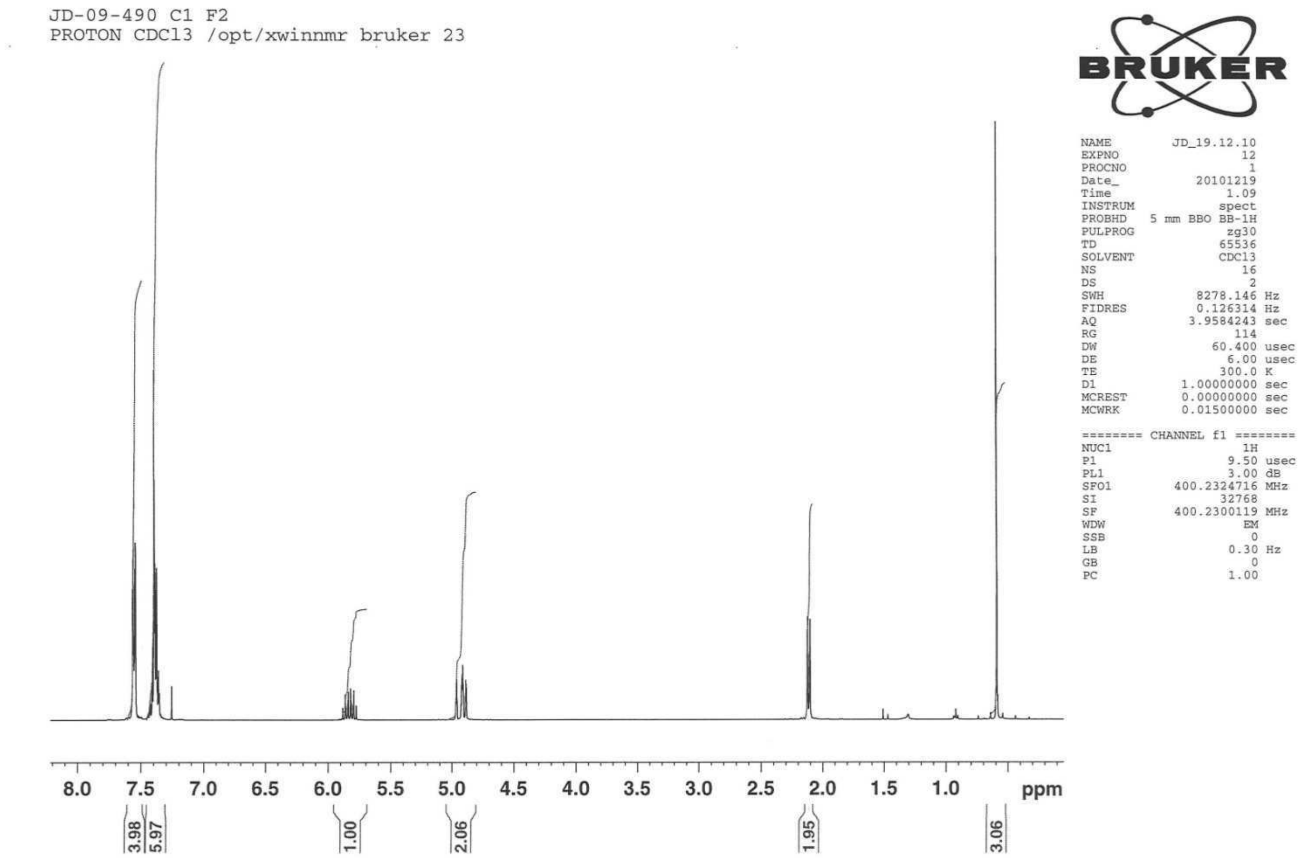
```
NAME           JD_290702
EXPNO                 11
PROCNO                 1
Date_           20090702
Time               20.33
INSTRUM            spect
PROBHD      5 mm QNP  1H
PULPROG          dept135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            25000.000 Hz
FIDRES          0.381470 Hz
AQ             1.3107700 sec
RG                 32768
DW                20.000 usec
DE                 28.57 usec
TE                 300.0 K
P1                  6.00 usec
P3                 14.50 usec
CNST2        145.0000000
HL1                    4 dB
D1            2.00000000 sec
S1                     4 dB
SFO2         400.1365000 MHz
DECNUC                1H
D2             0.0034483 sec
P4                  29.0 usec
P2                  12.0 usec
D13            0.0000040 sec
S2                    17 dB
SFO1         100.6253720 MHz
NUCLEUS              13C
CPDPRG           waltz16
P31                80.00 usec
SI                 32768
SF           100.6138575 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

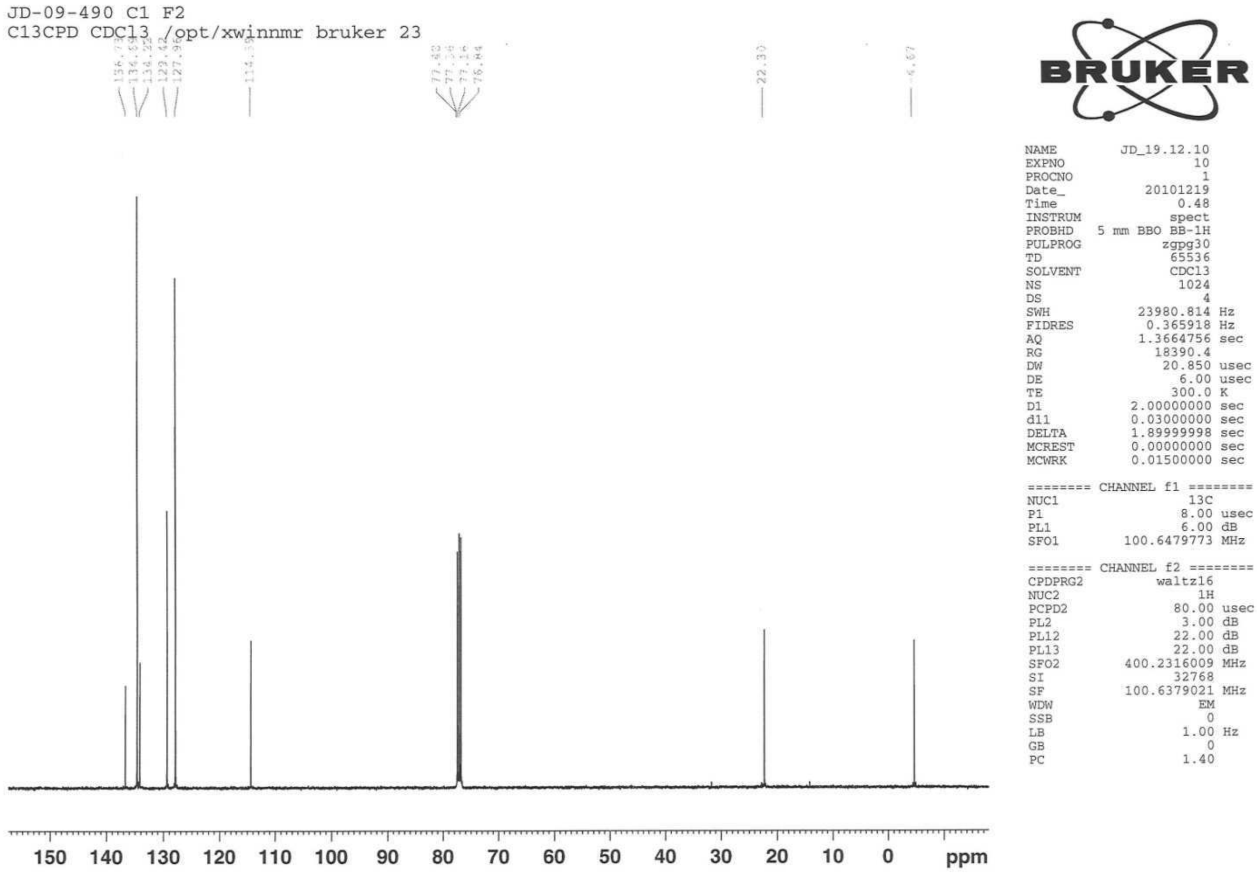
TABLE 1 ENTRY 4

Allyldiphenylmethylsilane



Dimethyl(iodomethyl)phenylsilane was prepared based on the procedure reported by Soderquist *et al*.[83] To a mixture of mechanically activated magnesium turnings (0.36 g, 15.0 mmol) and chloromethyldiphenylsilane (2.79 g, 2.53 mL, 12.0 mmol) in THF (15 mL) was added dropwise allylbromide (1.45 g, 1.01 mL, 12.0 mmol) at a rate to maintain gentle reflux. After being stirred at 25 °C for 15 h, the reaction mixture was poured onto ice. The aqueous layer was extracted with diethyl ether (2 × 20 mL) and the combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford a pale yellow oil (2.90 g). Purification by either Kugelrohr distillation or flash column chromatography [silica gel, hexane] gave the desired product (1.68 g, 7.05 mmol, 59%) as a colourless oil; bp 115-119 °C/1 mmHg, (lit.[viii] 93 °C/0.1 mmHg); R_f 0.23 [hexane]; ν_{max}(film)/cm^{-1} 3069, 2953, 2875, 1629 (C=C), 1427, 1251, 1112, 895; δ_H (400 MHz; $CDCl_3$) 0.59 (3H, s, SiC$\underline{H}_3$), 2.12 (2H, dt, *J* 8.0 and 1.1, C$\underline{H}_2$CH=CH$_2$), 4.89-4.97 (2H, m, overlapping signals CH$_2$CH=C$\underline{H}_2$), 5.83 (1H, ddt, *J* 17.0 10.1 and 8.0, CH$_2$C$\underline{H}$=CH$_2$), 7.36-7.43 (6H, m, Ar), 7.54-757 (4H, m, Ar); δ_C (100 MHz; $CDCl_3$) −4.7 (2 × CH_3), 22.3 ($\underline{C}$H$_2$CH=CH$_2$), 114.2 (CH$_2$CH=$\underline{C}$H$_2$), 128.0 (4 × *m*-CH, Ar), 129.4 (2 × *p*-CH, Ar), 134.2 (CH$_2\underline{C}$H=CH$_2$), 134.7 (4 × *o*-CH, Ar), 136.7 (2 × C, Ar); LRMS (EI$^+$, *m/z*) 238 ([M]$^+$, 2%), 223 (3), 197 (100), 181 (19), 165 (20), 119 (10), 105 (27); HRMS (EI$^+$, *m/z*) 238.1170 [M]$^+$, $C_{16}H_{18}Si$ requires 238.1172. The data is in good agreement with previously reported values.[ix]

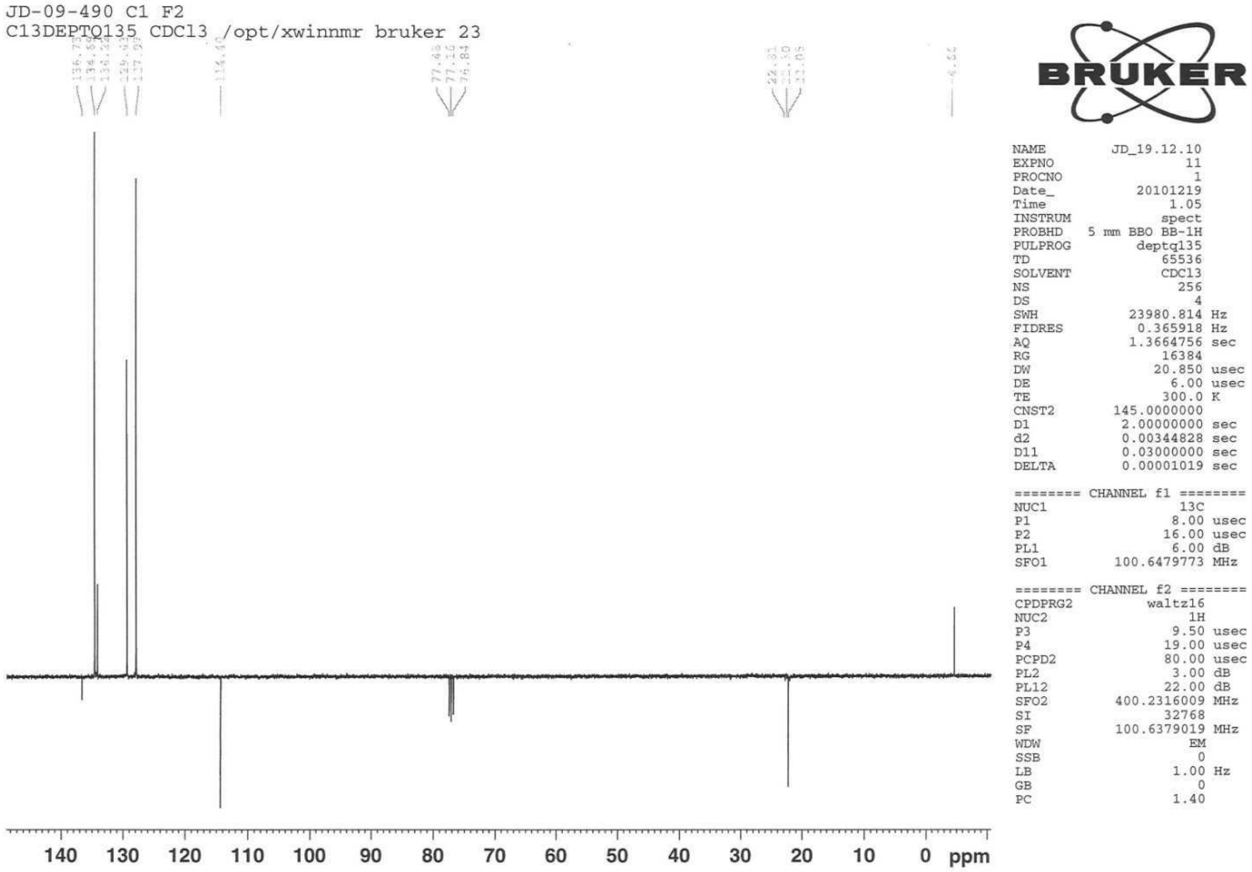




```
NAME           JD_19.12.10
EXPNO                   10
PROCNO                   1
Date_             20101219
Time                  0.48
INSTRUM              spect
PROBHD      5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379021 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



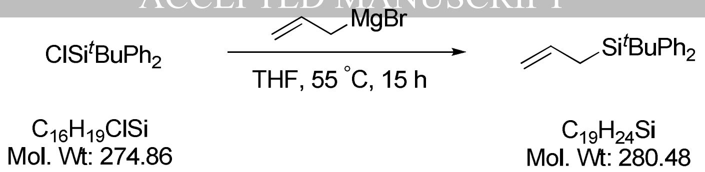
```
NAME           JD_19.12.10
EXPNO                   11
PROCNO                   1
Date_             20101219
Time                  1.05
INSTRUM              spect
PROBHD      5 mm BBO BB-1H
PULPROG          deptq135
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
D11             0.03000000 sec
DELTA           0.00001019 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
P2                   16.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

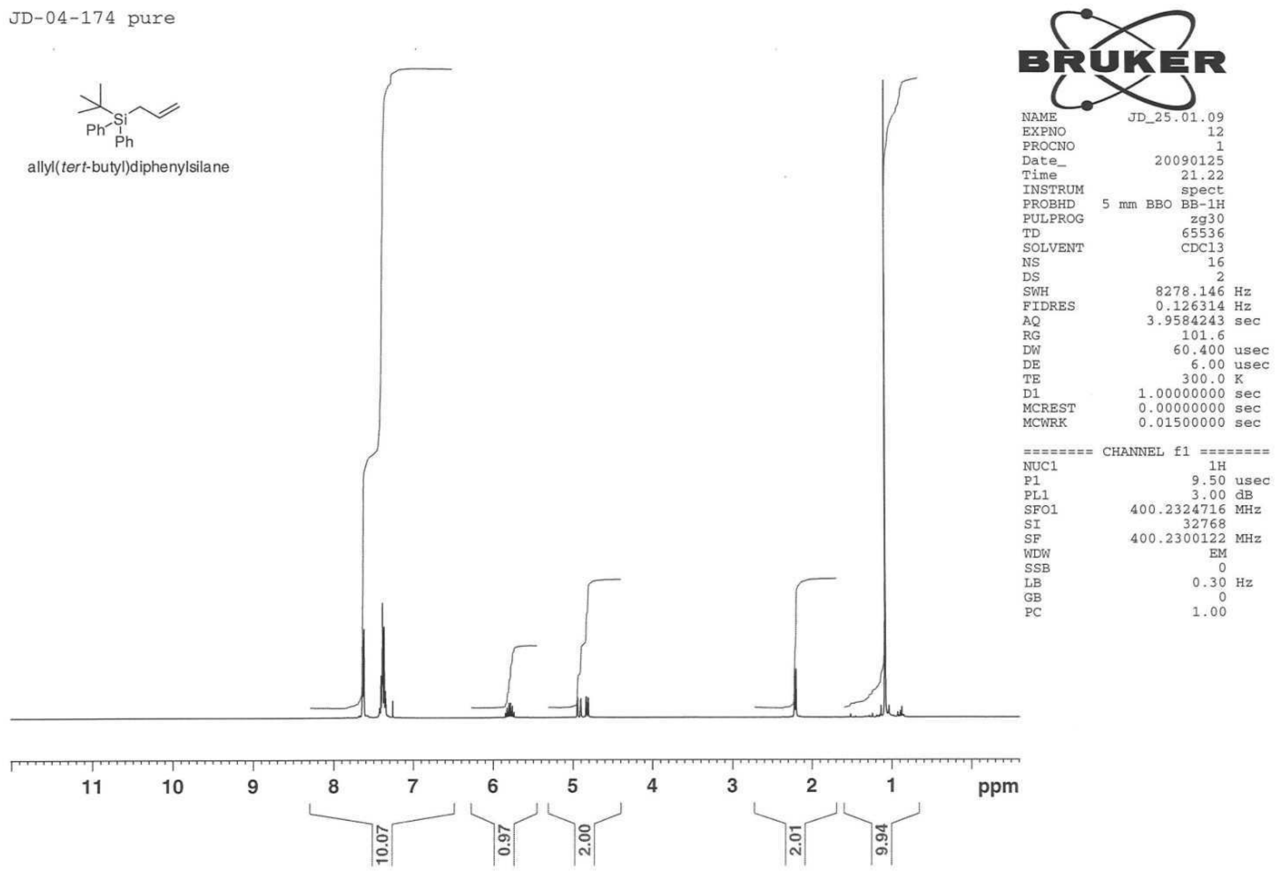
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
P3                    9.50 usec
P4                   19.00 usec
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379019 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

TABLE 1 ENTRY 5

Allyl-*tert*-butyldiphenylsilane

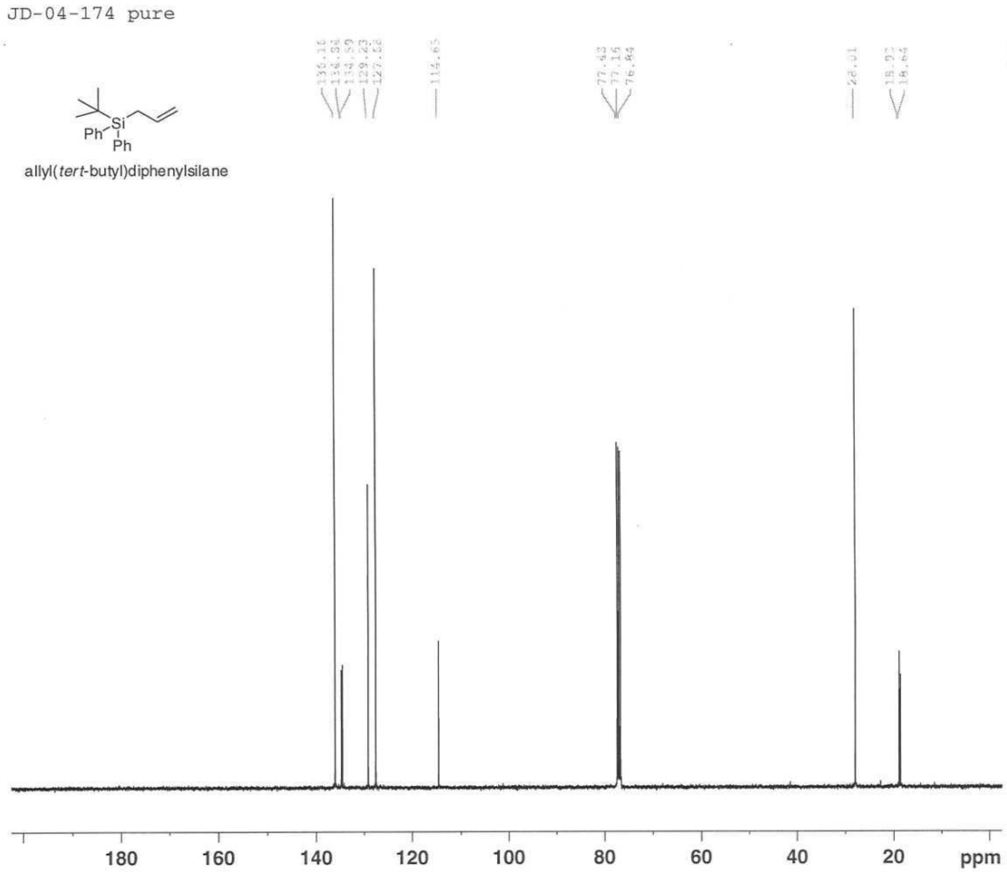


Following the general procedure A, *tert*-butyldiphenylchlorosilane (7.15 g, 6.76 mL, 26.0 mmol) furnished the impure product (7.02 g) as a pale yellow oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (6.67 g, 23.8 mmol, 92%) as a colourless oil; R_f 0.42 [hexane]; ν_{max}(film)/cm^{-1} 2929, 2857, 1630 (C=C), 1427, 1104, 895, 820; δ_H (400 MHz; CDCl$_3$) 1.09 (9H, s, ^{t}Bu), 2.21(2H, dt, *J* 7.8 and 1.2, $C\underline{H}_2CH{=}CH_2$), 4.82 (1H, ddt, *J* 10.0 2.0 and 1.2, $CH_2CH{=}C\underline{H}_{cis}H_{trans}$), 4.92 (1H, ddt, *J* 16.9 2.0 and 1.2, $CH_2CH{=}CH_{cis}\underline{H}_{trans}$), 5.79 (1H, ddt, *J* 16.9 10.0 and 7.8, $CH_2C\underline{H}{=}CH_{cis}H_{trans}$), 7.35-7.44 (6H, m, Ar), 7.62-7.64 (4H, m, Ar); δ_C (100.6 MHz; CDCl$_3$) 18.6 ($Si\underline{C}(CH_3)_3$), 18.9 ($\underline{C}H_2CH{=}CH_2$), 28.0 ($SiC(\underline{C}H_3)_3$), 114.7 ($CH_2CH{=}\underline{C}H_2$), 127.7 (4 × *m*-CH, Ar), 129.2 (2 × *p*-CH, Ar), 134.6 (2 × C, Ar), 134.8 ($CH_2\underline{C}H{=}CH_2$), 136.16 (4 × *o*-CH, Ar); LRMS (EI$^+$, *m/z*) 280 ([M]$^+$, 1%), 239 (71), 223 (100), 197 (52), 181 (36), 135 (100), 105 (40); HRMS (EI$^+$, *m/z*) 280.1643 [M]$^+$, $C_{19}H_{24}Si$ requires 280.1642. The data is in good agreement with previously reported values.^{x}



```
NAME           JD_25.01.09
EXPNO                   12
PROCNO                   1
Date_             20090125
Time                 21.22
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   101.6
DW                  60.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.50 usec
PL1                   3.00 dB
SFO1           400.2324716 MHz
SI                   32768
SF             400.2300122 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
NAME          JD_25.01.09
EXPNO                  10
PROCNO                  1
Date_            20090125
Time                21.02
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               18390.4
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379014 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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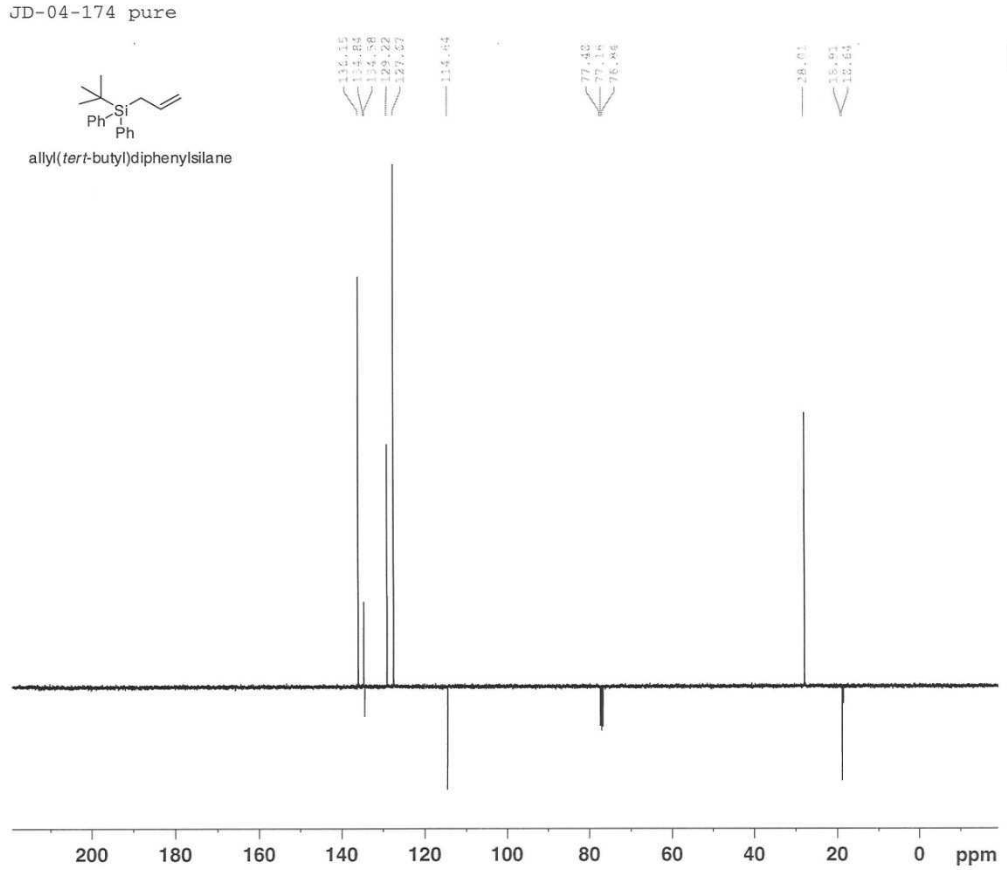

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EXPNO                  11
PROCNO                  1
Date_            20090125
Time                21.19
INSTRUM             spect
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PULPROG         deptq135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
P2                 16.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                  1H
P3                  9.50 usec
P4                 19.00 usec
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379022 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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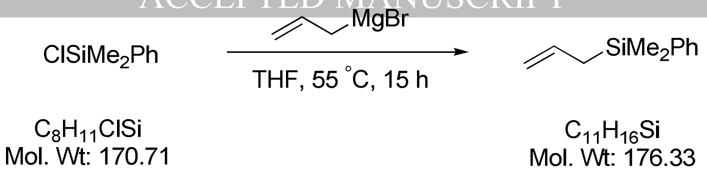
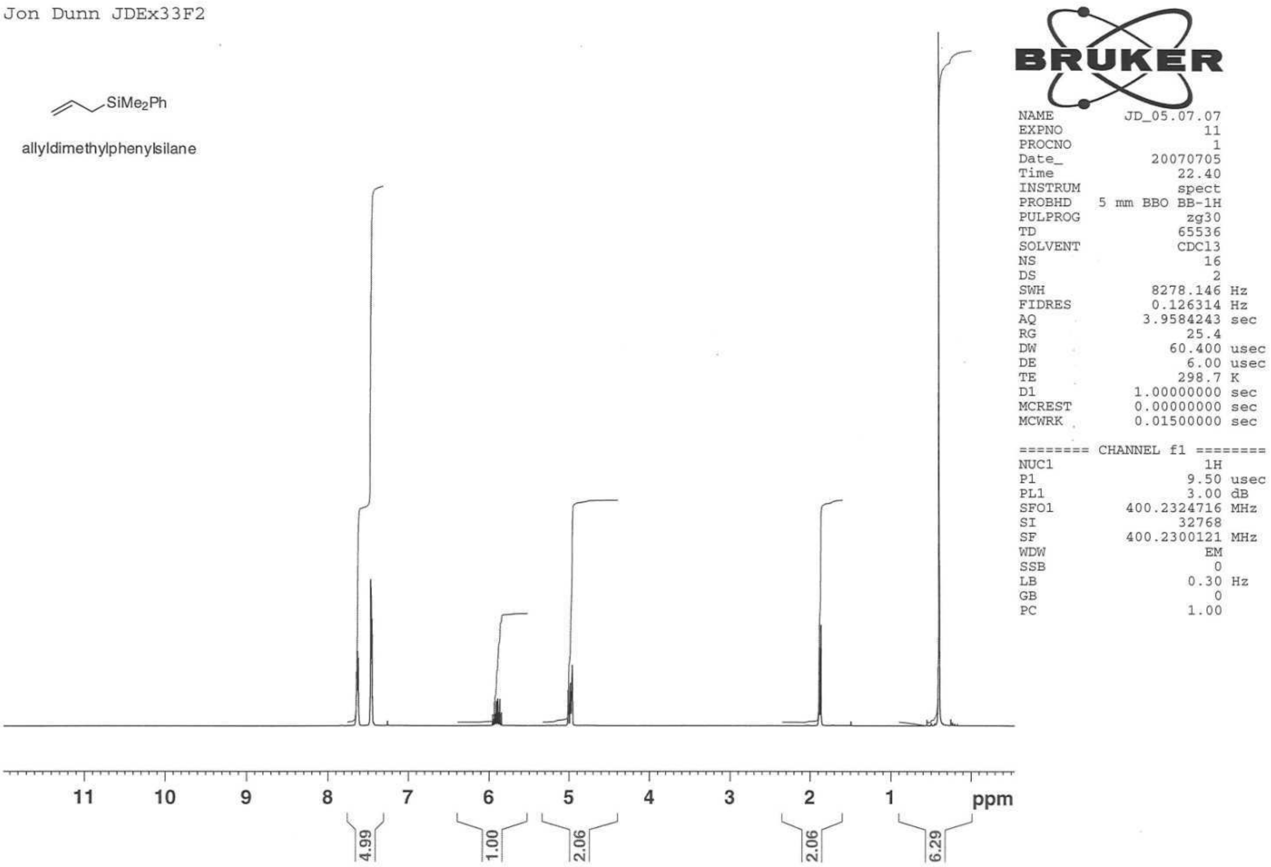
TABLE 1 ENTRY 6

Allyldimethylphenylsilane



Following the general procedure A, chlorodimethylphenylsilane (4.27 g, 5.01 mL, 25.0 mmol) furnished the impure product (5.22 g) as a pale yellow oil. Purification by flash column chromatography [silica gel, hexane] afforded the desired product (3.79 g, 21.5 mmol, 86%) as a colourless oil; R_f 0.49 [hexane]; bp 44-45 °C/0.07 mmHg, (lit.[83] 96-97 °C 14 mmHg); ν_{max}(film)/cm^{-1} 3071, 2956, 1630 (C=C), 1427, 1248, 1195, 890; δ_H (400 MHz; $CDCl_3$) 0.30 (6H, s, $SiMe_2$), 1.77 (2H, dt, *J* 8.1 and 1.0, $C\underline{H}_2CH=CH_2$), 4.86 (1H, ddt, *J* 10.1 2.1 and 1.0, $CH_2CH=C\underline{H}_{cis}H_{trans}$), 4.87 (1H, ddt, *J* 16.9 2.1 and 1.0, $CH_2CH=CH_{cis}\underline{H}_{trans}$), 5.79 (1H, ddt, *J* 16.9 10.1 and 8.1, $CH_2C\underline{H}=CH_2$), 7.35-7.38 (3H, m, Ph), 7.52-7.54 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −3.3 (3 × CH_3), 23.8 ($\underline{C}H_2CH=CH_2$), 113.6 ($CH_2CH=\underline{C}H_2$), 127.9 (2 × *m*-CH, Ph), 129.1 (*p*-CH, Ph), 133.8 (2 × *o*-CH, Ph), 134.8 ($CH_2\underline{C}H=CH_2$), 138.8 (C, Ph); LRMS (EI$^+$, *m/z*) 176 ([M]$^+$, 7%), 161 (6), 135 (100), 119 (11), 105 (15), 91 (7); HRMS (EI$^+$, *m/z*) 176.1017 [M]$^+$, $C_{11}H_{16}Si$ requires 176.1016. The data is in good agreement with previously reported values[xi]



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PROCNO                  1
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Time                22.40
INSTRUM             spect
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TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   25.4
DW                 60.400 usec
DE                   6.00 usec
TE                  298.7 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300121 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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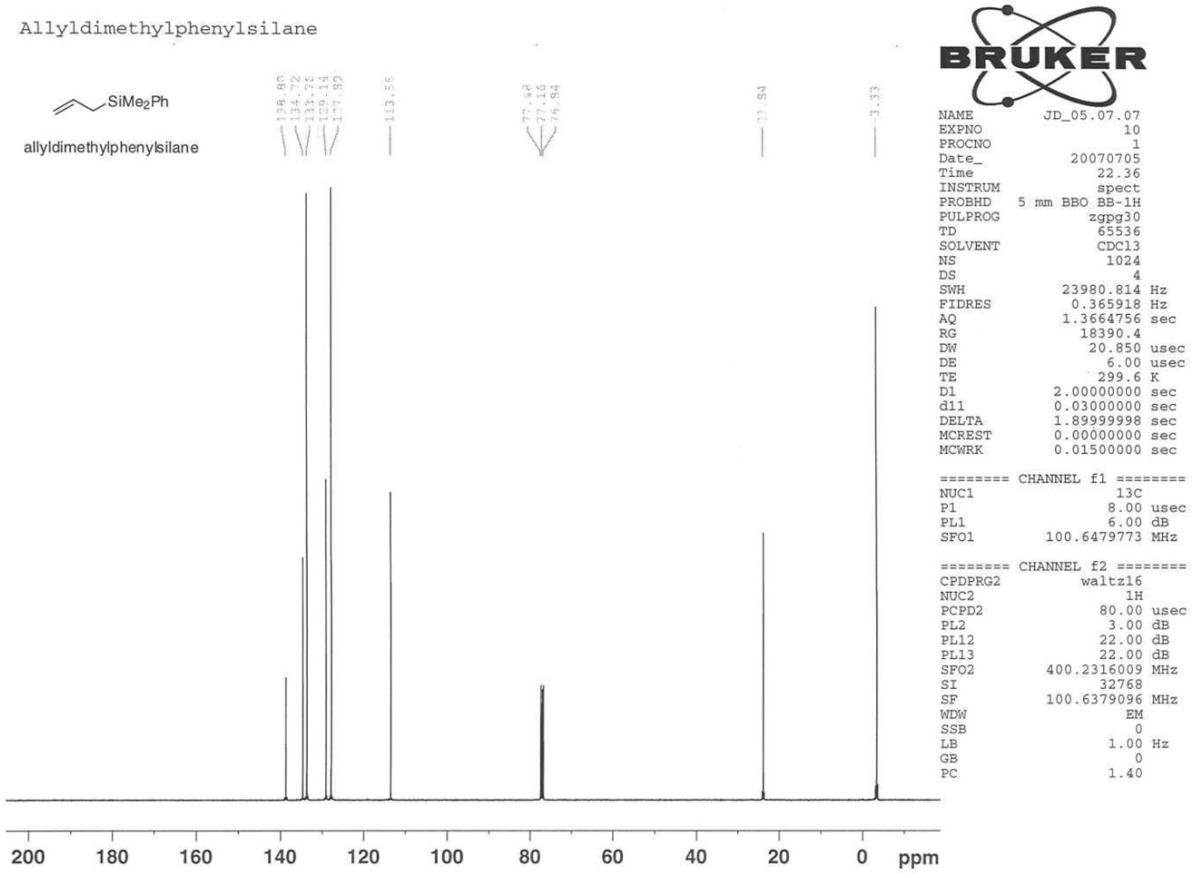

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PROCNO                  1
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Time                22.36
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  299.6 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379096 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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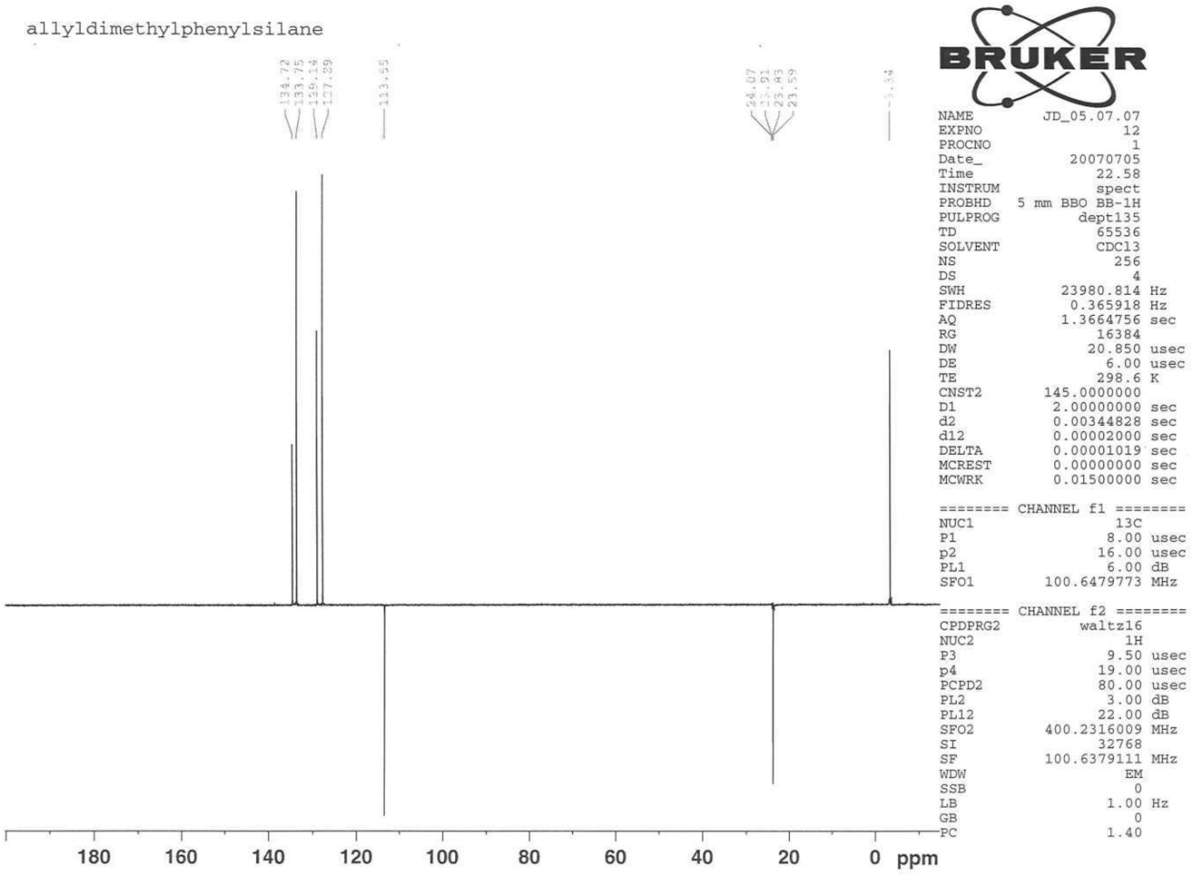

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PROCNO                  1
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Time                22.58
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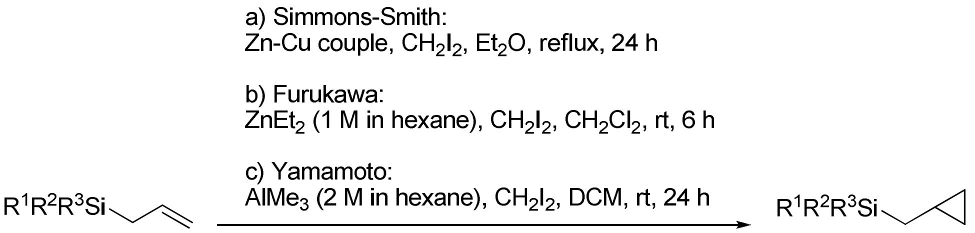
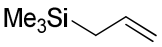
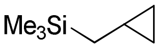
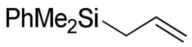
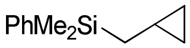
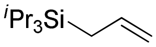
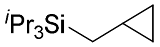
PULPROG           dept135
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  298.6 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
d12            0.00002000 sec
DELTA          0.00001019 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
p2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
p4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379111 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

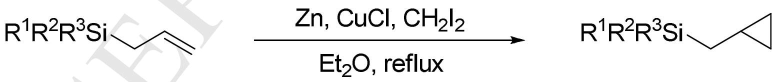
Table 2 Summary of different cyclopropanation methodologies used for the synthesis of silylmethylcyclopropane



Entry	Allylsilane	Product	Method	Yield (%)
1			Simmons Smith[a]	51
2			Simmons Smith[a]	54
3			Furukawa[b]	61
4			Yamamoto[c]	63
5			Simmons Smith	60
6			Yamamoto	56

[a] 1 eq. of allylsilane, 2 eq.diiodomethane, 5 eq. of copper chloride and 5 eq. of zinc powder in diethyl ether were heated at reflux temperature for 24 h. [b] 1eq. allylsilane, 5 eq. diiodomethane and 5 eq. of diethyl zinc in DCM were stirred at room temperature for 6 h.[c] 1eq. allylsilane, 2 eq. diiodomethane and 2 eq. of trimethylaluminium in DCM were stirred at room temperature for 24 h.

Table 3. Summary of silylmethylcyclopropanes synthesised using the Simmons-Smith reaction



Entry	R^1	R^2	R^3	Isolated yield of cyclopropane (%)	Recovered allylsilane (%)[a]
1	Et	Et	Et	42	7 (12)[b]
2	Bu	Bu	Bu	65	9 (13)
3	*i*Pr	*i*Pr	*i*Pr	77	8 (9)
4	Me	Me	Ph	82	6
5	Me	Ph	Ph	71	5
6	*t*Bu	Ph	Ph	86	5

[a] In several cases the recovered starting material could not be cleanly separated from the cyclopropane, the value in brackets is the percentage of cyclopropane that eluted with starting material determined by ^{1}H NMR analysis.

[b]The remaining material was identified as hexaethyldisiloxane by GCMS.

General Procedure B - Preparation of (cyclopropylmethyl)silanes (Simmons-Smith)

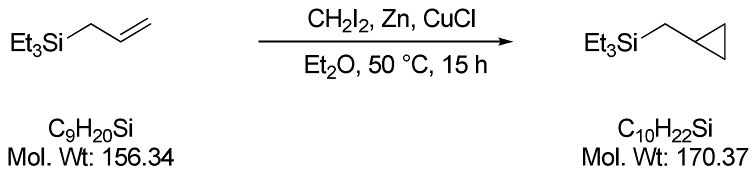
To a stirred suspension of zinc powder (5 eq.) and copper chloride (5 eq.) in anhydrous diethyl ether (5 mL/mmol), which had been heated at reflux temperature for 30 min and allowed to cool to room temperature, was added allylsilane (1 eq.) and diiodomethane (2 eq.). The reaction was heated at reflux temperature for 15 h, cooled to room temperature and filtered through celite washing with diethyl ether (2 mL/mmol). The filtrate was washed with 1 M HCl followed by 10% *w/v* sodium bicarbonate solution until pH 7. The combined aqueous layers were extracted with diethyl ether and the combined organic layers were washed with brine, 10% *w/v* sodium thiosulfate solution, separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product. Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica (1 : 3) eluting with hexane gave the desired product.

Typical procedure for the purification of (cyclopropylmethyl)silanes - Preparation of silver nitrate impregnated silica gel.

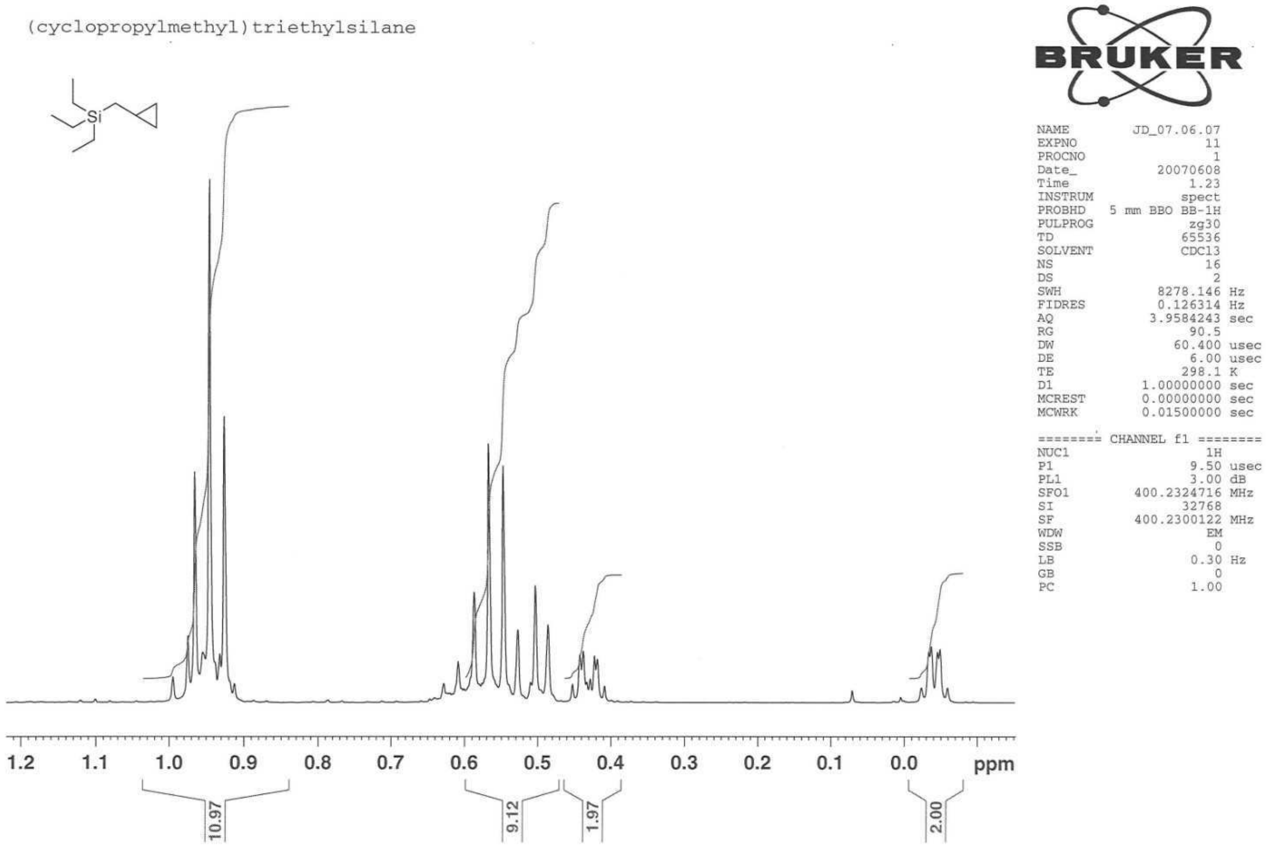
Silver nitrate (3 g) and methanol (300 mL) was stirred vigorously until the all the solid had dissolved. To this solution was added silica gel (30 g) and the resulting mixture stirred for 5 min. The slurry was then transferred to a round bottom flask covered with silver foil and the solvent removed *in vacuo* to give the impregnated silica gel as a bright white powder/gel. The column was made by pre-forming a slurry of silica gel (50 g) in hexane. Once this had settled the silver nitrate impregnated silica gel was added as a slurry in hexane creating a band of silver nitrate impregnated silica at the top of the column. The column was washed with three column lengths of hexane to wash through any residual methanol and run in the usual way.

TABLE 3 ENTRY 1

(Cyclopropylmethyl)triethylsilane



Following the general procedure B, allytriethylsilane (3.78 g, 24.0 mmol) furnished the impure product as a brown oil (2.90 g). Purification by flash column using 10% silver nitrate impregnated silica and standard silica eluting with hexane gave desired product (1.61 g, 9.45 mmol, 40%) as a colourless oil; R_f 0.81 [hexane]; ν_{max}(film)/cm^{-1} 3071 (CH cyclopropyl), 2952, 2875, 1457, 1416, 1239, 1013, 891; δ_H (400 MHz; $CDCl_3$) −0.06 to −0.02 (2H, m, CH_2 cyclopropyl), 0.41-0.45 (2H, m, CH_2 cyclopropyl), 0.49 (2H, d, *J* 6.9, 3 × CH_2), 0.56 (6H, q, *J* 8.0, 3 × $C\underline{H}_2CH_3$), 0.54-0.61 (1H, m, CH cyclopropyl); 0.95 (9H, t, *J* 8.0, 3 × CH_3); δ_C (100.6 MHz; $CDCl_3$) 3.7 (3 × CH_2), 6.3 (CH), 6.9 (2 × CH_2 cyclopropyl), 7.6 (3 × CH_3), 17.3 ($SiCH_2$); LRMS (EI^+, *m/z*) 170 ($[M]^+$ 1%), 141 (34),115 (61), 87 (100), 59 (35); HRMS (EI^+, *m/z*) 170.1483 $[M]^+$, $C_{10}H_{22}Si$ requires 170.1485.



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PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  90.5
DW                60.400 usec
DE                  6.00 usec
TE                 298.1 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.50 usec
PL1                 3.00 dB
SFO1         400.2324716 MHz
SI                 32768
SF           400.2300122 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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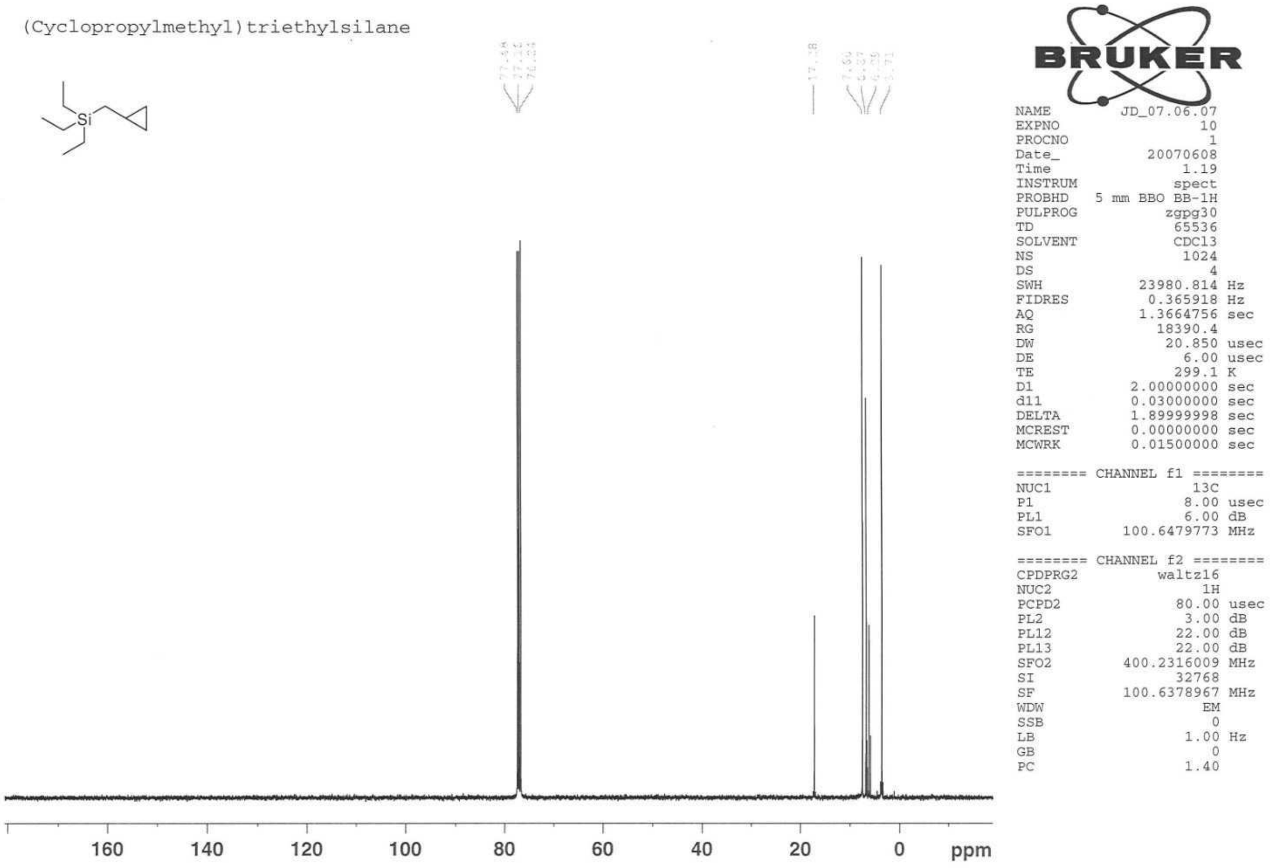

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PROCNO                   1
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Time                  1.19
INSTRUM              spect
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PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   299.1 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6378967 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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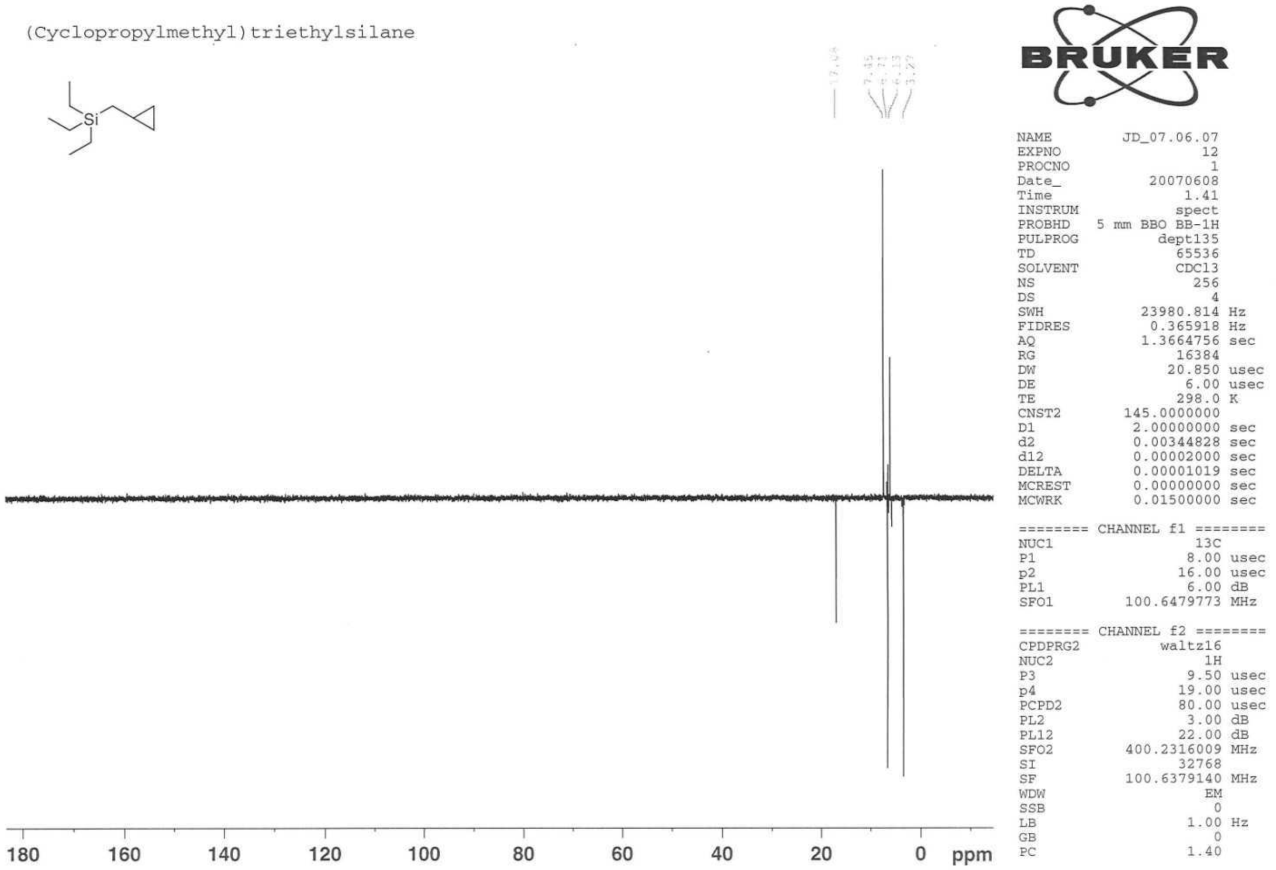

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PROCNO                   1
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Time                  1.41
INSTRUM              spect
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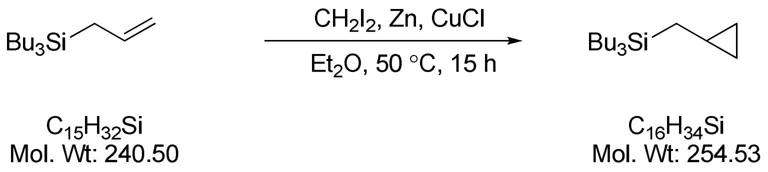
PULPROG            dept135
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   298.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001019 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
p2                   16.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

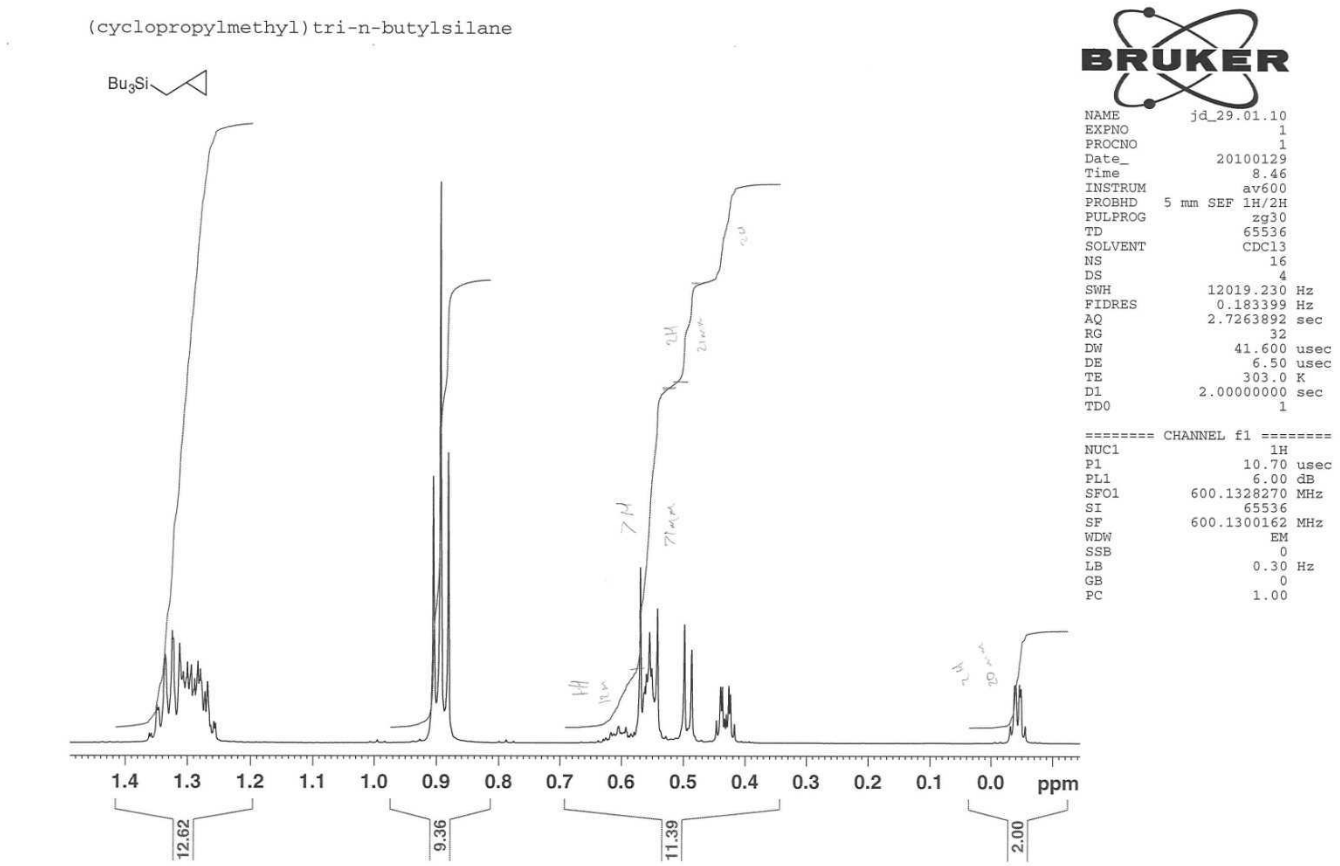
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
P3                    9.50 usec
p4                   19.00 usec
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379140 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

TABLE 3 ENTRY 2

(Cyclopropylmethyl)tri-*n*-butylsilane



Following the general procedure B, allyltri-*n*-butylsilane (3.78 g, 16.5 mmol) furnished the impure product as a colourless oil (3.78 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (2.73 g, 10.7 mmol, 65%) as a colourless oil; R_f 0.93 [hexane]; ν_{max}(film)/cm^{-1} 2918, 1463, 1197 (Si-C), 1081, 886 (Si-C); δ_H (600 MHz; $CDCl_3$) −0.06 to −0.03 (2H, m, CH_2 cyclopropyl), 0.42-0.45 (2H, m, CH_2 cyclopropyl), 0.49 (2H, d, *J* 7.0, $SiC\underline{H_2}CH$), 0.54-0.63 (7H, m, $SiCH_2C\underline{H}$ and 3 × CH_2 overlapping signals), 0.89 (9H, t, *J* 7.0, 3 × $C\underline{H_3}$), 1.26-1.36 (12H, m, 6 × $C\underline{H_2}$ Bu); δ_C (100.6 MHz; $CDCl_3$) 6.4 (CH cyclopropyl), 6.9 (2 × CH_2 cyclopropyl), 12.5 (3 × CH_2, Bu), 14.0 (3 × CH_3), 18.3 ($Si\underline{C}H_2CH$), 26.4 (3 × CH_2), 27.1 (3 × CH_2); LRMS (EI^+, *m/z*) 199 ($[M-C_4H_7]^+$, 45%), 143 (100), 101 (29), 87 (22), 59 (29); HRMS (EI^+, *m/z*) 253.2348 $[M-H]^+$, $C_{16}H_{33}Si$ requires 253.2346.



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PROCNO                  1
Date_            20100129
Time                 8.46
INSTRUM             av600
PROBHD   5 mm SEF 1H/2H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      4
SWH             12019.230 Hz
FIDRES           0.183399 Hz
AQ              2.7263892 sec
RG                     32
DW                 41.600 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.70 usec
PL1                  6.00 dB
SFO1          600.1328270 MHz
SI                  65536
SF            600.1300162 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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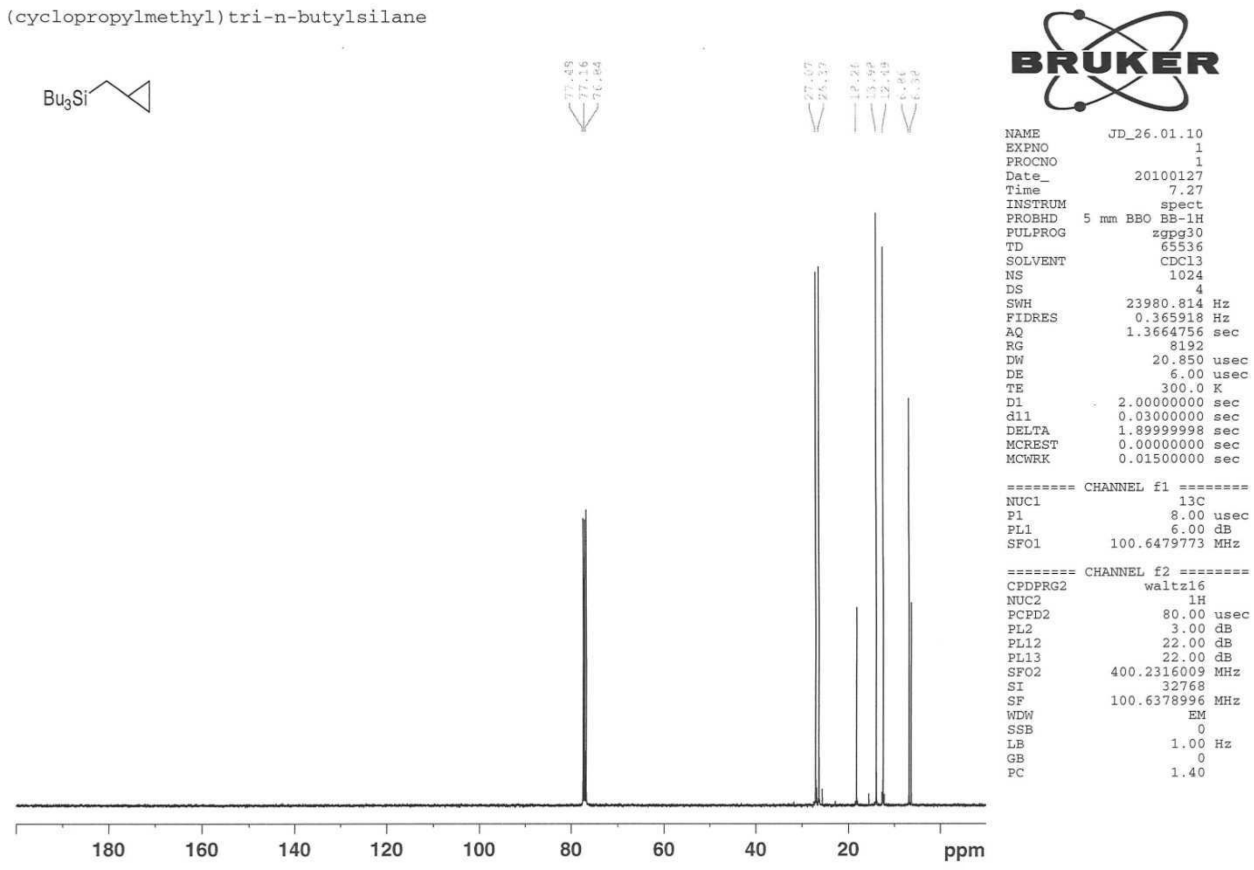

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PROCNO                  1
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Time                 7.27
INSTRUM             spect
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PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6378996 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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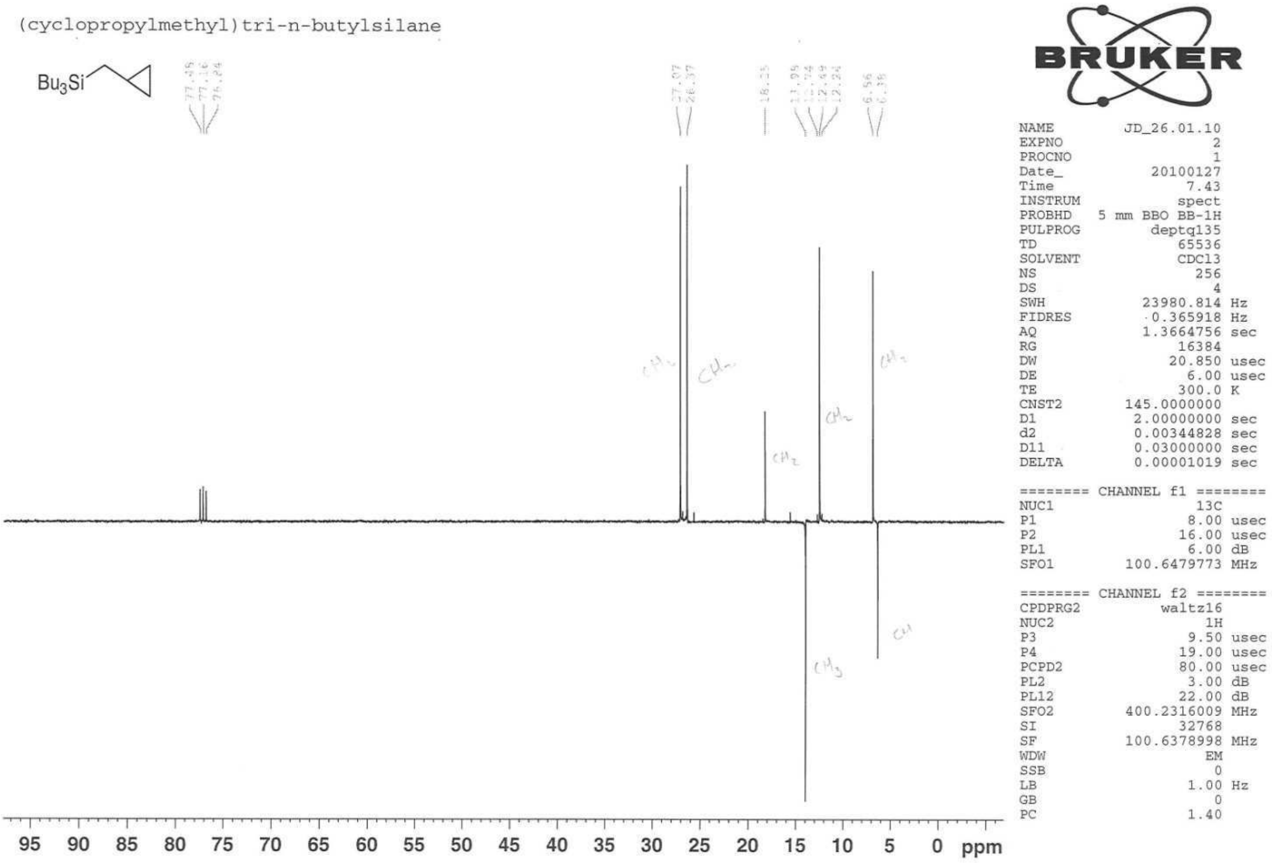

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NAME          JD_26.01.10
EXPNO                   2
PROCNO                  1
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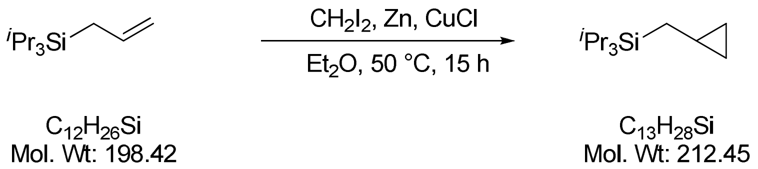
Time                 7.43
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG         deptq135
TD                 65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

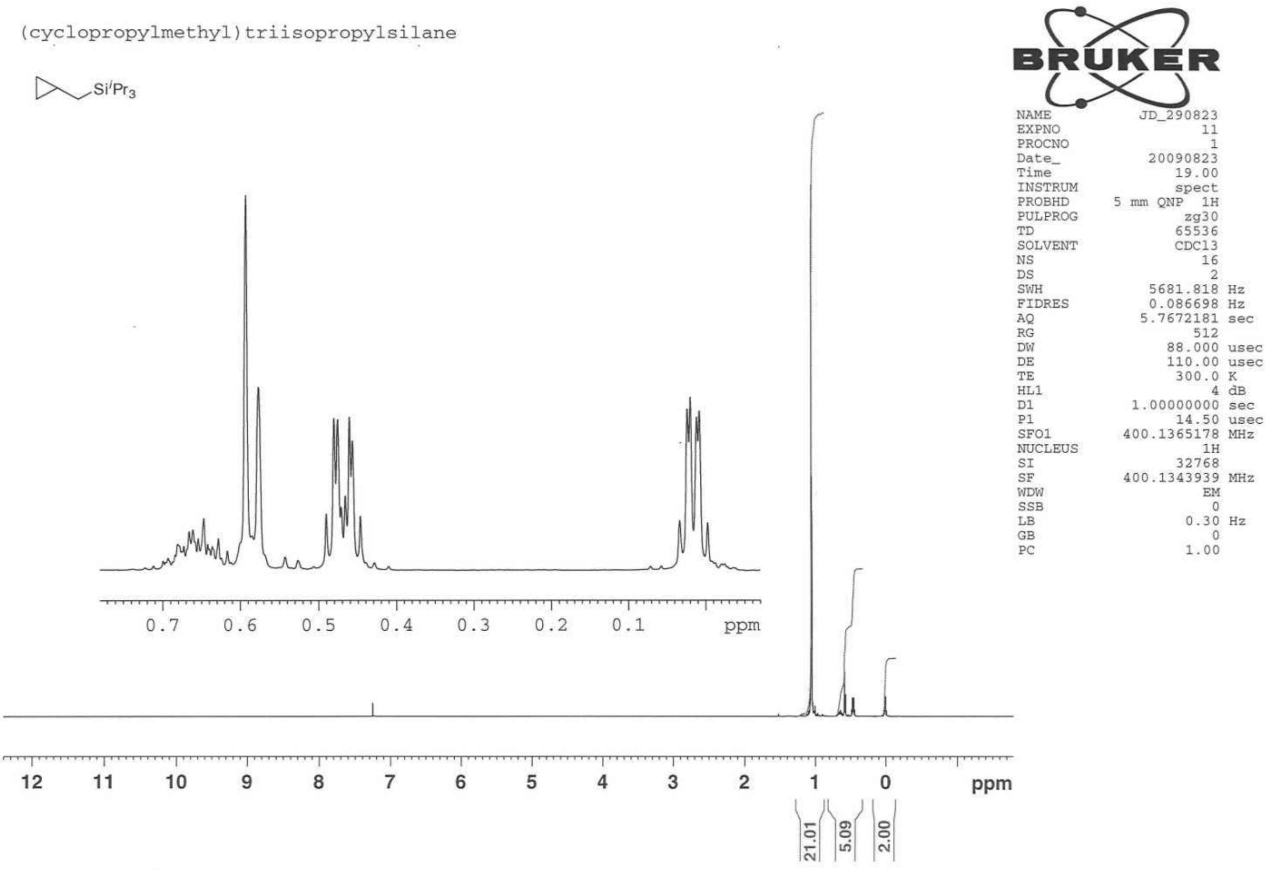
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6378998 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

TABLE 3 ENTRY 3

(Cyclopropylmethyl)triisopropylsilane

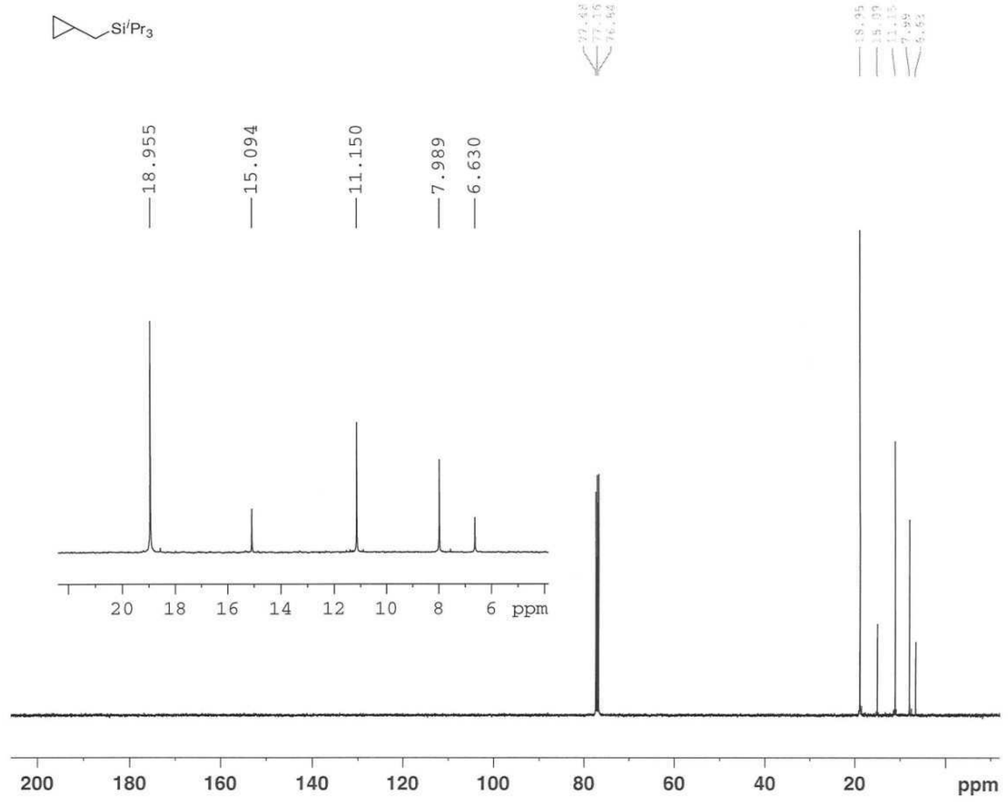


Following the general procedure B, allyltriisopropylsilane (5.77 g, 21.0 mmol) furnished the impure product as a yellow oil (5.04 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (3.45 g, 16.2 mmol, 77%) as a colourless oil; R_f 0.88 [hexane]; ν_{max}(film)/cm^{-1} 3074 (C-H cyclopropyl), 2941 (C-H), 1464, 1015, 881 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.00-0.03 (2H, m, CH_2 cyclopropyl), 0.46-0.49 (2H, m, CH_2 cyclopropyl), 0.58 (2H, d, *J* 6.5, $SiC\underline{H}_2CH$), 0.61-0.71 (1H, m, $SiCH_2C\underline{H}$), 1.04-1.12 (21H, m, overlapping signals 6 × CH_3 and 3 × CH, ^{i}Pr); δ_C (100.6 MHz; $CDCl_3$) 6.6 (CH cyclopropyl), 8.0 (2 × CH_2 cyclopropyl), 11.1 (3 × CH, ^{i}Pr), 15.1 ($Si\underline{C}H_2CH$), 19.0 (6 × CH_3); LRMS (EI^+, *m/z*) M^+ not visible, 169 ([M−^{i}Pr]$^+$, 13%), 157 (80), 127 (88), 115 (100), 99 (56), 87 (58), 73 (78), 59 (81); HRMS (EI^+, *m/z*) 213.2034 $[M+H]^+$, $C_{13}H_{29}Si$ requires 213.2033.



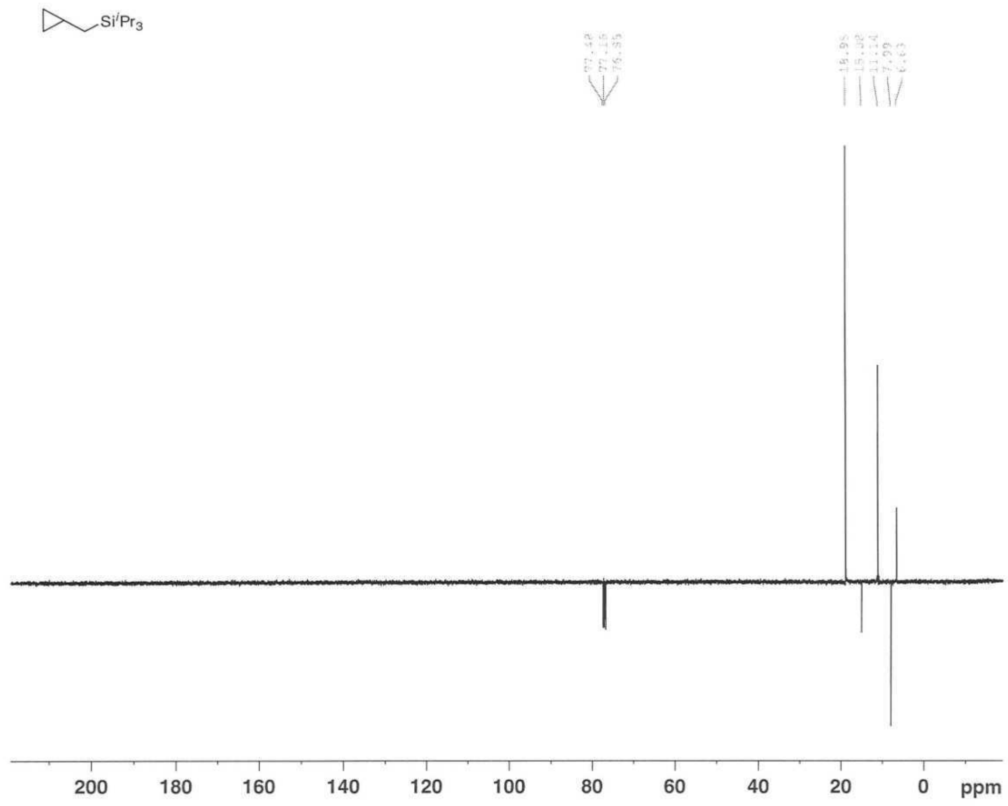
```
NAME          JD_290823
EXPNO                11
PROCNO                1
Date_          20090823
Time              19.00
INSTRUM           spect
PROBHD     5 mm QNP  1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            5681.818 Hz
FIDRES         0.086698 Hz
AQ            5.7672181 sec
RG                  512
DW               88.000 usec
DE               110.00 usec
TE                300.0 K
HL1                   4 dB
D1           1.00000000 sec
P1                14.50 usec
SFO1        400.1365178 MHz
NUCLEUS              1H
SI                32768
SF          400.1343939 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

(cyclopropylmethyl)triisopropylsilane



```
NAME          JD_290823
EXPNO                10
PROCNO                1
Date_          20090823
Time              18.58
INSTRUM           spect
PROBHD     5 mm QNP  1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH          26315.789 Hz
FIDRES        0.401547 Hz
AQ           1.2452340 sec
RG                32768
DW               19.000 usec
DE                27.14 usec
TE                300.0 K
HL1                   4 dB
D1           2.00000000 sec
CPDPRG          waltz16
P31               80.00 usec
S4                   20 dB
D11          0.0300000 sec
S2                   17 dB
P1                 6.00 usec
SFO1       100.6251166 MHz
NUCLEUS             13C
SI                32768
SF         100.6138553 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

(cyclopropylmethyl)triisopropylsilane



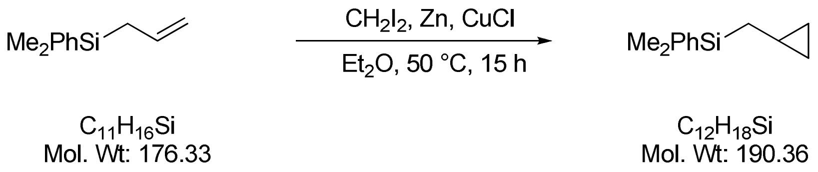
```
NAME          JD_19.07.09
EXPNO                22
PROCNO                1
Date_          20090719
Time              21.45
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG        deptq135
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ           1.3664756 sec
RG                16384
DW               20.850 usec
DE                 6.00 usec
TE                300.0 K
CNST2       145.0000000
D1           2.00000000 sec
d2           0.00344828 sec
D11          0.03000000 sec
DELTA        0.00001019 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
P2                16.00 usec
PL1                6.00 dB
SFO1       100.6479773 MHz

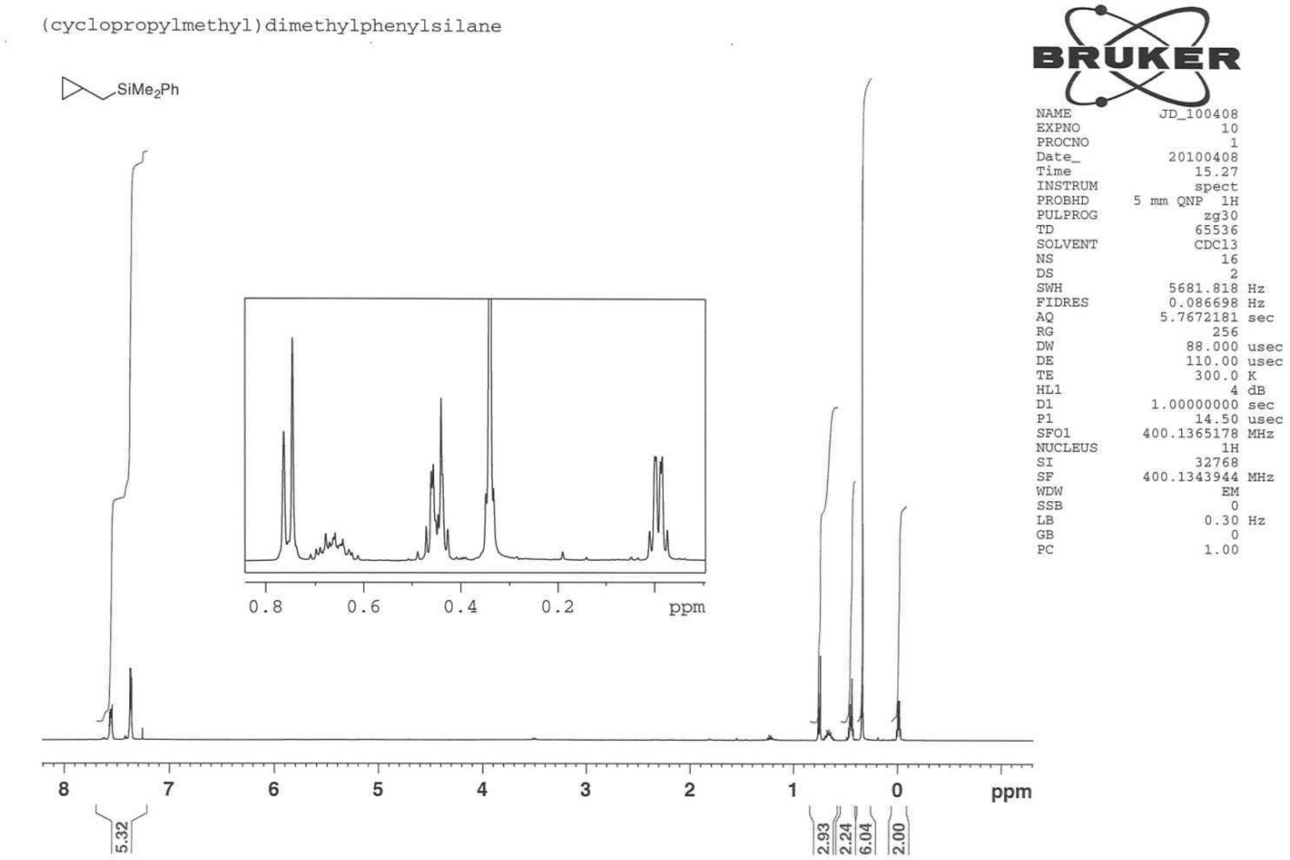
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
P3                 9.50 usec
P4                19.00 usec
PCPD2             80.00 usec
PL2                3.00 dB
PL12              22.00 dB
SFO2       400.2316009 MHz
SI                32768
SF         100.6378992 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

TABLE 3 ENTRY 4

(Cyclopropylmethyl)dimethylphenylsilane

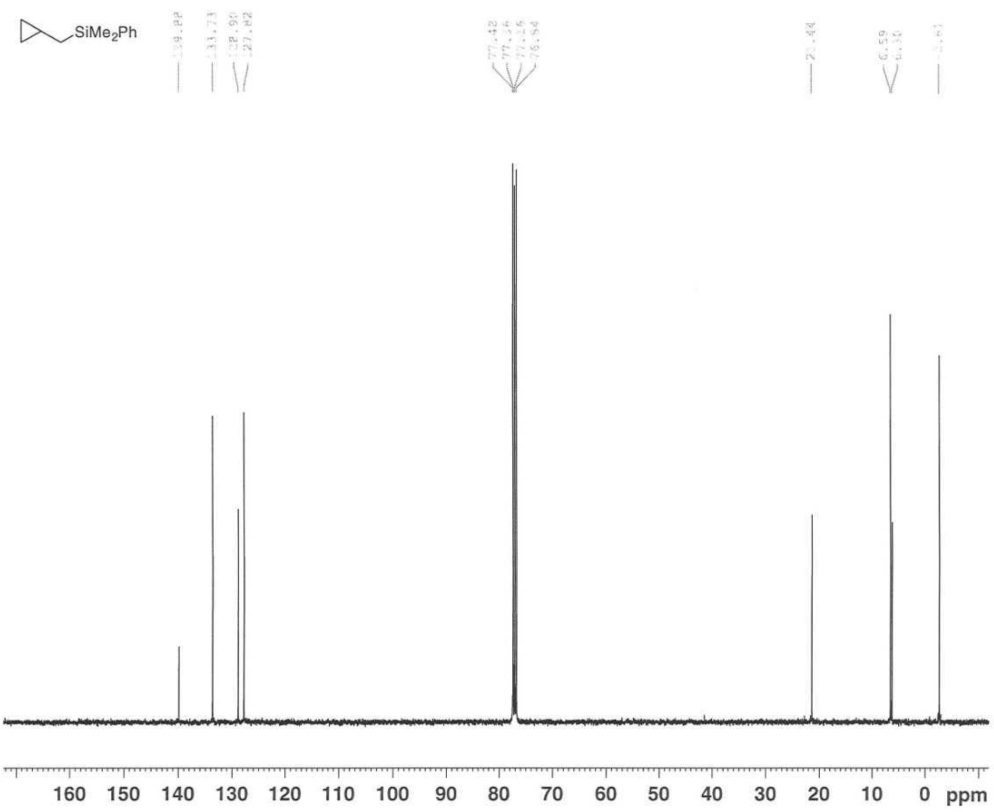


Following the general procedure B, allyldimethylphenylsilane (3.88 g, 22.0 mmol) furnished the impure product as a yellow oil (3.24 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (2.79 g, 14.7 mmol, 67%) as a colourless oil; R_f 0.53 [hexane]; ν_{max}(film)/cm^{-1} 3070 (C-H cyclopropyl), 2956, 1426, 1247, 1113, 835; δ_H (400 MHz; $CDCl_3$) −0.03-0.01 (2H, m, CH_2 cyclopropyl), 0.34 (6H, s, 2 × CH_3), 0.43-0.47 (2H, m, CH_2 cyclopropyl), 0.61-0.71 (1H, m, $SiCH_2C\underline{H}$), 0.75 (2H, d, *J* 6.9, $SiC\underline{H}_2CH$),7.36-7.39 (3H, m, Ph), 7.54-7.58 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −2.6 (2 × CH_3), 6.3 (CH cyclopropyl), 6.6 (2 × CH_2 cyclopropyl), 21.4 ($Si\underline{C}H_2$), 127.8 (2 × *m*-CH, Ph), 128.9 (*p*-CH, Ph), 133.7 (2 × *o*-CH, Ph), 139.9 (C, Ph); LRMS (EI$^+$, *m/z*) 190 ([M]$^+$, 2%), 175 (9), 135 (100), 105 (12); HRMS (EI$^+$, *m/z*) 190.1173 [M]$^+$, $C_{12}H_{18}Si$ requires 190.1172.



```
NAME             JD_100408
EXPNO                   10
PROCNO                   1
Date_             20100408
Time                 15.27
INSTRUM              spect
PROBHD      5 mm QNP   1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               5681.818 Hz
FIDRES            0.086698 Hz
AQ               5.7672181 sec
RG                     256
DW                  88.000 usec
DE                  110.00 usec
TE                   300.0 K
HL1                      4 dB
D1              1.00000000 sec
P1                   14.50 usec
SFO1           400.1365178 MHz
NUCLEUS                 1H
SI                   32768
SF             400.1343944 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

(cyclopropylmethyl)dimethylphenylsilane

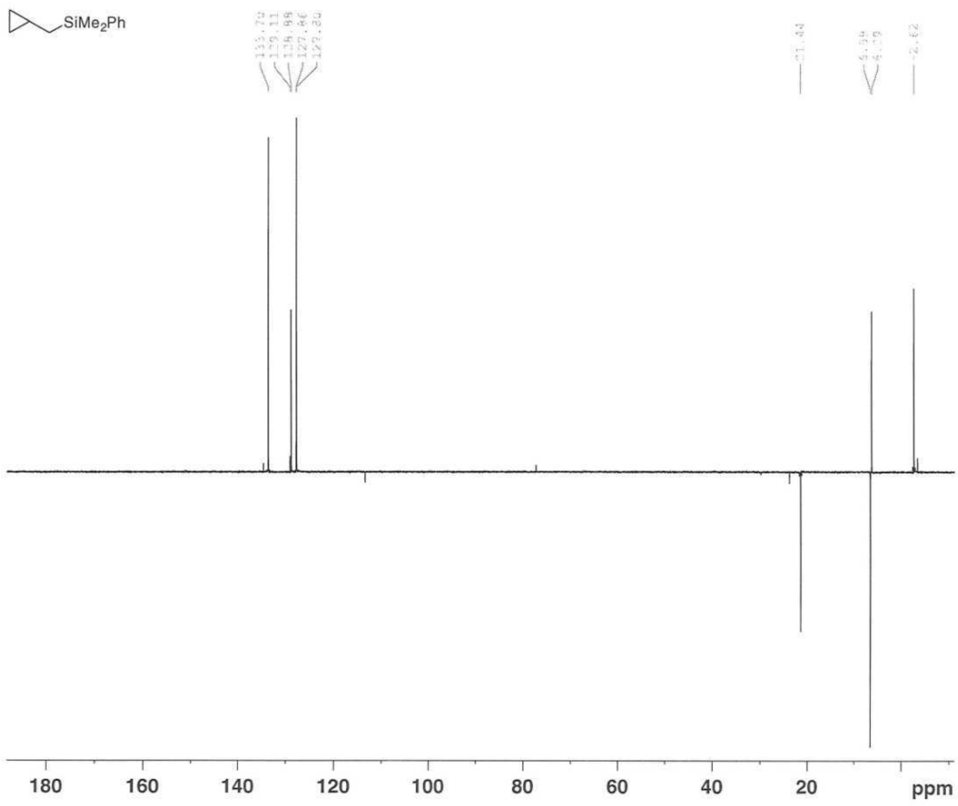


```
NAME           JD_27.06.09
EXPNO                   31
PROCNO                   1
Date_             20090626
Time                 23.30
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379011 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

(cyclopropylmethyl)dimethylphenylsilane



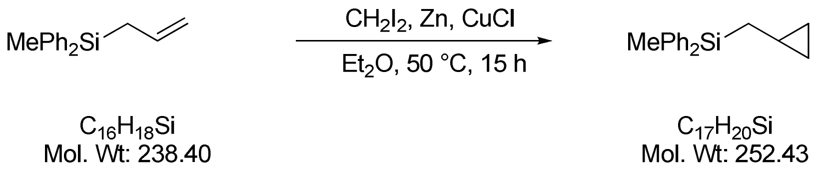
```
NAME           JD_05.12.07
EXPNO                   11
PROCNO                   1
Date_             20071206
Time                 10.23
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG            dept135
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   298.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001019 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
p2                   16.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

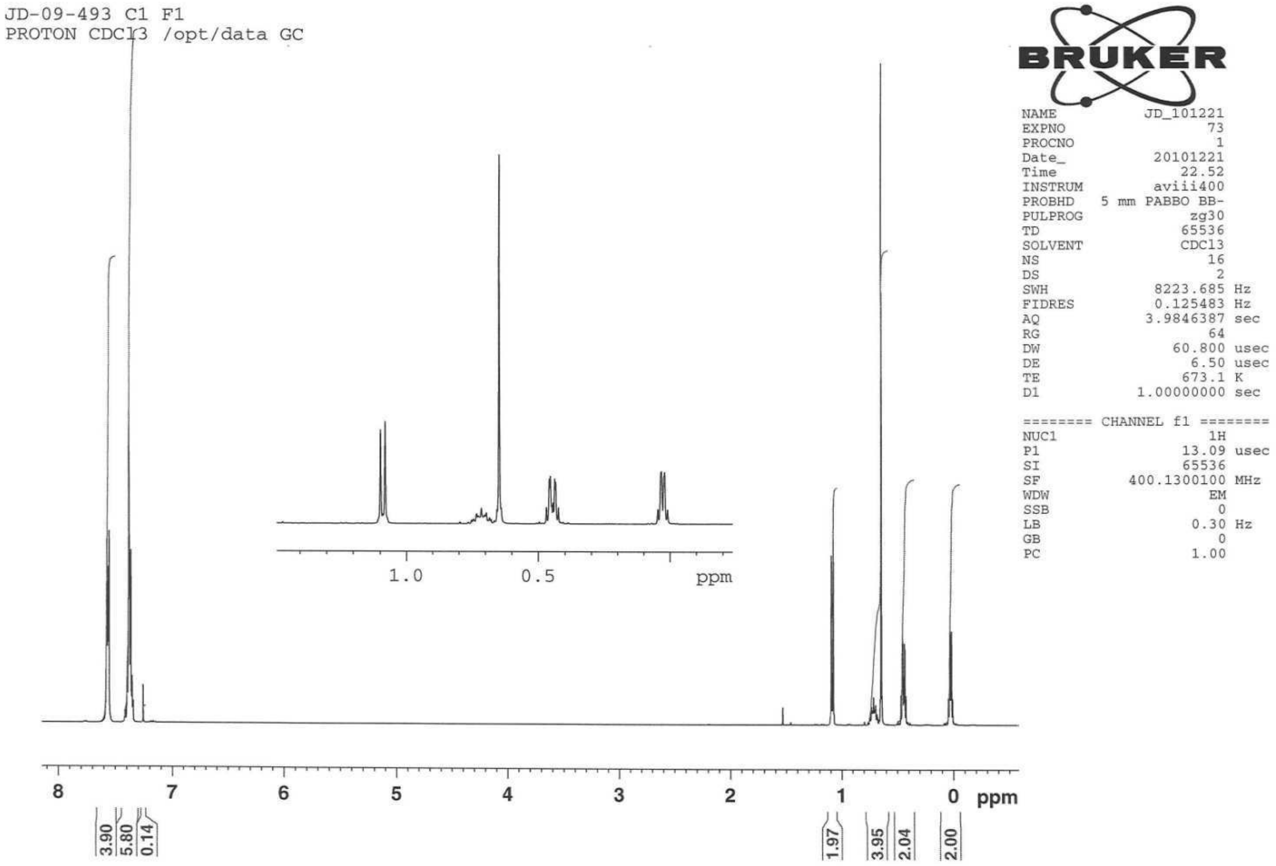
======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
P3                    9.50 usec
p4                   19.00 usec
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379100 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

TABLE 3 ENTRY 5

(Cyclopropylmethyl)(methyl)diphenylsilane

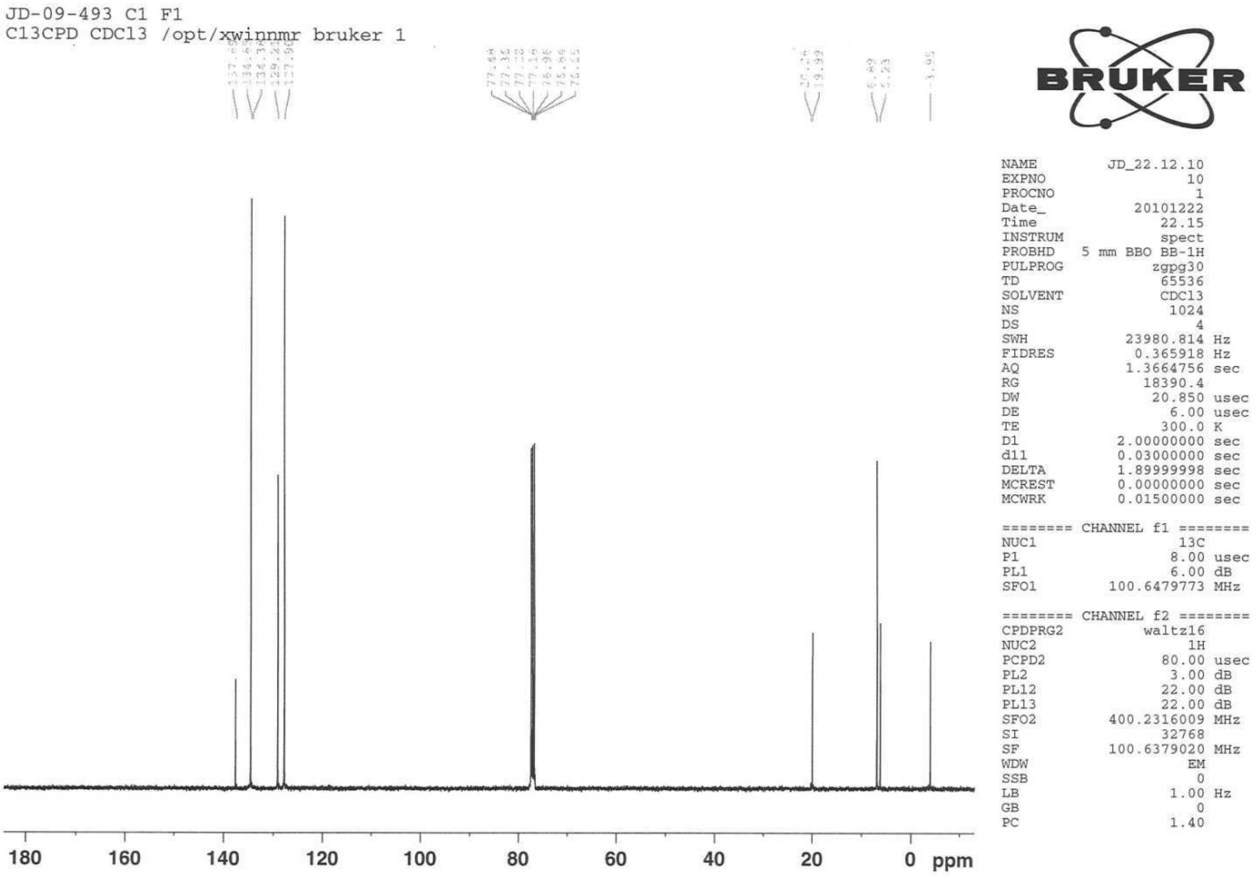


Following the general procedure B, allyl(methyl)diphenylsilane (4.32 g, 18.0 mmol) furnished the impure product as a yellow oil (3.94 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (3.21 g, 12.7 mmol, 71%) as a colourless oil; R_f 0.32 [hexane]; ν_{max}(film)/cm^{-1} 3069 (C-H cyclopropyl), 2998 (CH_3), 1427, 1250, 1108, 802, 727, 697; δ_H (400 MHz; $CDCl_3$) 0.01-0.05 (2H, m, CH_2 cyclopropyl), 0.43-0.47 (2H, m, CH_2 cyclopropyl), 0.65 (3H, s, SiMe), 0.68-0.77 (1H, m, CH cyclopropyl), 1.09 (2H, d, *J* 7.0, $SiC\underline{H}_2$), 7.35-7.42 (6H, m, Ar), 7.54-7.60 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −4.0 ($SiMe_2$), 6.2 (CH cyclopropyl), 6.9 (2 × CH_2 cyclopropyl), 20.0 ($Si\underline{C}H_2$), 127.9 (4 × *m*-CH, Ar), 129.2 (2 × *p*-CH, Ar), 134.7 (4 × *o*-CH, Ar), 137.7 (2 × C, Ar); LRMS (EI$^+$, *m/z*) 252 ([M]$^+$, 8%), 237 (4), 224 (13), 197 (100), 181 (13), 165 (11), 105 (20); HRMS (EI$^+$, *m/z*) 252.1329 [M]$^+$, $C_{17}H_{20}Si$ requires 252.1329.



```
NAME           JD_101221
EXPNO                 73
PROCNO                 1
Date_           20101221
Time               22.52
INSTRUM          aviii400
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                    64
DW                60.800 usec
DE                  6.50 usec
TE                 673.1 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.09 usec
SI                 65536
SF           400.1300100 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

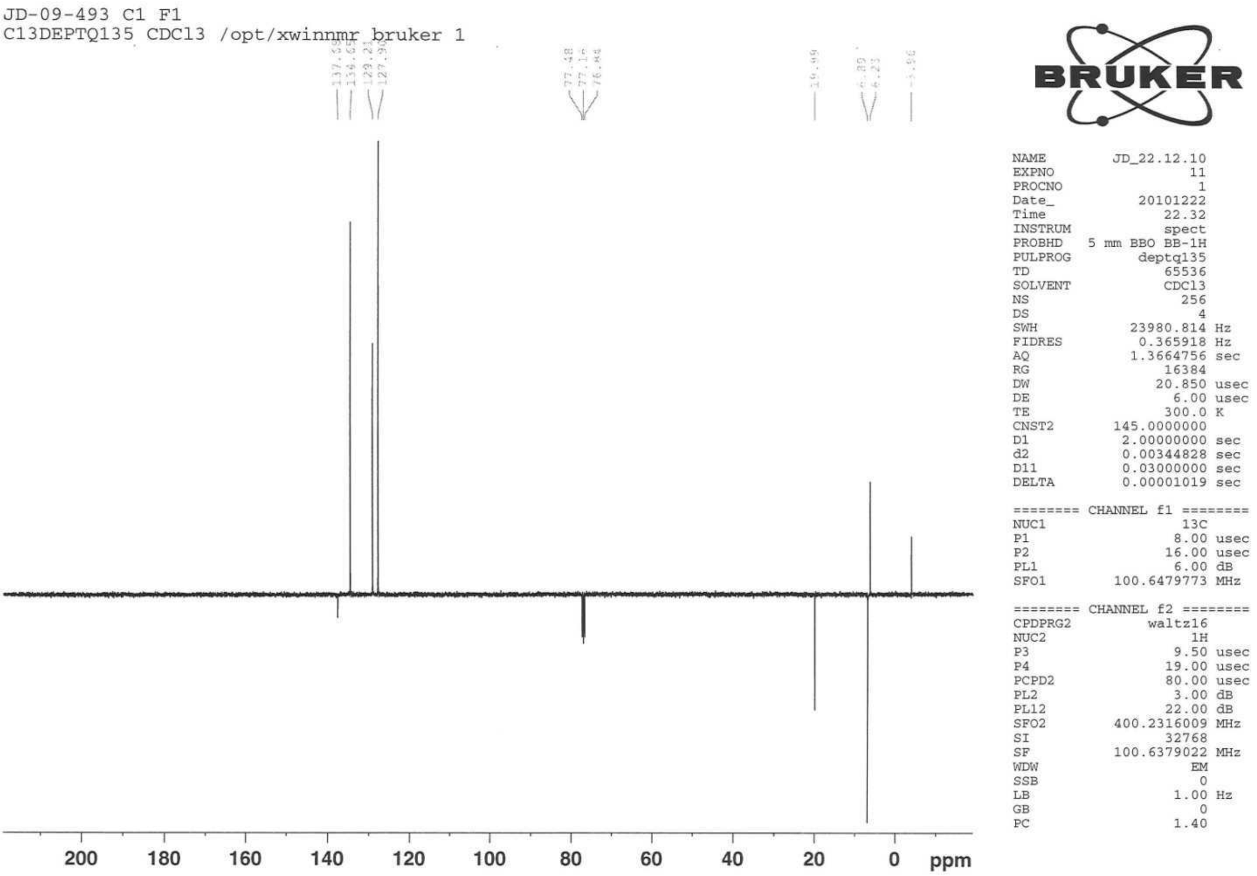


```
JD-09-493 C1 F1
C13CPD CDCl3 /opt/xwinnmr bruker 1
```

```
NAME         JD_22.12.10
EXPNO                 10
PROCNO                 1
Date_           20101222
Time               22.15
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               18390.4
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379020 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



```
JD-09-493 C1 F1
C13DEPTQ135 CDCl3 /opt/xwinnmr bruker 1
```

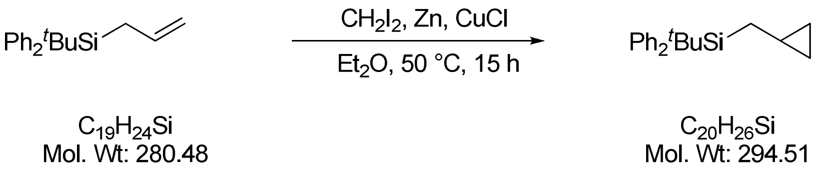
```
NAME         JD_22.12.10
EXPNO                 11
PROCNO                 1
Date_           20101222
Time               22.32
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG        deptq135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
P2                 16.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

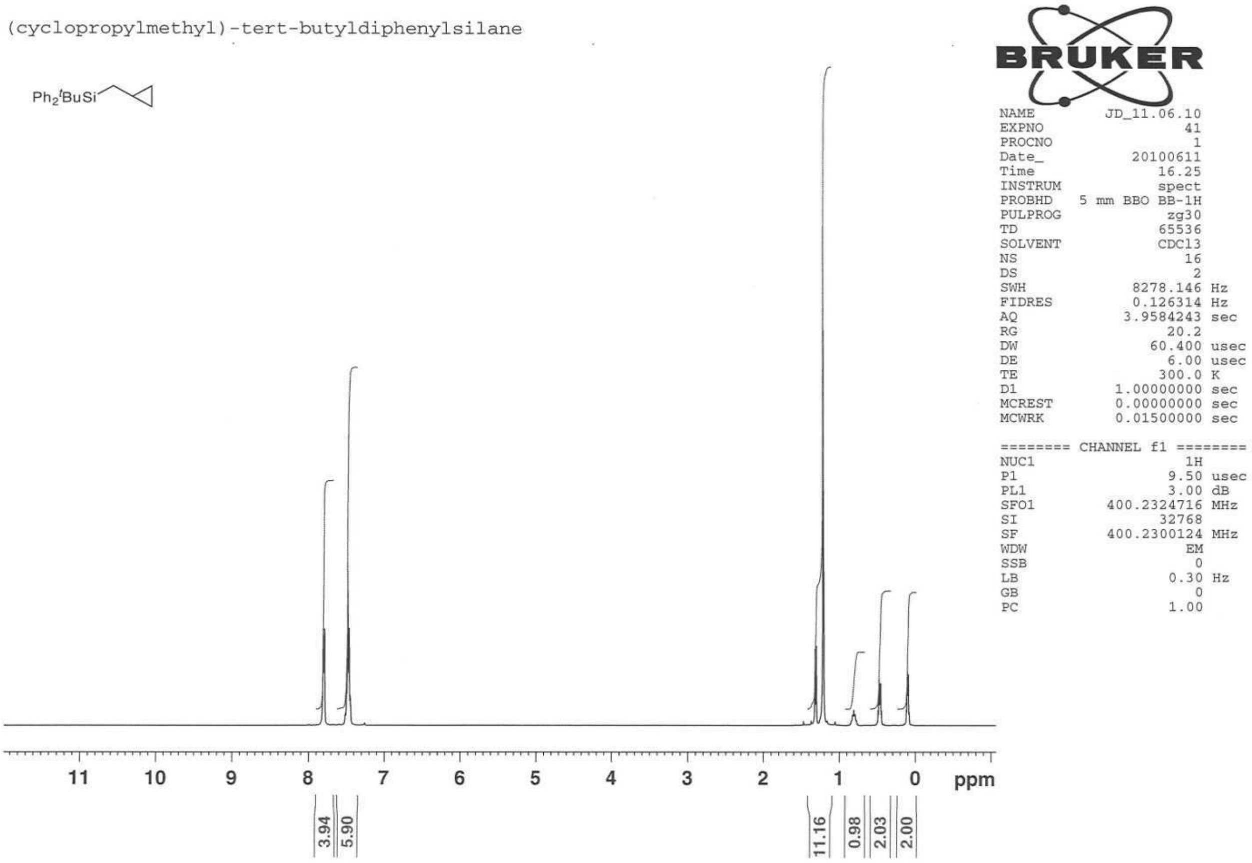
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  9.50 usec
P4                 19.00 usec
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379022 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

TABLE 3 ENTRY 6

(Cyclopropylmethyl)-*tert*-butyldiphenylsilane

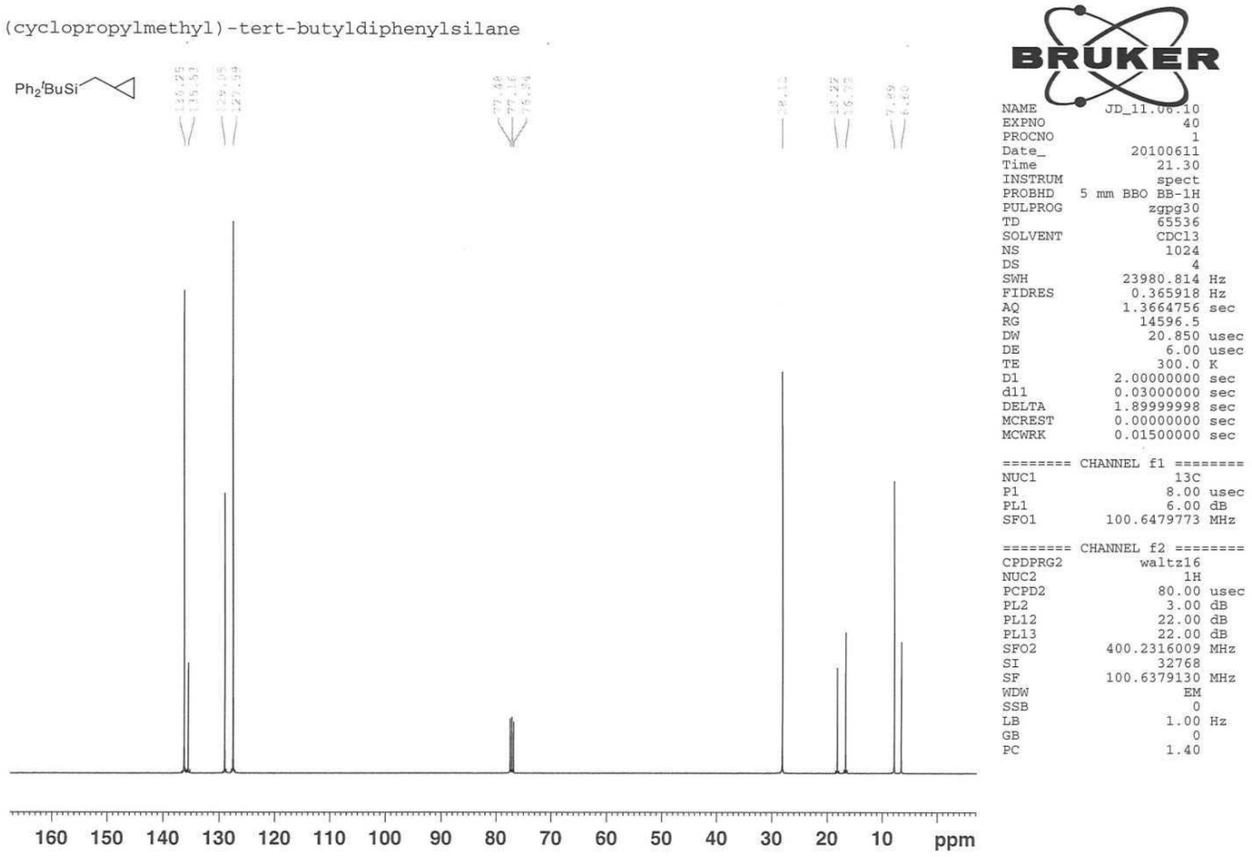


Following the general procedure B, allyl-*tert*-butyldiphenylsilane (3.50 g, 12.5 mmol) furnished the impure product as a colourless oil (3.65 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica eluting with hexane gave the desired product (2.16 g, 7.33 mmol, 59%) as a colourless oil; R_f 0.62 [hexane]; ν_{max}(film)/cm^{-1} 3072, 2929, 2856, 1427, 1103, 818; δ_H (600 MHz; $CDCl_3$) 0.08-0.12 (2H, m, CH_2 cyclopropyl), 0.45-0.49 (2H, m, CH_2 cyclopropyl), 0.76-0.86 (1H, m, CH cyclopropyl), 1.21 (9H, s, 3 × CH_3), 1.31 (2H, d, *J* 6.6, $SiC\underline{H}_2CH$), 7.44-7.54 (6H, m, Ar), 7.79-7.81 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 6.6 (CH cyclopropyl), 7.9 (2 × CH_2 cyclopropyl), 16.7 ($Si\underline{C}H_2CH$), 18.2 ($Si\underline{C}(CH_3)_3$), 28.1 (3 × CH_3), 127.6 (4 × *m*-CH, Ar), 129.1 (2 × *p*-CH, Ar), 135.5 (2 × C, Ar), 136.3 (4 × *o*-CH, Ar); LRMS (EI^+, *m/z*) M^+ not visible, 237 ($[M-{}^tBu]^+$, 100%), 197 (54), 183 (100), 159 (62), 135 (100), 105 (44); HRMS (CI^+, *m/z*) 312.2141 $[M+NH_4]^+$, $C_{20}H_{30}NSi$ requires 312.2142.



```
NAME          JD_11.06.10
EXPNO                  41
PROCNO                  1
Date_            20100611
Time                16.25
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   20.2
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300124 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



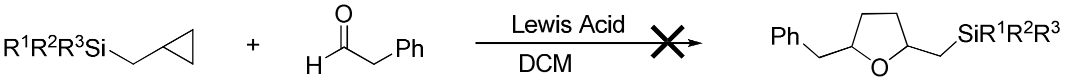
(cyclopropylmethyl)-tert-butyldiphenylsilane

```
NAME           JD_11.06.10
EXPNO                   40
PROCNO                   1
Date_             20100611
Time                 21.30
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 14596.5
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379130 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

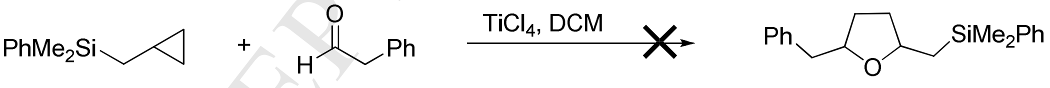
Unsuccessful attempted Lewis acid promoted cyclisations of silylmethylcyclopropanes



Entry	R^1	R^2	R^3	Lewis Acid	Temp (°C)	Major Product
1	Me	Me	Ph	$TiCl_4$	-78	Chlorosilane/aldehyde
2	Me	Me	Ph	$TiCl_4$	0	Chlorosilane/Aldol
3	Me	Me	Ph	$SnCl_4$	-78	Chlorosilane/silanol
4	Me	Me	Ph	$SnCl_4$	0	Chlorosilane/silanol
5	Me	Me	Ph	$BF_3.OEt_2$ (THF)	-78 to 0	Starting material
6	Me	Me	Ph	$BF_3.OEt_2$	-78 to 0	Starting material
7	Me	Me	Ph	$InCl_3$	0 to 21	Starting material
8	^{i}Pr	^{i}Pr	^{i}Pr	$TiCl_4$	-78	Chlorosilane/Aldehyde
9	^{i}Pr	^{i}Pr	^{i}Pr	$TiCl_4$	0	Chlorosilane/Aldol
10	^{i}Pr	^{i}Pr	^{i}Pr	$SnCl_4$	-78	silanol
11	^{i}Pr	^{i}Pr	^{i}Pr	$SnCl_4$	0	Chlorosilane/silanol
12	^{i}Pr	^{i}Pr	^{i}Pr	$BF_3.OEt_2$	-78 to 0	Starting material
13	^{i}Pr	^{i}Pr	^{i}Pr	$InCl_3$	0 to 21	Starting material/ Chlorosilane

One feature of these studies was that the cyclopropane was never recovered using $TiCl_4$ or

The cyclisation of cyclopropylmethyldimethylphenylsilane and phenylacetaldehyde with titanium tetrachloride



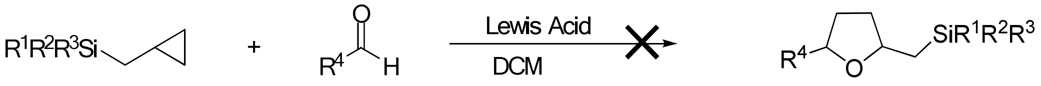
143 **164** **165**

Entry	Order of reagents[a]	Temperature (°C)	Time (h)	Product[b]
1	Aldehyde : cyclopropane : $TiCl_4$	0	2	Decomposition/Aldol
2	Aldehyde : $TiCl_4$: cyclopropane	0	2	Decomposition/Aldol
3	Aldehyde : $TiCl_4$: cyclopropane	-78	2	Aldehyde/Aldol
4	Aldehyde : cyclopropane : $TiCl_4$	-78	2	Decomposition/ Aldehyde
5	Aldehyde : $TiCl_4$ (at 0 °C) : cyclopropane (at -78 °C)	-78	2	Decomposition/Aldol
6	Aldehyde : $TiCl_4$: cyclopropane	-78 to rt	2	Decomposition/Aldol

[a] all reactions were performed using the following ratio of cyclopropane : $TiCl_4$: phenylacetaldehyde 1 : 1.1 : 2 equivalents.

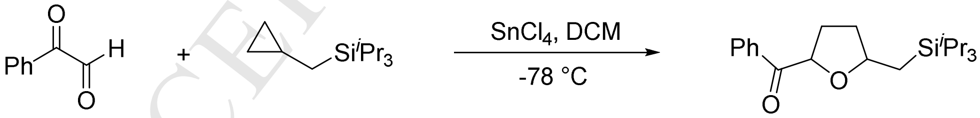
[b] Products were identified by GCMS and NMR analysis. If there was no evidence by ^{1}H NMR or GCMS analysis for starting material or the desired THF present in the reaction mixture no purification was attempted.

Attempted cyclisation of silylmethylcyclopropanes with a range of different aldehydes



Entry	R^1	R^2	R^3	R^4	Lewis Acid	Temp (°C)	Major Products
1	Me	Me	Ph	$CH_3(CH_2)_4$	$TiCl_4$	-78	Disilylether/Aldol
2	Me	Me	Ph	$CH_3(CH_2)_4$	$SnCl_4$	-78	Disilylether/Aldol
3	Me	Me	Ph	NO_2Ph	$TiCl_4$	-78	Disilylether/aldehyde
4	Me	Me	Ph	NO_2Ph	$SnCl_4$	-78	Disilylether/aldehyde
5	Me	Me	Ph	PhCO	$TiCl_4$	-78 to 0	Disilylether
6	Me	Me	Ph	PhCO	$SnCl_4$	-78 to 0	Disilylether
7	Me	Me	Ph	PhCO	$SnCl_4$	0	Disilylether
8	^{i}Pr	^{i}Pr	^{i}Pr	PhCO	$TiCl_4$	-78	Chlorosilane/silanol
9	^{i}Pr	^{i}Pr	^{i}Pr	PhCO	$SnCl_4$	-78	Chlorosilane/silanol
10	Me	Me	Ph	EtO_2C	$TiCl_4$	-78	Chlorosilane/silanol
11	Me	Me	Ph	EtO_2C	$SnCl_4$	-78	Chlorosilane/silanol

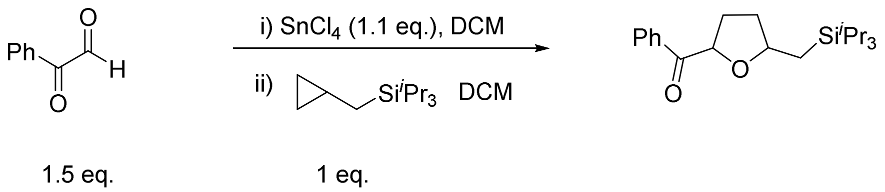
Summary of the Work-up conditions tested



Entry	Work-up Conditions	Yield of isolated THF (%)[a]
1	No work-up (concentrated *in vacuo*)	23
2	1 M HCl	21
3	Sat. $NaHCO_3$ solution	24
4	H_2O	24
5	Acetone/ H_2O (-78 °C)	21

[a] the product extracted with DCM, the solvent was removed under reduced pressure and the pure product was obtained by flash column chromatography of the resulting residue.

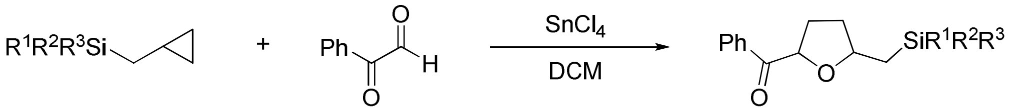
The effect of concentration on the yield of the cyclisation

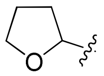


Entry	Cyclopropane added in mLs of DCM (mL)	Tin tetrachloride added in mLs of DCM (mL)	Phenyl glyoxal in DCM (mL)	Initial temp (°C)	Temp $SnCl_4$ added (°C)	Temp triisopropylsilylmethylcyclopropane added (°C)	Final Temp (°C)	Time (h)	Yield of THF (%)
1	1	1	2	-78	-78	-78	0	1.5	23
2	1	1	2	-78	-78	-78	-78	1.5	23
3	1	1	2	-78	-78	-78	-78	1.5	21
4	2	1	2	-78	-78	-78	-78	1.5	54
5	2	1	2	-78	-78	-78	-78	2.5	53
6	2	1	2	0	0	0	0	2	8
7	2	1	2	0	0	0	0	1.5	9
8	3	2	2	-78	-78	-78	0	1	63
9	3	2	2	-78	-78	-78	-78	1.5	52
10	3	2	2	-78	-78	-78	-78	1	69
11	3	2	2	-78	-78	-78	0	2	28[a]
12	3	3	3	0	0	0	0	1	13
13	3	3	3	-78	-78	-78	-78	1	65
14	3	3	3	-78	-78	0	0	1	6
15	4	4	4	-78	-78	-78	-78	1	37
16	4	4	4	-78	-78	-78	-78	2.5	45
17	4	4	4	-78	-78	-78	-78	4	50
18	4	4	4	0	0	0	0	2	24

[a] Triisopropylsilylmethylcyclopropane and phenyl glyoxal were mixed before the addition of $SnCl_4$.

TABLE 5



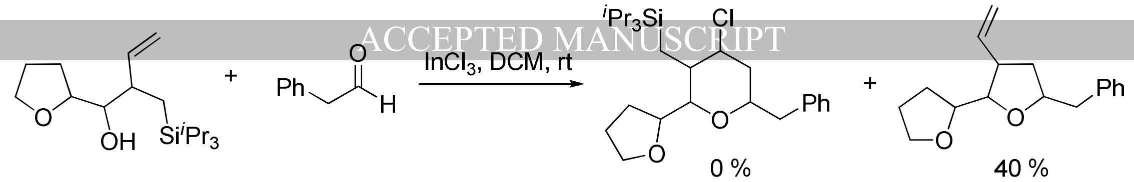
Entry	R^1	R^2	R^3	R	Temperature (°C)[a]	Yield (%)	*dr* (*cis/trans*)
1	^{i}Pr	^{i}Pr	^{i}Pr	Ph	-78	67	1.6 : 1
2	^{i}Pr	^{i}Pr	^{i}Pr	Ph	-78 to 0	85	Only *trans*
3	^{i}Pr	^{i}Pr	^{i}Pr	tBu	-78 to 0	5[b]	
4	^{i}Pr	^{i}Pr	^{i}Pr	OEt	-78 to 0/2 h	42[c]	
5	^{i}Pr	^{i}Pr	^{i}Pr		-78 to 0/ 6 h	0[d]	
6	^{t}Bu	Ph	Ph	Ph	-78	66	2.1 : 1
7	^{t}Bu	Ph	Ph	Ph	-78 to 0	72	1 : 1.1
8	Me	Me	Ph	Ph	-78	53	2.1 : 1
9	Me	Me	Ph	Ph	-78 to 0	18	Only *trans*
10	Me	Me	Ph	OEt	-78 to 0	53	Only *trans*
11	Me	Me	Ph	p-NO_2-C_6H_4	-78	25	2.6:1
12	Me	Me	Ph	p-NO_2-C_6H_4	-78 to 0	3	Only *trans*
13	Me	Me	Ph	p-Br-C_6H_4	-78	55	1.8:1
14	Me	Me	Ph	p-Br-C_6H_4	-78 to 0	34	Only *trans*
15	Me	Ph	Ph	Ph	-78	40	2 : 1
16	Me	Ph	Ph	Ph	-78 to 0	38	1 : 2.4
17	Et	Et	Et	Ph	-78	21	2.3 : 1
18	Et	Et	Et	Ph	-78 to 0	53	1 : 10
19	^{n}Bu	^{n}Bu	^{n}Bu	Ph	-78	43	1 : 1.4
20	^{n}Bu	^{n}Bu	^{n}Bu	Ph	-78 to 0	31	1 : 11

[a] Conditions: A solution of tin tetrachloride in DCM was added to a solution of phenyl glyoxal in DCM at -78 °C. After stirring at this temperature for approx. 5 min a solution of silylmethylcyclopropane in DCM was added. The reaction was either kept at -78 °C or allowed to warm to 0 °C and the product was isolated by column chromatography.

[b] Additionally 63% TiPs-Cl and 26% TiPS-OH were recovered.

[c] Additionally 11% TiPs-Cl and 10% TiPS-OH were recovered.

[d] While none of the desired adduct was obtained, the following were isolated: 26% TiPs-Cl and 6% TiPS-OH and 5% unreacted cyclopropane were recovered. A further additional product **14** was observed in 23% yield (combined diastereomers). As an aside, this was utilised in a Prins reaction utilising our established method employing $InCl_3$ as the Lewis acid, and gave a bis-THF product **15** in 40% yield.

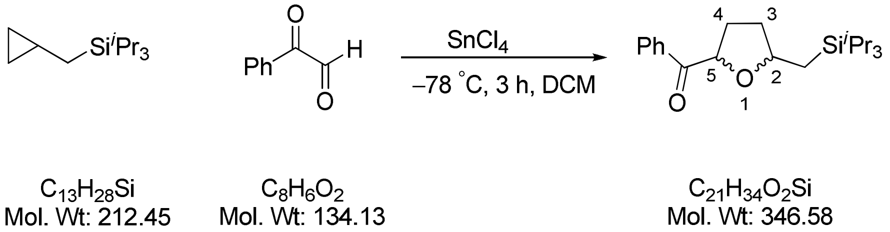


General Procedure C - Cyclisation of silylmethylcyclopropanes with α-keto-aldehydes

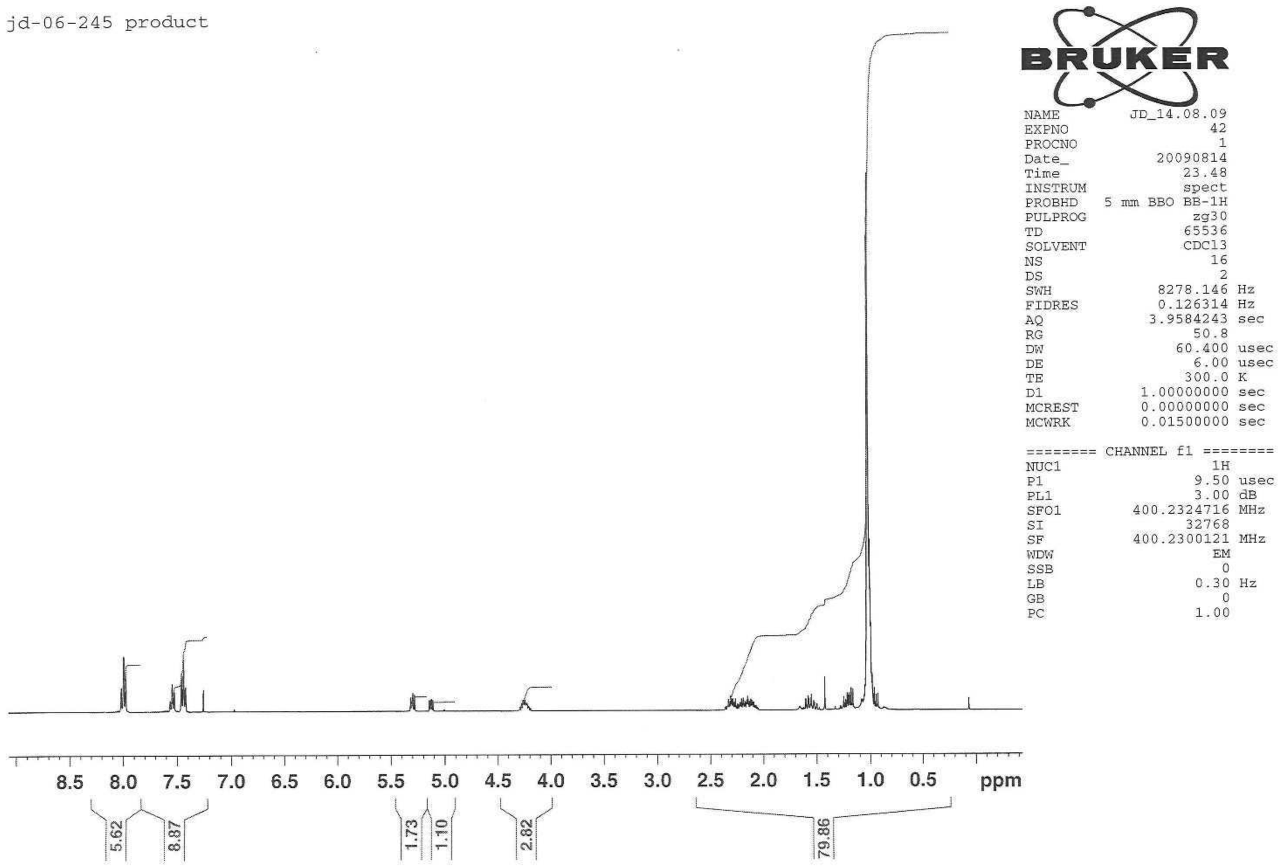
To a stirred mixture of freshly distilled glyoxal or glyoxalate (1.5 eq.) and silylmethylcyclopropane (1 eq.) in anhydrous dichloromethane (9 mL/mmol of silylmethylcyclopropane) cooled to the required temperature (−78 or 0 °C) and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.8 eq.) in anhydrous dichloromethane (3 mL/mmol of tin tetrachloride). The reaction was stirred at the required temperature and monitored by TLC, after 3 h the reaction was quenched by the addition of wet acetone (1 mL/mmol of silylmethylcyclopropane) if the reaction was performed at −78 °C or water (1 mL/mmol of silylmethylcyclopropane) if the reaction was at 0 °C. The organic layer was separated and the aqueous layer further extracted with dichloromethane. The combined organic phases were washed with brine, separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a yellow oil. The products were purified by flash column chromatography.

TABLE 5 ENTRY 1

(±)-Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanone



Following the general procedure C, (cyclopropylmethyl)tri*iso*propylsilane (0.13 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at −78 °C furnished the impure product (0.27 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.14 g, 0.40 mmol, 67%, *dr* (*trans* : *cis*) 1 : 1.6) as a colourless oil; R_f 0.63 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2947 (C-H), 1690 (C=O), 1430 (C-H), 1230 (Si-C), 1115 (C-O), 885; *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.93-1.05 (22H, m, overlapping signals $Si(C\underline{H}(C\underline{H}_3)_2)_3$ and $SiC\underline{H}_aH_b$), 1.23 (1H, dd, *J* 12.5 and 6.6, $SiCH_a\underline{H}_b$), 1.46-1.63 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 2.05-2.38 (3H, m, overlapping signals CH_2 C-4 and $CH_a\underline{H}_b$ C-3 THF), 4.19-4.29 (1H, m, CH C-2 THF), 5.13 (1H, dd, *J* 8.7 and 5.0, CH C-5 THF), 7.42-7.57 (3H, m, Ph), 7.98-8.02 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (SiCH, ^{i}Pr), 16.8 ($SiCH_2$), 18.9 (6 × CH_3, ^{i}Pr), 29.2 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 79.8 (CH, C-2 THF), 79.8 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 198.3 (C=O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.96 (1H, dd, *J* 14.4 and 7.5, $SiC\underline{H}_aH_b$), 1.02-1.04 (21H, m, overlapping signals 3 × CH and 6 × CH_3), 1.20 (1H, dd, *J* 14.4 and 6.6, $SiCH_a\underline{H}_b$), 1.53-1.64 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 2.09-2.23 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 2.27-2.37 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.23-4.30 (1H, m, CH C-2 THF), 5.31 (1H, dd, *J* 8.3 and 6.1, CH C-5 THF), 7.45 (2H, app t, *J* 7.7, 2 × *m*-CH, Ph), 7.55 (1H, app tt, *J* 7.4 and 1.4, *p*-CH, Ph), 7.99 (2H, app dd, *J* 8.3 and 1.4, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH, ^{i}pr), 16.9 ($SiCH_2$), 19.0 (6 × CH_3, ^{i}Pr), 29.3 (CH_2, C-4 THF), 35.1 (CH_2, C-3 THF), 78.7 (CH, C-2 THF), 79.3 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 303 ([M−^{i}Pr]$^+$, 14%), 261 (100), 241 (7), 157 (22), 105 (30), 77 (22); HRMS (CI$^+$, *m/z*) 347.2405 [M+H]$^+$, $C_{21}H_{35}O_2Si$ requires 347.2401. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.13 *cis* and 5.30 *trans*.



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DS                    2
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FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                 50.8
DW               60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
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PL1                3.00 dB
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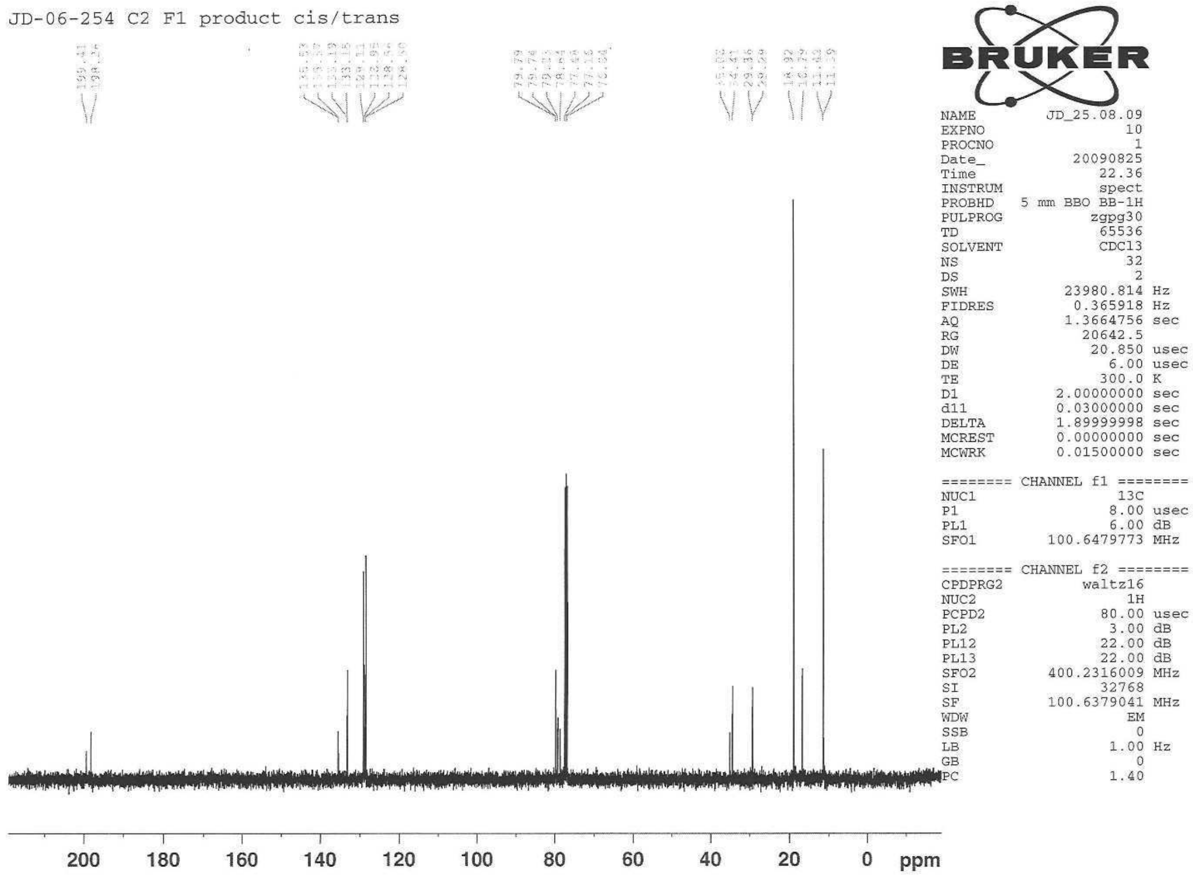

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TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
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AQ            1.3664756 sec
RG              20642.5
DW               20.850 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
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======== CHANNEL f1 ========
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PL1                6.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
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PCPD2             80.00 usec
PL2                3.00 dB
PL12              22.00 dB
PL13              22.00 dB
SFO2        400.2316009 MHz
SI                32768
SF          100.6379041 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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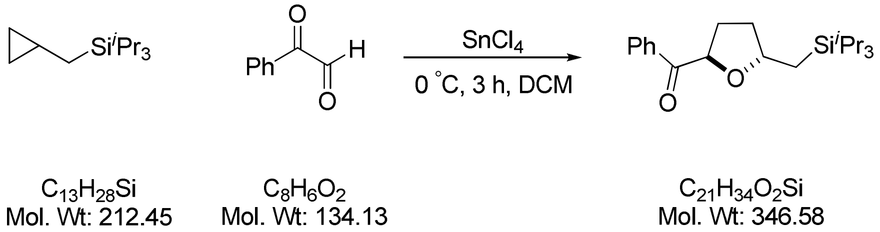
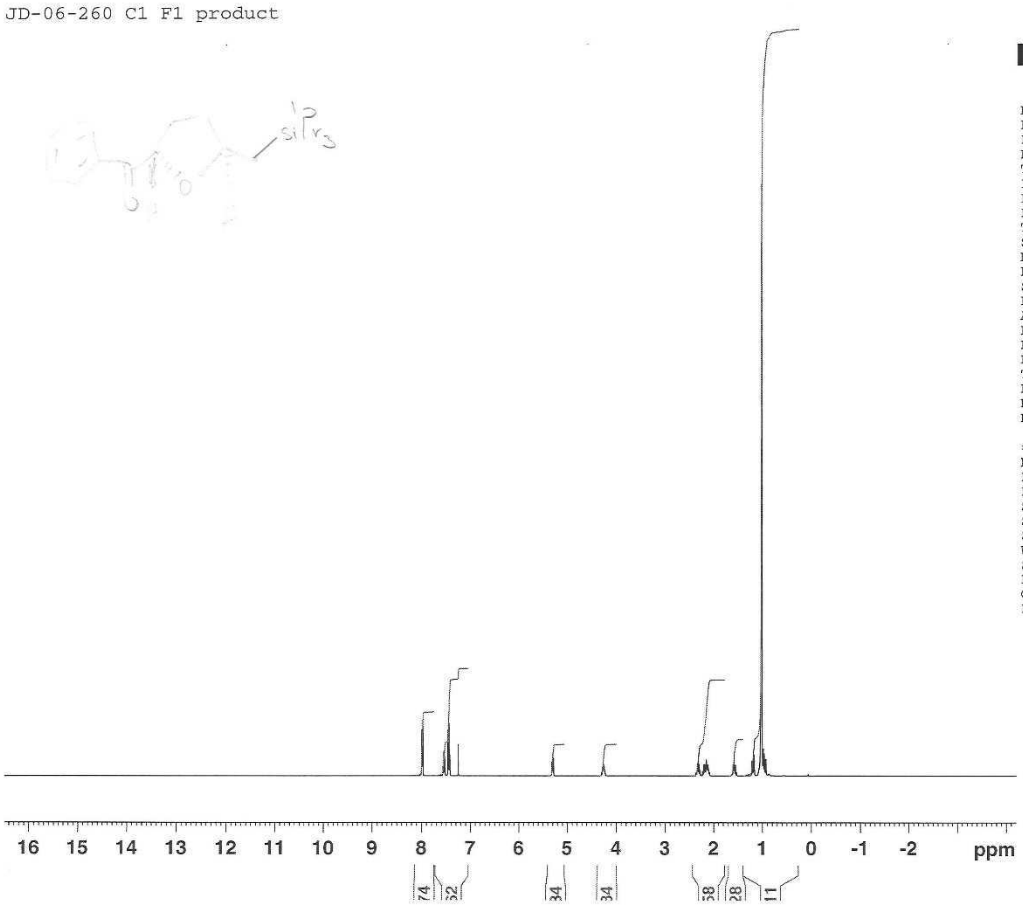
TABLE 5 ENTRY 2

(±)-(Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanone



Following the general procedure C, (cyclopropylmethyl)tri*iso*propylsilane (0.13 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at 0 °C furnished the impure product (0.25 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.18 g, 0.51 mmol, 85%) as a colourless oil; R_f 0.63 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2947 (C-H), 1690 (C=O), 1430 (C-H), 1230 (Si-C), 1115 (C-O), 885; *trans*-diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.96 (1H, dd, *J* 14.4 and 7.5, SiC$\underline{H}_a$H$_b$), 1.02-1.04 (21 H, m, overlapping signals 3 × CH and 6 × CH$_3$), 1.20 (1H, dd, *J* 14.4 and 6.6, SiCH$_a\underline{H}_b$), 1.53-1.64 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 2.09-2.23 (2H, m, overlapping signals CH$_a\underline{H}_b$ C-3 and C$\underline{H}_a$H$_b$ C-4 THF), 2.27-2.37 (1H, m, CH$_a\underline{H}_b$ C-4 THF), 4.23-4.30 (1H, m, CH C-2 THF), 5.31 (1H, dd, *J* 8.26 and 6.1, CH C-5 THF), 7.45 (2H, app t, *J* 7.7, 2 × *m*-CH Ph), 7.55 (1H, app tt, *J* 7.4 and 1.4, *p*-CH Ph), 7.99 (2H, dd, *J* 8.3 and 1.4, 2 × *o*-CH Ph); δ_C (100.6 MHz; CDCl$_3$) 11.4 (3 × CH, ^{i}Pr), 16.9 (SiCH$_2$), 19.0 (6 × CH$_3$, ^{i}Pr), 29.3 (CH$_2$, C-4 THF), 35.1 (CH$_2$, C-3 THF), 78.7 (CH, C-2 THF), 79.3 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 303 ([M−^{i}Pr]$^+$, 14%), 261 (100), 241 (7), 157 (22), 105 (30), 77 (22); HRMS (CI$^+$, *m/z*) 347.2405 [M+H]$^+$, C$_{21}$H$_{35}$O$_2$Si requires 347.2401.

JD-06-260 C1 F1 product



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FIDRES           0.126314 Hz
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RG                  143.7
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DE                   6.00 usec
TE                  300.0 K
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MCREST         0.00000000 sec
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======== CHANNEL f1 ========
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GB                      0
PC                   1.00
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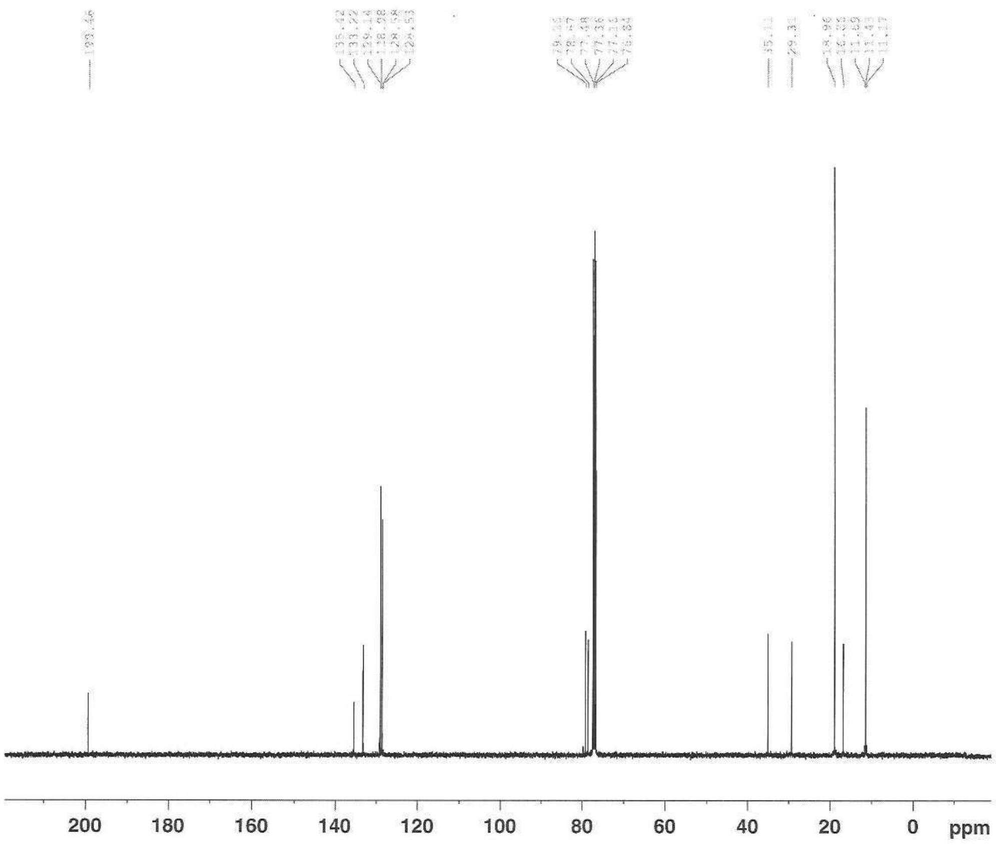
JD-06-247 C2F1



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DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
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DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
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SI                  32768
SF            100.6379011 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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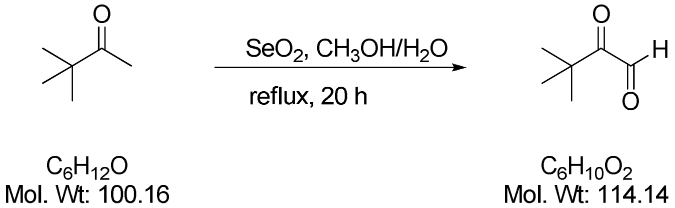
TABLE 5 ENTRY 3

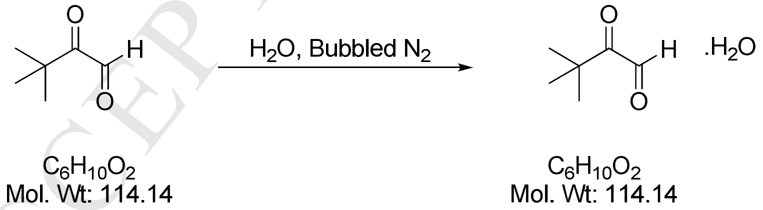
***tert*-Butylglyoxal**



tert-Butylglyoxal was prepared from commercially available pinacolone as previously reported. A stirred mixture of methanol (6 mL), water (0.3 mL) and selenium dioxide (5.55 g, 50.0 mmol) was gently heated until the selenium dioxide had dissolved and pinacolone (4.90 g, 6.10 mL, 49.0 mmol) was rapidly added. The colourless reaction mixture became yellow then red and finally black after 5 min. The reaction mixture was heated at reflux temperature with vigorous stirring for 20 h, cooled to room temperature and filtered under gravity. The filtrate was distilled under atmospheric pressure and the distillate boiling between 95-125 °C was collected. Purification by fractional distillation using a Vigreux fractionating column gave the desired product (1.20 g, 10.5 mmol, 21%) as a bright yellow oil; bp 110-115 °C/760 mmHg, (lit.[108] 114-115 °C/760 mmHg). Owing to rapid decomposition of the compound, the material was used immediately.

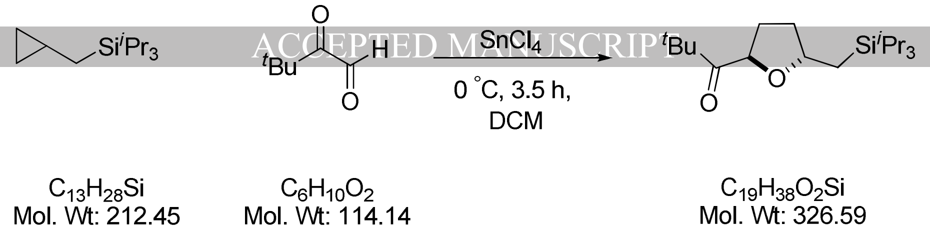
It should be noted that pure *tert*-butyl glyoxal was unstable but could be stored by pouring into water and agitating by bubbling nitrogen through the mixture to give the stable hydrate, which could be recrystallised from benzene; the hydrate could be dehydrated by reduced pressure distillation giving the glyoxal in higher purity than direct distillation of the selenium dioxide reaction mixture).

***tert*-Butylglyoxal dimer hydrate**

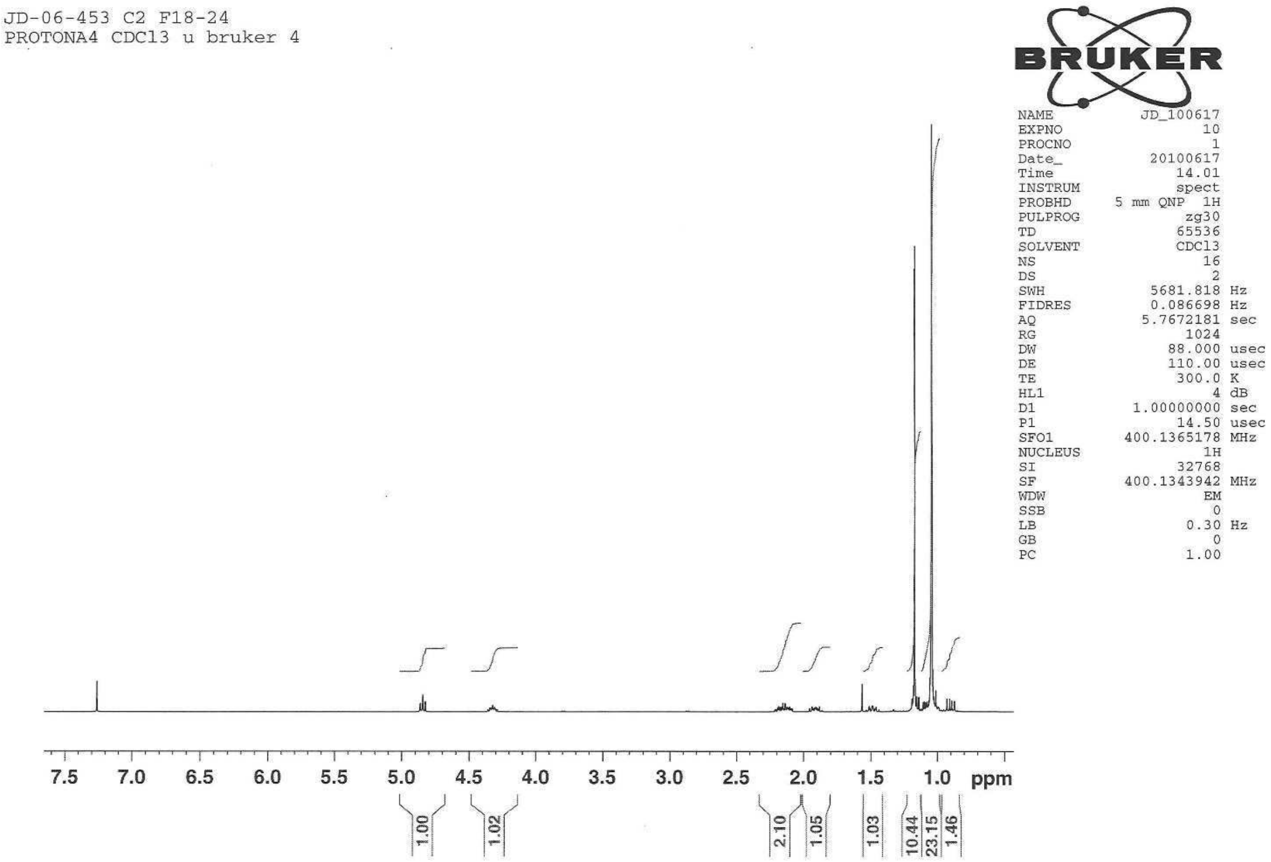


Owing to rapid decomposition of the compound the material was stored as the hydrate, synthesised as follows: freshly distilled *tert*-butylglyoxal (1.50 g) was added to water (10 mL). Nitrogen was bubbled though the resulting mixture for 2 h and then allowed to stand over night to form pale yellow solid. The reaction mixture was filtered to yield the impure product as a pale yellow solid. Purification by recrystallisation from the minimum amount of hot benzene gave the desired product (0.42 g, 3.68 mmol) as a white crystalline solid; mp 91-93 °C (from C_6H_6) (lit.[108] 91-92 °C); ν_{max}(film)/cm^{-1} 3337 (O-H), 2965 (C-H), 1413, 1368, 1016 (C-O); HRMS (EI$^+$, *m/z*) 264.1802 [M+NH$_4^+$], $C_{12}H_{26}O_5N_1$ requires 264.1805.

(±)-2,2-Dimethyl-1-(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)propan-1-one



To a stirred solution of freshly distilled *tert*-butyl glyoxal (0.17 g, 1.50 mmol) in anhydrous DCM (2 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at 0 °C for 5 min followed by the dropwise addition of a solution of (cyclopropylmethyl)tri*iso*propylsilane (0.13 g, 0.60 mmol) in anhydrous DCM (3 mL). Stirring was continued at 0 °C for 3.5 h and the reaction was monitored by TLC. After this time the reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.12 g) as a colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.01 g, 0.03 mmol, 5%) as a colourless oil; R_f 0.67 [20% diethylether : hexane]; ν_{max}(film)/cm^{-1} 2942 (C-H), 2866 (C-H), 1716 (C=O), 1464, 1059, 883 (Si-C); δ_H (400 MHz; $CDCl_3$); 0.90 (1H, dd, *J* 14.4 and 8.1, SiC$\underline{H}_a$H$_b$), 1.02-1.08 (21H, m, overlapping signals: 6 × CH_3 and 3 × CH), 1.17 (1H, dd, *J* 14.4 and 6.2, SiCH$_a\underline{H}_b$), 1.18 (9H, s, CH_3 ^{t}Bu), 1.49 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.86-1.95 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 2.08-2.21 (2H, m, CH$_a\underline{H}_b$ C-3 and CH$_a\underline{H}_b$ C-4 THF), 4.32 (1H, app tt, *J* 8.1 and 5.7, CH C-2 THF), 4.84 (1H, t, *J* 7.4, CH C-5 THF); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH, ^{i}Pr), 16.8 ($SiCH_2$), 19.0 (6 × CH_3, ^{i}Pr), 26.4 (CH_3, ^{t}Bu), 30.5 (CH_2, C-4), 35.3 (CH_2, C-3 THF), 40.5 (C, ^{t}Bu), 77.5 (CH, C-5 THF), 78.9 (CH, C-2 THF), 215.9 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 283 ([M-^{i}Pr]$^+$, 37%), 241 (66), 199 (53), 157 (100), 115 (58), 87 (35), 57 (98); HRMS (CI$^+$, *m/z*) 344.2979 [M+NH$_4$]$^+$, $C_{19}H_{42}O_2NSi$ requires 344.2979.



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JD-06-453 C2 F18-24
PROTONA4 CDCl3 u bruker 4
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PROCNO                    1
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TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                5681.818 Hz
FIDRES             0.086698 Hz
AQ                5.7672181 sec
RG                     1024
DW                   88.000 usec
DE                   110.00 usec
TE                    300.0 K
HL1                       4 dB
D1               1.00000000 sec
P1                    14.50 usec
SFO1            400.1365178 MHz
NUCLEUS                  1H
SI                    32768
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WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
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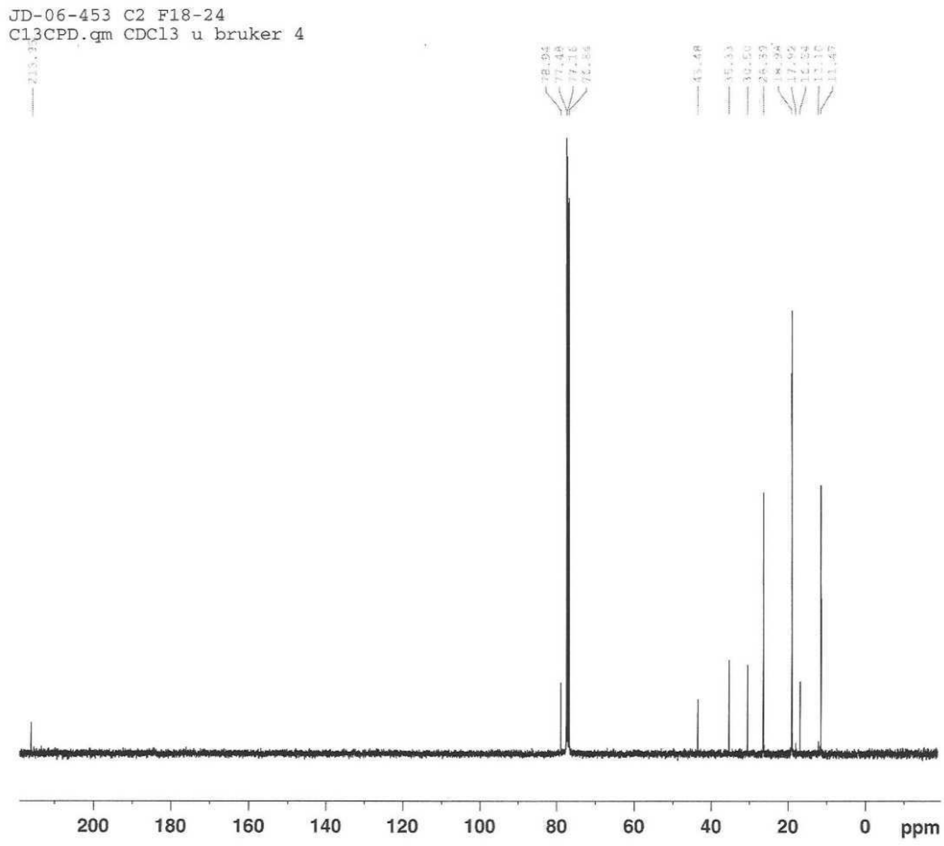

JD-06-453 C2 F18-24
C13CPD.qm CDCl3 u bruker 4

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PROCNO	1
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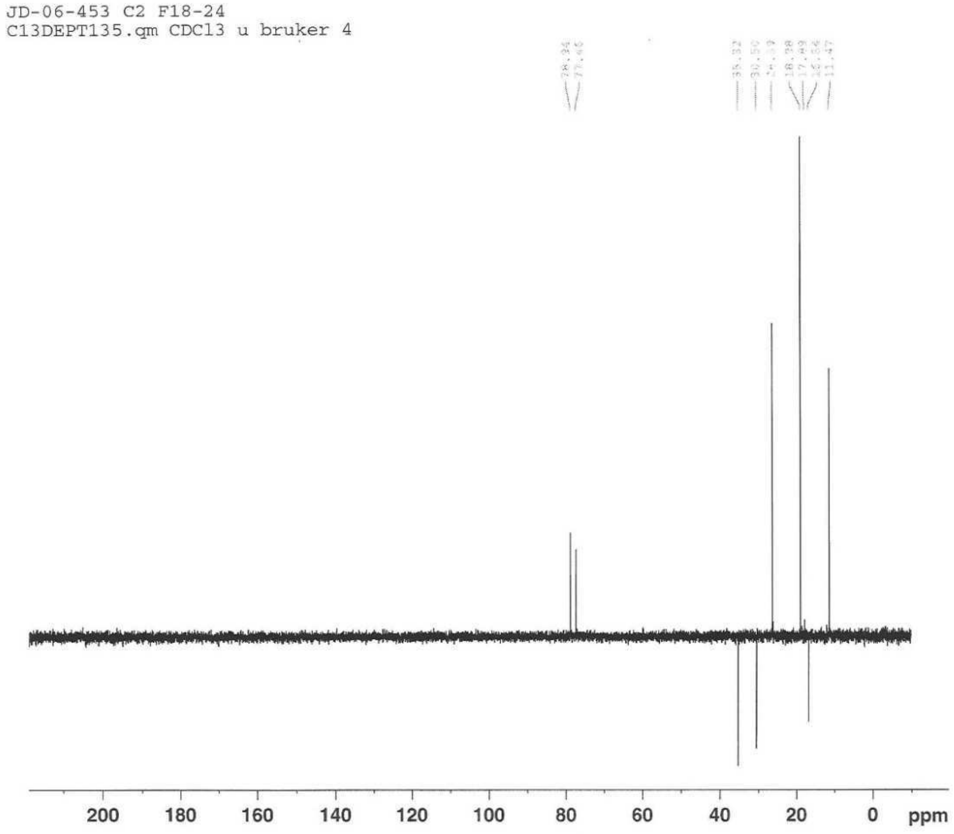
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	26315.789 Hz
FIDRES	0.401547 Hz
AQ	1.2452340 sec
RG	32768
DW	19.000 usec
DE	27.14 usec
TE	300.0 K
HL1	4 dB
D1	2.00000000 sec
CPDPRG	waltz16
P31	80.00 usec
S4	20 dB
D11	0.0300000 sec
S2	17 dB
P1	6.00 usec
SFO1	100.6251166 MHz
NUCLEUS	13C
SI	32768
SF	100.6138554 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

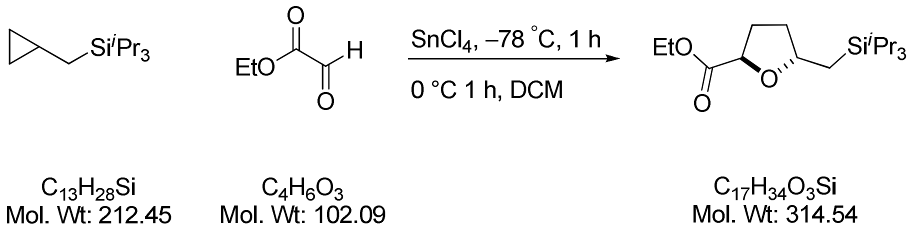


JD-06-453 C2 F18-24
C13DEPT135.qm CDCl3 u bruker 4

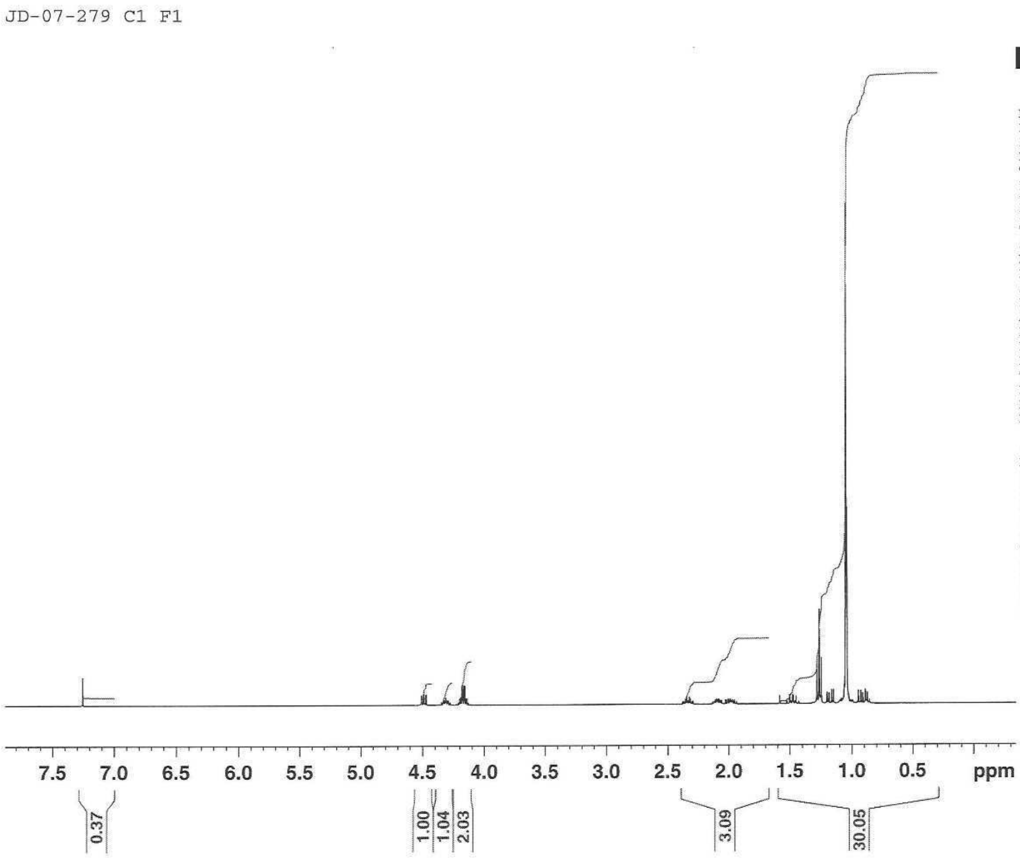
NAME	JD_100617
EXPNO	12
PROCNO	1
Date_	20100617
Time	15.28
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	dept135
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	25000.000 Hz
FIDRES	0.381470 Hz
AQ	1.3107700 sec
RG	32768
DW	20.000 usec
DE	28.57 usec
TE	300.0 K
P1	6.00 usec
P3	14.50 usec
CNST2	145.0000000
HL1	4 dB
D1	2.00000000 sec
S1	4 dB
SFO2	400.1365000 MHz
DECNUC	1H
D2	0.0034483 sec
P4	29.0 usec
P2	12.0 usec
D13	0.0000040 sec
S2	17 dB
SFO1	100.6253720 MHz
NUCLEUS	13C
CPDPRG	waltz16
P31	80.00 usec
SI	32768
SF	100.6138558 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

TABLE 5 ENTRY 4

(±)-Ethyl-2-((triisopropylsilyl)methyl)tetrahydrofuran-5-carboxylate



To a stirred solution of freshly distilled ethyl glyoxalate (0.10 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of a solution of (cyclopropylmethyl)triisopropylsilane (0.13 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 1 h the reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.15 g) as a colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.08 g, 0.25 mmol, 42%) as a colourless oil; R_f 0.50 [20% diethylether : hexane]; ν_{max}(film)/cm^{-1} 2940 (C-H), 2865 (C-H), 1752 (C=O), 1735 (C=O), 1264, 1230 (Si-C), 1183 (C-O), 1094 (C-O), 882 (Si-C); δ_H (400 MHz; $CDCl_3$); 0.92 (1H, dd, *J* 14.4 and 8.1, SiC$\underline{H}_a$H$_b$), 1.00-1.10 (21H, m, overlapping signals: 6 × CH_3 and 3 × CH), 1.18 (1H, dd, *J* 14.4 and 6.1, SiCH$_a\underline{H}_b$), 1.27 (3H, t, *J* 7.1, OCH$_2$C$\underline{H}_3$), 1.48 (1H, dq, *J* 11.7 and 8.0, C$\underline{H}_a$H$_b$ C-3 THF), 1.98 (1H, app dtd, *J* 12.6 8.6 and 6.3, C$\underline{H}_a$H$_b$ C-4 THF), 2.10 (1H, dddd, *J* 11.7 8.0 5.3 and 3.5, CH$_a\underline{H}_b$ C-3 THF), 2.34 (1H, app dtd, *J* 12.5 8.4 and 3.2, CH$_a\underline{H}_b$ C-4 THF), 4.18 (2H, qd, *J* 7.1 and 2.4, OC$\underline{H}_2$CH$_3$), 4.32 (1H, app tt, *J* 8.3and 5.8, CH C-2 THF), 4.49 (1H, dd, *J* 8.4 and 6.3, CH C-5 THF); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH, ^{i}Pr), 14.3 (O CH$_2\underline{C}$H$_3$), 16.7 (SiCH$_2$), 19.0 (6 × CH$_3$, ^{i}Pr), 30.8 (CH$_2$, C-4 THF), 34.5 (CH$_2$, C-3 THF), 60.8 (O$\underline{C}$H$_2$CH$_3$), 76.1 (CH, C-5 THF), 78.9 (CH, C-2 THF), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 271 ([M−^{i}Pr]$^+$, 100%), 241 (11), 225 (15), 198 (19), 157 (58), 145 (42), 131 (88), 103 (59); HRMS (CI$^+$, *m/z*) 332.2615 [M+NH$_4$]$^+$, $C_{17}H_{38}O_3NSi$ requires 332.2615.



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PROCNO                  1
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Time                15.07
INSTRUM             spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  143.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
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SI                  32768
SF            400.2300123 MHz
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GB                      0
PC                   1.00
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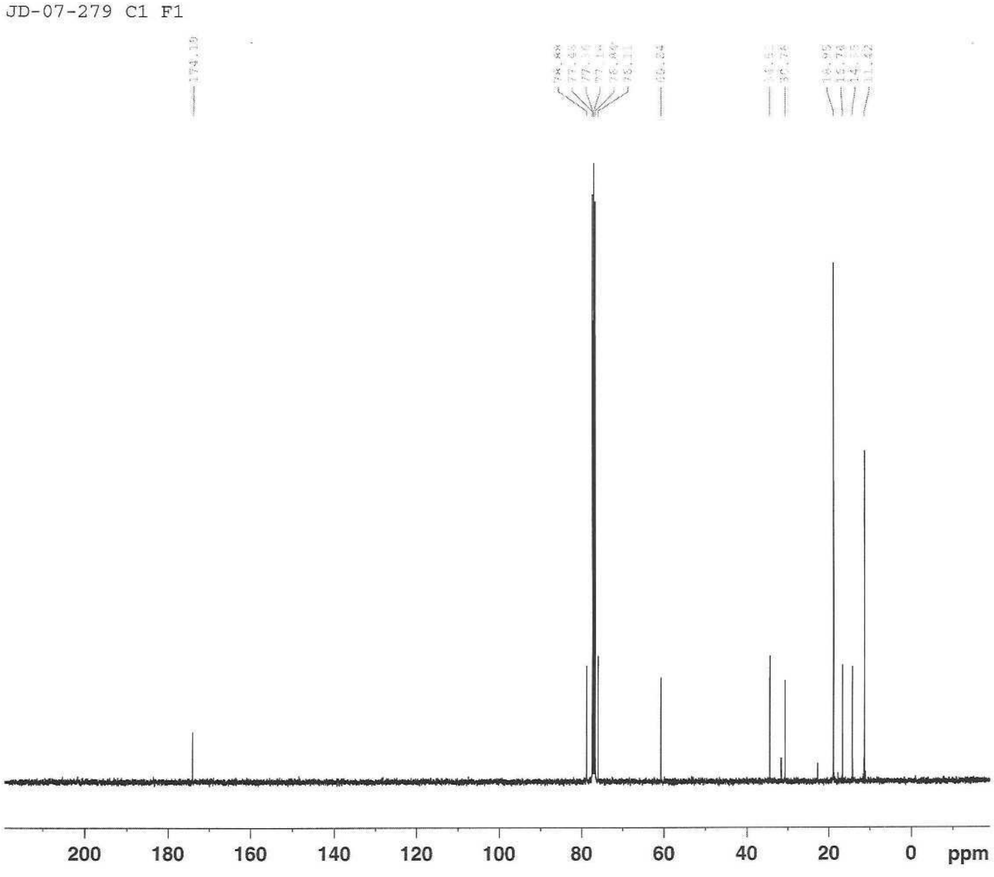

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PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379005 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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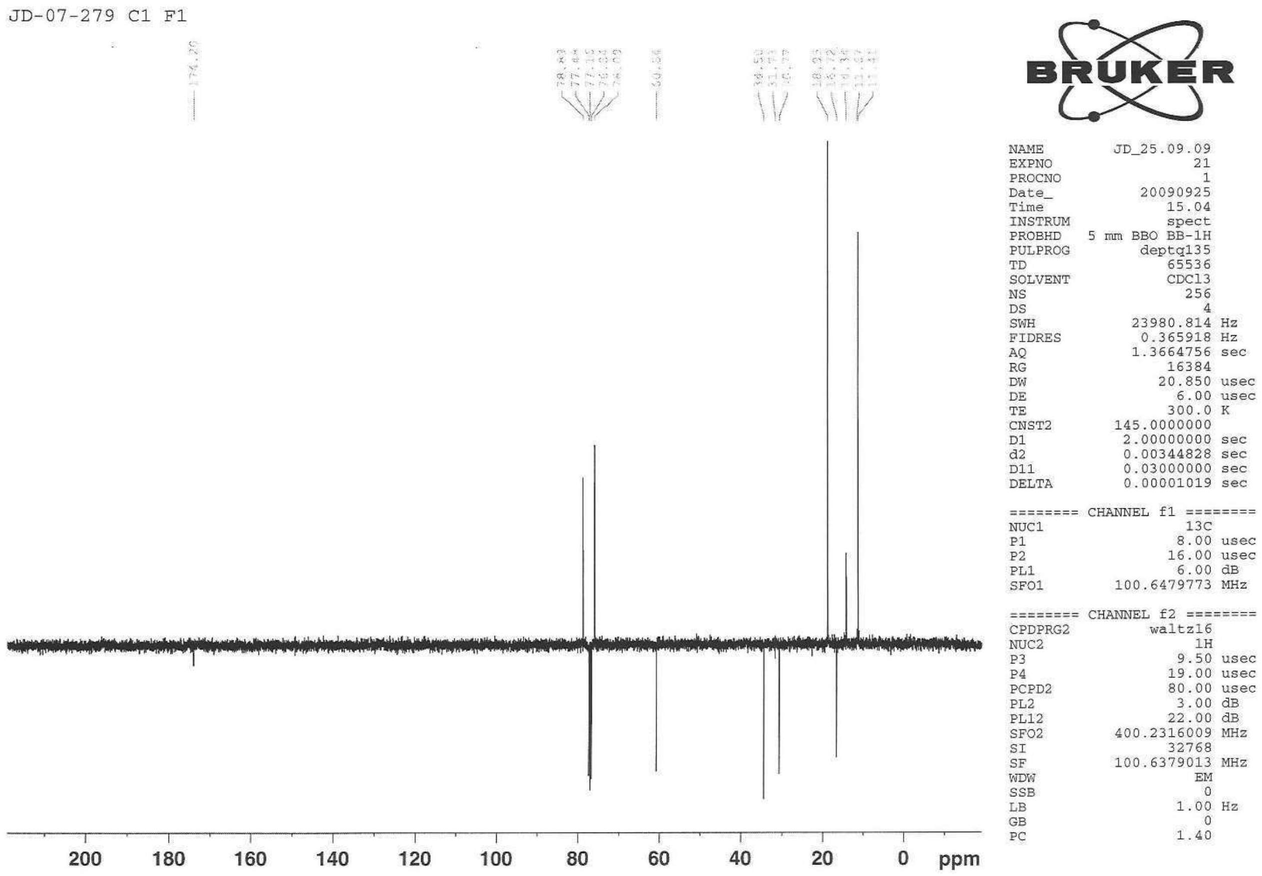

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PROCNO                 1
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Time               15.04
INSTRUM            spect
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PULPROG        deptq135
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
P2                 16.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  9.50 usec
P4                 19.00 usec
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379013 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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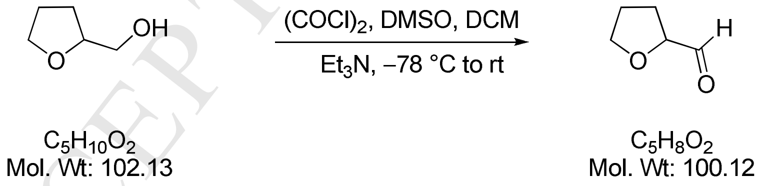
TABLE 5 ENTRY 5

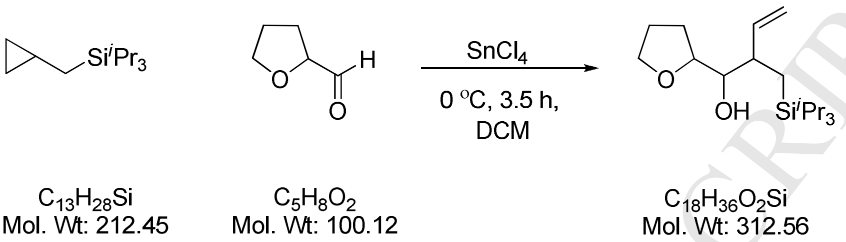
(±)-Tetrahydrofuran-2-carbaldehyde



Tetrahydrofuran-2-carbaldehyde was prepared from commercially availably racemic tetrahydrofurfuryl alcohol according to the method previously reported.[104] To a stirred solution of oxalyl chloride (4.14 g, 2.80 mL, 33.0 mmol) in anhydrous dichloromethane (15 mL) at −78 °C was added dropwise a solution of DMSO (4.29 g, 3.90 mL, 55.0 mmol) in dichloromethane (70 mL). The mixture was stirred for 20 min and then a solution of tetrahydrofurfuryl alcohol (2.64 g, 2.50 mL, 12.9 mmol) in dichloromethane (20 mL) was added dropwise. The mixture was stirred for 10 min and then triethylamine (18 mL) was slowly added dropwise and the reaction was allowed to warm to room temperature. After 1 h stirring at room temperature the reaction mixture was poured onto saturated aqueous ammonium chloride solution (25 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were washed with brine (20 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a pale yellow oil (2.63 g). Purification by flash column chromatography [silica gel, 30% ethyl acetate : hexane] followed by bulb-to-bulb distillation gave the desired compound (0.23 g, 2.30 mmol, 18%) as a colourless oil; R_f 0.18 [30% ethyl acetate : hexane], bp 64-65 °C/23mmHg, (lit.[xii] 43-46 °C/15mmHg), ν_{max}(film)/cm^{-1} 2979, 2875, 1731

(C=O), 1461, 1069 (C-O); δ_H (400 MHz; CDCl$_3$) 1.84-2.01 (3H, m, overlapping signals CH$_2$ and C$\underline{\text{H}}_a$H$_b$ THF), 2.09-2.18 (1H, m, CH$_a\underline{\text{H}}_b$ THF), 3.93 (2H, t, *J* 6.6, OCH$_2$), 4.25 (1H, ddd, *J* 8.4 5.9 and 1.7, OCH), 9.65 (1H, d, *J* 1.7, CHO); δ_C (100.6 MHz; CDCl$_3$) 25.7 (CH$_2$, C-4), 27.5 (CH$_2$, C-3), 69.7 (CH$_2$, C-5), 82.9 (CH), 202.9 (CHO); LRMS (EI$^+$, *m/z*) 101 ([M]$^+$, 2%), 71 (90), 43 (100), 41 (98), 39 (73); HRMS (EI$^+$, *m/z*) 118.0863 [M+NH$_4$]$^+$, $C_5H_{12}O_2N_1$ requires 118.0863. The data is in good agreement with previously reported values.

1-(Tetrahydrofuran-2-yl)-2-((triisopropylsilyl)methyl)but-3-en-1-ol



To a stirred solution of tetrahydrofurfuryl aldehyde (0.09 g, 0.90 mmol) and triisopropylsilylmethylcycopropane (0.13 g, 0.61 mmol) in DCM (6 mL) at 0 °C was added dropwise using a syringe pump (rate = 9 mL/h) a solution of tin tetrachloride (0.19 g, 0.73 mmol) in DCM (3 mL). The reaction was allowed to warm to room temperature and monitored by TLC, after 18 h TLC and GCMS analysis showed all the staring material had been consumed and the reaction was quenched by the addition of water (5 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried (MgSO$_4$), filtered and concentrated *in vacuo* to give the impure product (0.20 g) as a brown oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% ethyl acetate : hexane] afforded a separable mixture of two diastereoisomers of the *title compound* (combined yield 0.04 g, 0.14 mmol, 23%) as colourless oils:

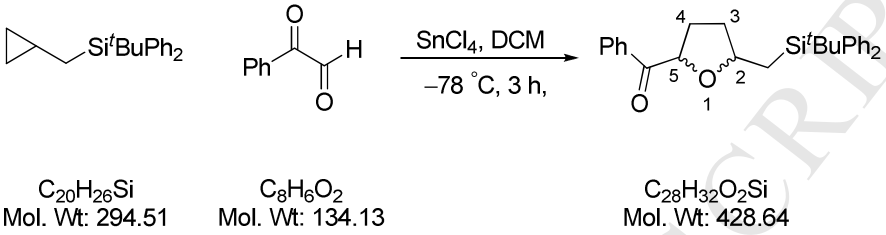
Major diastereoisomer (0.04 g, 0.11 mmol, 19%); R_f 0.25 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3450 (br), 2941(C-H), 2867 (C-H), 2362, 1465 (O-H bend), 1245 (Si-C), 1059 (C-O), 1000, 883; δ_H (400 MHz; CDCl$_3$); 0.84 (1H, dd, *J* 15.1 and 8.8, SiC$\underline{\text{H}}_a$H$_b$), 0.96 (1H, dd, *J* 15.1 and 4.7, SiCH$_a\underline{\text{H}}_b$), 1.00-1.08 (21H, m, overlapping signals 3 × CH and 6 × CH$_3$ ^{i}Pr), 1.48-1.59 (1H, m, C-4/3 THF), 1.82-1.97 (3H, m, C-4/3 THF), 2.31-2.38 (1H, m, C$\underline{\text{H}}$CH=CH$_2$), 2.41 (1H, d, *J* 3.0, OH), 3.31 (1H, app dt, *J* 7.3 and 3.2, C$\underline{\text{H}}$OH), 3.73-3.84 (3H, m, overlapping signals C-5 and C-2), 4.98 (1H, dd, *J* 17.3 and 2.0, CH=CH$_{cis}\underline{\text{H}}_{trans}$), 5.02 (1H, dd, *J* 10.2 and 1.9, CH=C$\underline{\text{H}}_{cis}H_{trans}$), 5.82 (1H, app dt, *J* 17.3 and 9.8, C$\underline{\text{H}}$=CH$_{cis}$H$_{trans}$); δ_C (100.6 MHz; CDCl$_3$) 11.6 (3 × CH$_2$, Si^{i}Pr$_3$), 12.5 (SiCH$_2$), 19.1 (6 × CH$_3$, Si^{i}Pr$_3$), 26.4 (CH$_2$, THF), 27.9 (CH$_2$, THF), 42.6 (SiCH$_2\underline{\text{C}}$H), 68.0 (CH$_2$, THF), 78.8 (H$\underline{\text{C}}$OH), 80.7 (CH THF), 115.5 (CH=$\underline{\text{C}}$H$_2$), 140.7 ($\underline{\text{C}}$H=CH$_2$); LRMS (EI$^+$, *m/z*): 269 ([M–^{i}Pr]$^+$, 16%), 157 (31), 131 (100), 103 (75), 75 (55), 71 (46); HRMS (CI$^+$, *m/z*) 330.2827 [M+NH$_4$]$^+$, $C_{18}H_{40}O_2NSi$ requires 330.2823.

Minor diastereoisomer (0.01 g, 0.03 mmol, 5%); R_f 0.32 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3450 (br), 2941(C-H), 2867 (C-H), 2362, 1465 (O-H bend), 1245 (Si-C), 1059 (C-O), 1000, 883; δ_H (400 MHz; CDCl$_3$); 0.67 (1H, dd, *J* 14.9 and 11.2, SiC$\underline{\text{H}}_a$H$_b$), 0.99-1.04 (22H, m, overlapping signals SiCH$_a\underline{\text{H}}_b$ and Si^{i}Pr$_3$) 1.75-1.94 (4H, m, overlapping signals C-3 and C-4 THF), 2.24 (1H, d, *J* 8.2, OH), 2.41 (1H, dddd, *J* 11.2 9.4 6.1 and 2.4, C$\underline{\text{H}}$CH=CH$_2$), 3.21 (1H, ddd, *J* 8.2 6.1 and 3.2, $\underline{\text{H}}$COH), 3.74-3.86 (1H, m, C-5 THF), 4.01 (1H, td, *J* 7.0 and 3.2, CH C-2 THF), 5.04 (1H, dd, *J* 10.2 and 1.9, CH=C$\underline{\text{H}}_{cis}H_{trans}$), 5.09 (1H, dd, *J* 17.2 and1.9, CH=CH$_{cis}\underline{\text{H}}_{trans}$), 5.69 (1H, app dt, *J* 17.2 10.2 and 9.4, C$\underline{\text{H}}$=CH$_{cis}$H$_{trans}$); δ_C

(100.6 MHz; $CDCl_3$) 10.5 (CH_2, $SiCH_2CH$), 11.6 (3 × CH Si^iPr_3), 19.1 (CH_3), 19.1 (CH_3), 26.4 (CH_2, THF), 29.3 (CH_2, THF), 44.9 ($SiCH_2C\underline{H}$), 68.9 (CH_2, C-5 THF), 77.8 ($C\underline{H}OH$), 78.4 (CH, C-2 THF), 116.0 ($CH{=}\underline{C}H_2$), 141.8 ($\underline{C}H{=}CH_2$); LRMS (EI^+, *m/z*): 269 ($[M-{}^iPr]^+$, 16%), 157 (31), 131 (100), 103 (75), 75 (55), 71 (46); HRMS (CI^+, *m/z*) 330.2825 $[M+NH_4]^+$, $C_{18}H_{40}O_2NSi$ requires 330.2823.

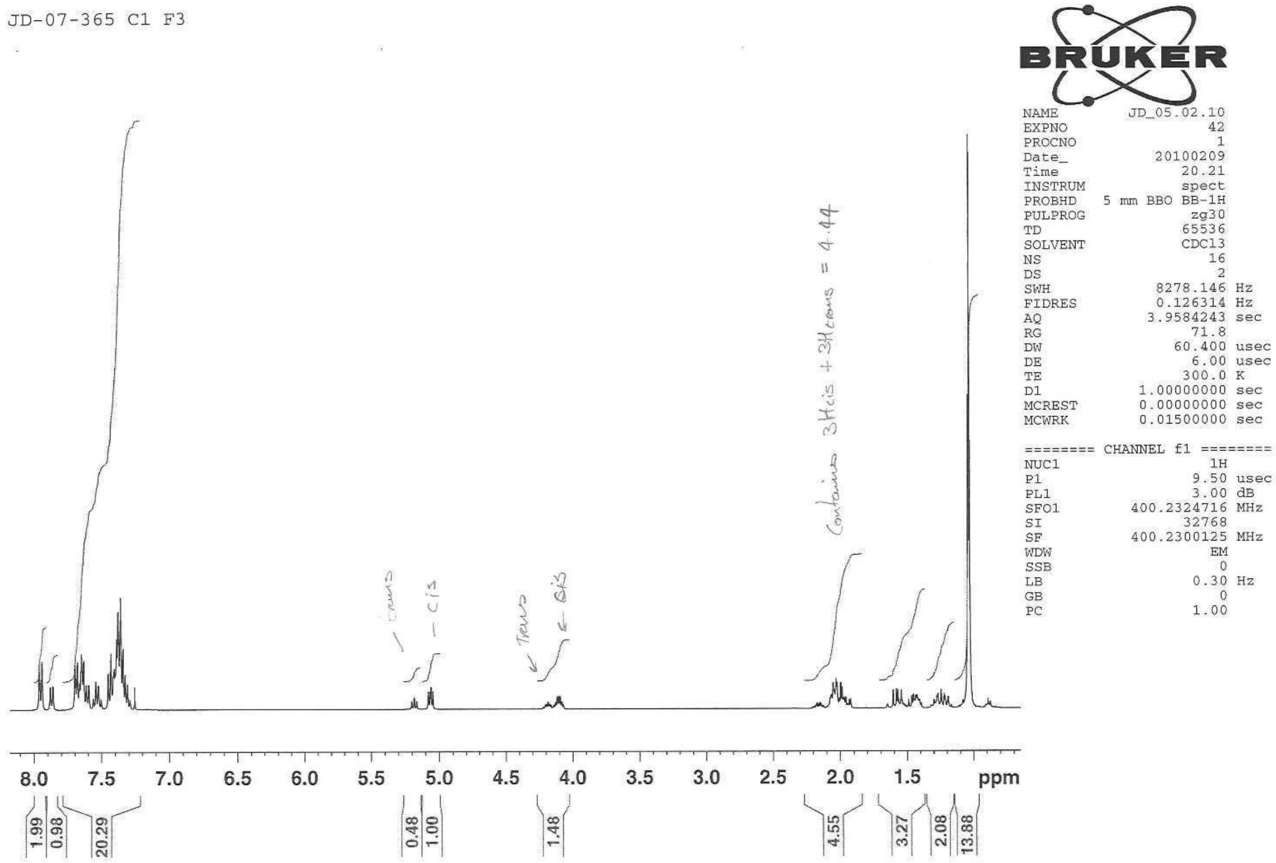
TABLE 5 ENTRY 6

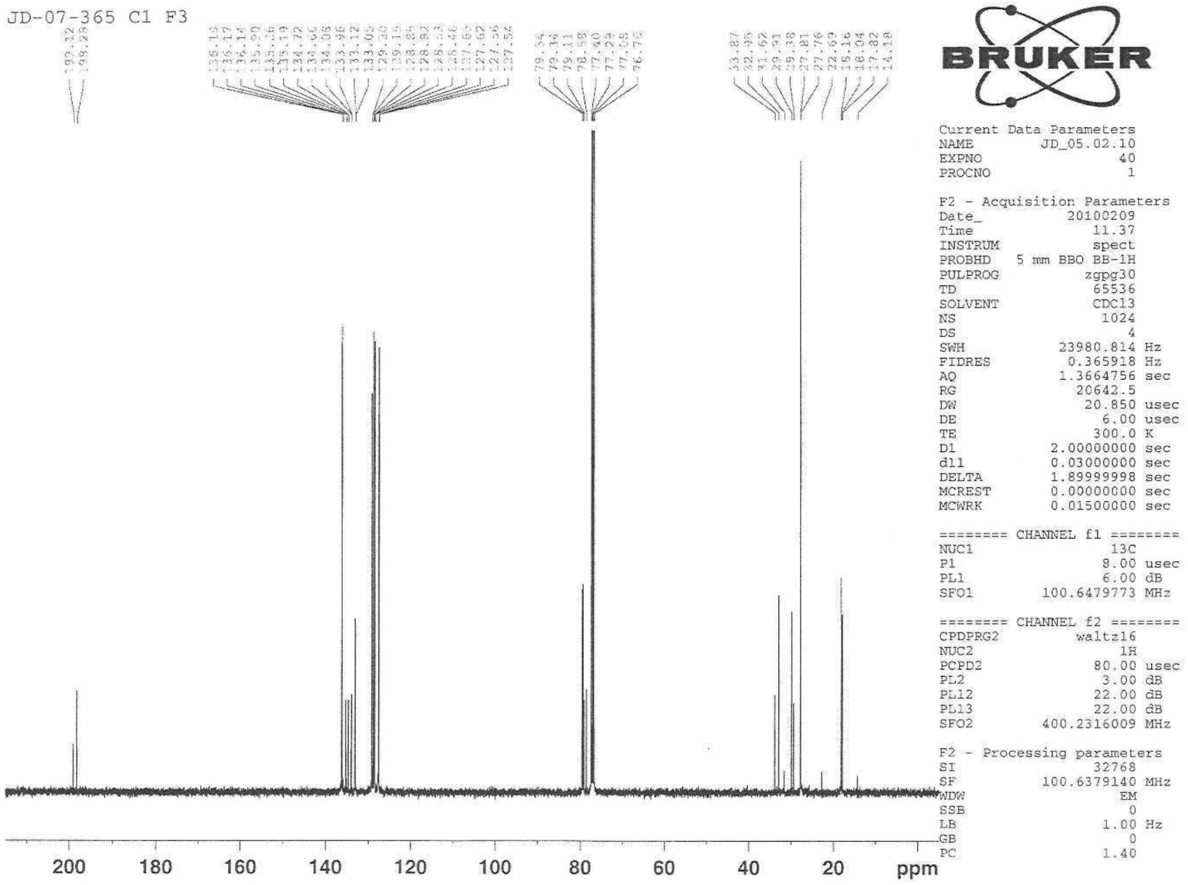
(±)-2-((*tert*-Butyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of *tert*-butyl(cyclopropylmethyl)diphenylsilane (0.18 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.29 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : cyclohexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.17 g, 0.40 mmol, 66%, *dr* (*trans* : *cis*) 1 : 2.1) as a colourless oil; R_f 0.41 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2930 (C-H), 2857 (C-H), 1691 (C=O), 1448 (C-H), 1228 (Si-C), 1104 (C-O); *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 1.04 (9H, s, $Si\underline{C}(CH_3)_3$), 1.17-1.32 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.40-1.47 (1H, m, $CH_a\underline{H}_b$, C-3 THF), 1.58 (1H, dd, *J* 14.5 and 9.8, $SiC\underline{H}_aH_b$), 2.02 (1H, dd, 14.5 and 4.1 $SiCH_a\underline{H}_b$), 2.03-2.08 (2H, m, CH_2 C-4 THF), 4.14 (1H, app tt, 9.5 and 4.8, CH C-2 THF), 5.07 (1H, dd, *J* 8.4 and 5.5, CH C-5 THF), 7.29-7.70 (13H, m, Ar), 7.94-7.96 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 17.9 ($SiCH_2$), 18.2 ($Si\underline{C}(CH_3)_3$), 29.8 (CH_2, C-4 THF), 33.0 (CH_2, C-3 THF), 79.4 (CH, C-5 THF), 79.6 (CH, C-2 THF), 127.6 (2 × *o*-CH, Ar), 127.7 (2 × *o*-CH, Ar), 128.6 (2 × *m*-CH, -C(=O)Ph), 128.9 (2 × *o*-CH, -C(=O)Ph), 129.3 (2 × *p*-CH, Ar), 133.2 (*p*-CH, -C(=O)Ph), 134.1 (C, Ar), 134.7 (C, Ar), 135.4 (*ipso*-C, -C(=O)Ph), 136.2 (2 × *m*-CH, Ar), 136.3 (2 × *m*-CH, Ar), 198.4 (C=O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 1.05 (9H, s, Si $C(CH_3)_3$), 1.17-1.32 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.46 (1H, dd, *J* 14.4 and 9.2, $SiC\underline{H}_aH_b$), 1.51-1.56 (1H, m, $CH_a\underline{H}_b$, C-3 THF), 1.95 (1H, dd, *J* 14.4 and 5.0, $SiCH_a\underline{H}_b$), 1.95-2.00 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 2.16 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.20 (1H, app tt, 8.9 and 5.2, CH C-2 THF), 5.19 (1H, dd, *J* 8.0 and 7.0, CH C-5 THF), 7.29-7.70 (13H, m, Ar), 7.86-7.88 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; $CDCl_3$) 18.1 ($SiCH_2$), 18.2 ($Si\underline{C}(CH_3)_3$), 29.4 (CH_2, C-4 THF), 34.0 (CH_2, C-3 THF), 78.6 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.6 (2 × *o*-CH, Ar), 127.7 (2 × *o*-CH, Ar), 128.5 (2 × *m*-CH, -C(=O)Ph), 128.9 (2 × *o*-CH, -C(=O)Ph), 129.2 (2 × *p*-CH, Ar), 133.1 (*p*-CH, -C(=O)Ph), 134.2 (C, Ar), 134.8 (C, Ar), 135.3 (*ipso*-C, -C(=O)Ph), 136.2 (2 × *m*-CH, Ar), 136.3 (2 × *m*-CH, Ar), 199.2 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, ($[M-{}^tBu]^+$ 18%), 329 (87), 183 (42), 135 (100), 105 (72), 77 (33); HRMS

(CI$^+$, *m/z*) 446.2512 $[M+NH_4]^+$, $C_{28}H_{36}O_2NSi$ requires 446.2510. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the C-5 protons of the THF ring, 5.07 *cis* and 5.19 *trans*.





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PROCNO                  1

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TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               20642.5
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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P1                  8.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2         400.2316009 MHz

F2 - Processing parameters
SI                 32768
SF           100.6379140 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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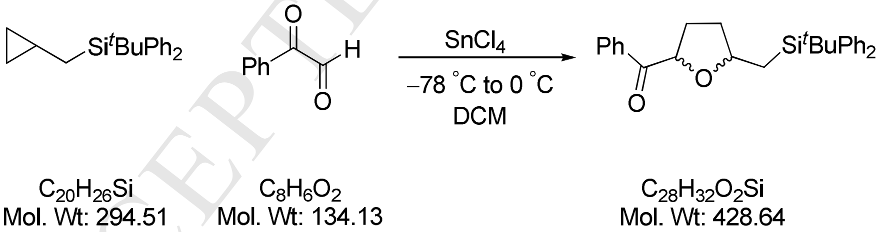
TABLE 5 ENTRY 7

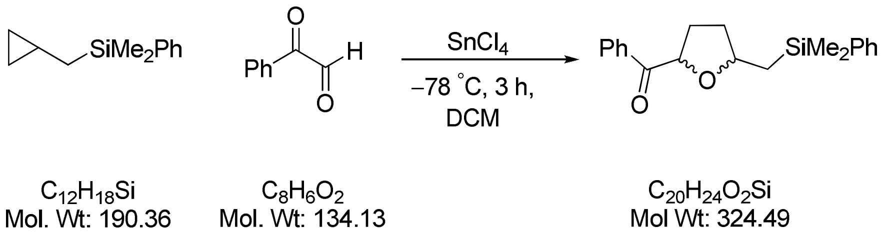
(±)-2-((*tert*-Butyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



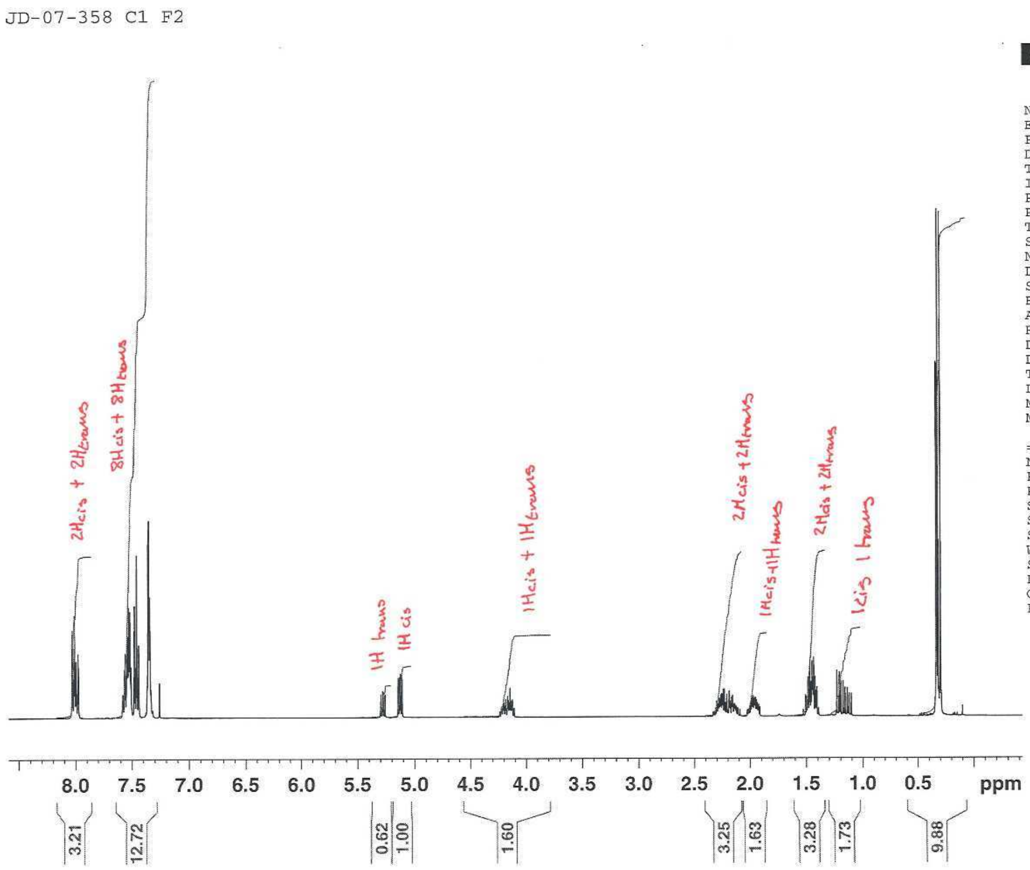
To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of *tert*-butyl(cyclopropylmethyl)diphenylsilane (0.18 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 1 h the reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.24 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ethyl : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.18 g, 0.43 mmol, 72%, *dr* (*trans* : *cis*) 1 : 1.1) as a colourless oil. Data is in agreement with that previously recorded.

TABLE 5 ENTRY 8

(±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



Following the general procedure C, (cyclopropylmethyl)dimethylphenylsilane (0.12 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at −78 °C furnished the impure product (0.27 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.10 g, 0.32 mmol, 53%, *dr* (*trans* : *cis*) 1 : 1.6) as a colourless oil; R_f 0.22 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3070, 2957 (C-H), 2886 (C-H), 1692 (C=O), 1451 (C-H), 1429, 1230 (Si-C), 1115 (C-O); *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$); 0.30 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$), 1.21 (1H, dd, *J* 14.2 and 8.5, SiC$\underline{H}_a$H$_b$), 1.42-1.51 (2H, m, overlapping signals SiH$_a$$\underline{H}_b$ and C$\underline{H}_a$H$_b$ C-3 THF), 1.92-2.02 (1H, m, CH$_a$$\underline{H}_b$ C-3 THF), 2.09-2.33 (2H, m, CH_2 C-4 THF), 4.15 (1H, app tt, *J* 8.7 and 5.8, CH C-2 THF), 5.13 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.33-7.59 (8H, m, Ar), 8.01-8.04 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 23.6 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 33.6 (CH_2, C-3 THF), 78.5 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh), 128.5 (2 × *m*-CH, -C(=O)Ph), 129.0 (2 × *o*-CH, -C(=O)Ph), 129.1 (*p*-CH, SiPh), 133.2 (*p*-CH, -C(=O)Ph), 133.7 (2 × *o*-CH, SiPh), 135.5 (*ipso*-C, -C(=O)Ph), 139.0 (C, SiPh), 198.4 (C=O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$); 0.32 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.12 (1H, dd, *J* 14.2 and 8.1, SiC$\underline{H}_a$H$_b$), 1.42 (1H, dd, *J* 14.2 and 6.2, SiH$_a$$\underline{H}_b$), 1.39-1.52 (1H, m, C$\underline{H}_aH_b$ C-3 THF), 1.98 (1H, dddd, *J* 12.1 8.1 5.5 and 3.6, CH$_a$$\underline{H}_b$ C-3 THF), 2.13 (1H, app dtd, *J* 12.7 8.5 and 6.6, C$\underline{H}_a$H$_b$ C-4 THF), 2.25 (1H, app dtd, *J* 12.7 8.4 and 3.6, CH$_a$$\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.4 and 5.9, CH C-2 THF), 5.27 (1H, dd, *J* 8.2 and 6.6, CH C-5 THF), 7.32-7.36 (3H, m, overlapping signals 2 × *o*-CH and *p*-CH Ar), 7.45 (2H, t, *J* 7.6, 2 × *m*-CH Ar), 7.49-7.52 (2H, m, 2 × *m*-CH Ar), 7.56 (1H, app tt, *J* 7.4 and 1.4, *p*-CH Ar), 7.96-7.99 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −2.0 ($SiCH_3$), 23.5 ($SiCH_2$), 29.3 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 78.6 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.9 (2 × *m*-CH, Ar), 128.6 (2 × *m*-CH, -C(=O)Ph), 129.0 (2 × *o*-CH, -C(=O)Ph), 129.0 (*p*-CH, Ar), 133.3 (*p*-CH, -C(=O)Ph), 133.7 (2 × *o*-CH, Ar), 135.3 (*ipso*-C, -C(=O)Ph), 139.1 (C, Ar), 199.4 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 309 ([M−CH$_3$]$^+$, 2%), 267 (5), 239 (10), 219 (16), 135 (100), 105 (21), 77 (15); HRMS (CI$^+$, *m/z*) 342.1878 [M+NH$_4$]$^+$, $C_{20}H_{28}O_2NSi$ requires 342.1884. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.13 *cis* and 5.27 *trans*.



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NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                     64
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TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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PL1                  3.00 dB
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SI                  32768
SF            400.2300120 MHz
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GB                      0
PC                   1.00
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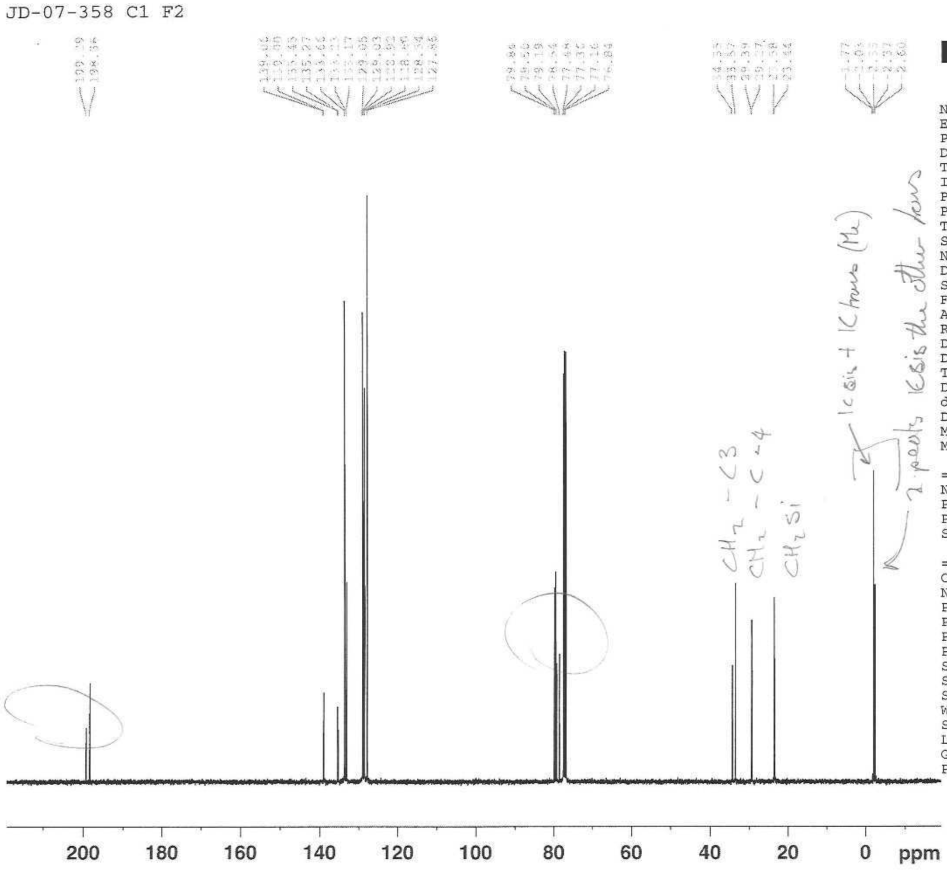

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DS                      4
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RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379085 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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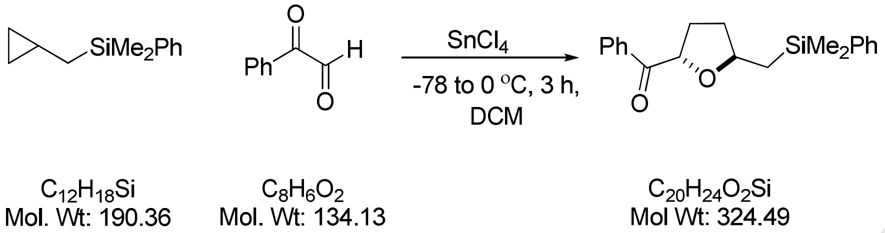
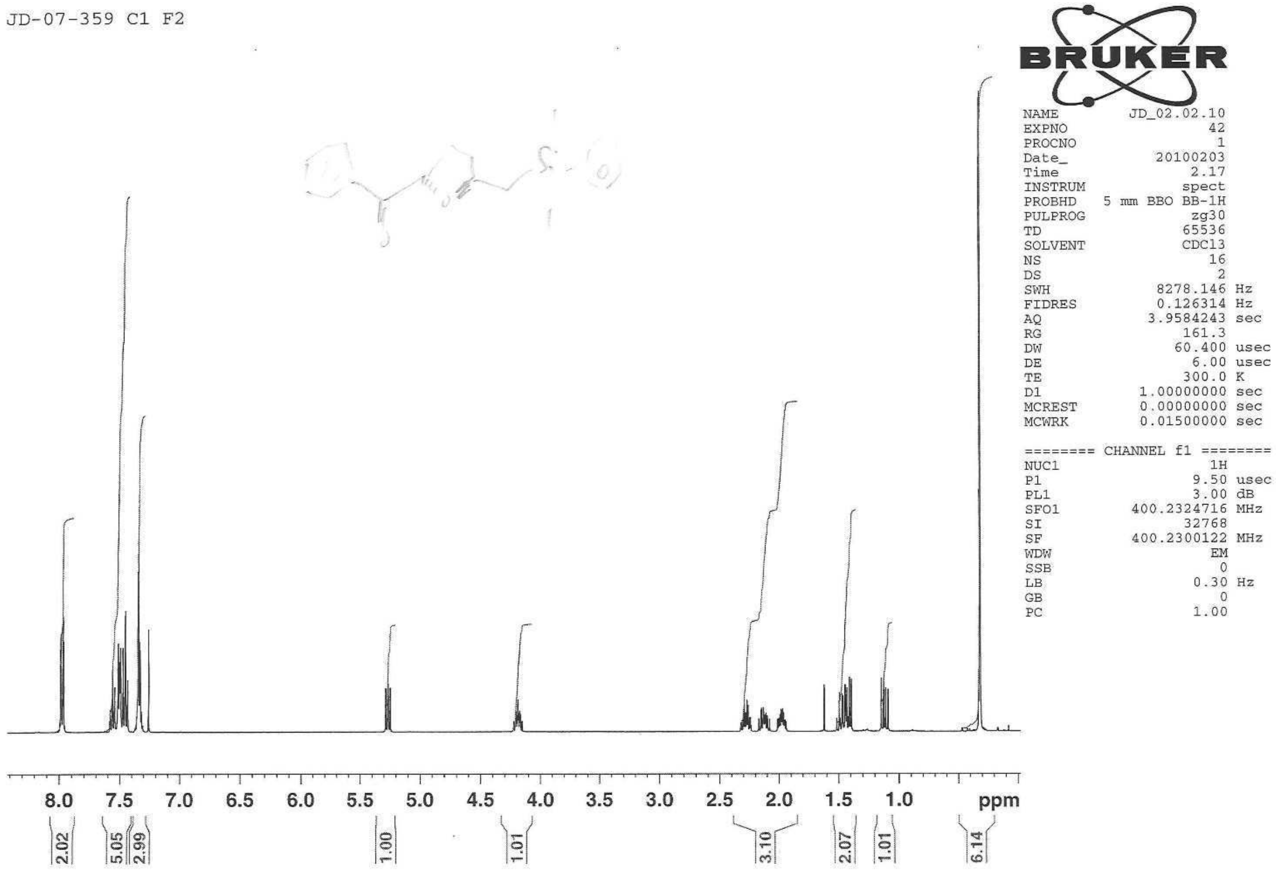
TABLE 5 ENTRY 9

(±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



Following the general procedure C, (cyclopropylmethyl)dimethylphenylsilane (0.12 g, 0.60 mmol) and phenyl glyoxal (0.12 g, 0.90 mmol) at 0 °C furnished the impure product (0.26 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.03 g, 0.11 mmol, 18%) as a colourless oil; R_f 0.41 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3070, 2957 (C-H), 2886 (C-H), 1692 (C=O), 1451 (C-H), 1429, 1230 (Si-C), 1115 (C-O); δ_H (400 MHz; CDCl$_3$); 0.32 (3H, s, SiCH$_3$), 0.33 (3H, s, SiCH$_3$), 1.12 (1H, dd, *J* 14.2 and 8.1, SiC$\underline{H}_a$H$_b$), 1.42 (1H, dd, *J* 14.2 and 6.2, SiH$_a\underline{H}_b$), 1.39-1.52 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.98 (1H, dddd, *J* 12.1 8.1 5.5 and 3.6, CH$_a\underline{H}_b$ C-3 THF), 2.13 (1H, app dtd, *J* 12.7 8.5 and 6.6, C$\underline{H}_a$H$_b$ C-4 THF), 2.25 (1H, app dtd, *J* 12.7 8.4 and 3.6, CH$_a\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.4 and 5.9, CH C-2 THF), 5.27 (1H, dd, *J* 8.2 and 6.6, CH C-5 THF), 7.32-7.36 (3H, m, overlapping signals 2 × *o*-CH and *p*-CH Ar), 7.45 (2H, t, *J* 7.6, 2 × *m*-CH Ar), 7.49-7.52 (2H, m, 2 × *m*-CH Ar), 7.56 (1H, tt, *J* 7.4 and 1.4, *p*-CH Ar), 7.96-7.99 (2H, m, 2 × *o*-CH Ar); δ_C (100.6 MHz; CDCl$_3$) −2.4 (SiCH$_3$), −2.0 (SiCH$_3$), 23.5 (SiCH$_2$), 29.3 (CH$_2$, C-4 THF), 34.4 (CH$_2$, C-3 THF), 78.6 (CH, C-2 THF), 79.2 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh), 128.6 (2 × *m*-CH, -C(=O)Ph), 129.0 (2 × *o*-CH, -C(=O)Ph), 129.0 (*p*-CH, SiPh), 133.3 (*p*-CH, -C(=O)Ph), 133.7 (2 × *o*-CH, SiPh), 135.3 (*ipso*-C, -C(=O)Ph), 139.1 (C, SiPh), 199.4 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 309 ([M−CH$_3$]$^+$, 2%), 267 (5), 239 (10), 219 (16), 135 (100), 105 (21), 77 (15); HRMS (CI$^+$, *m/z*) 342.1888 [M+NH$_4$]$^+$, $C_{20}H_{28}O_2NSi$ requires 342.1884.



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AQ              3.9584243 sec
RG                  161.3
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DE                   6.00 usec
TE                  300.0 K
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MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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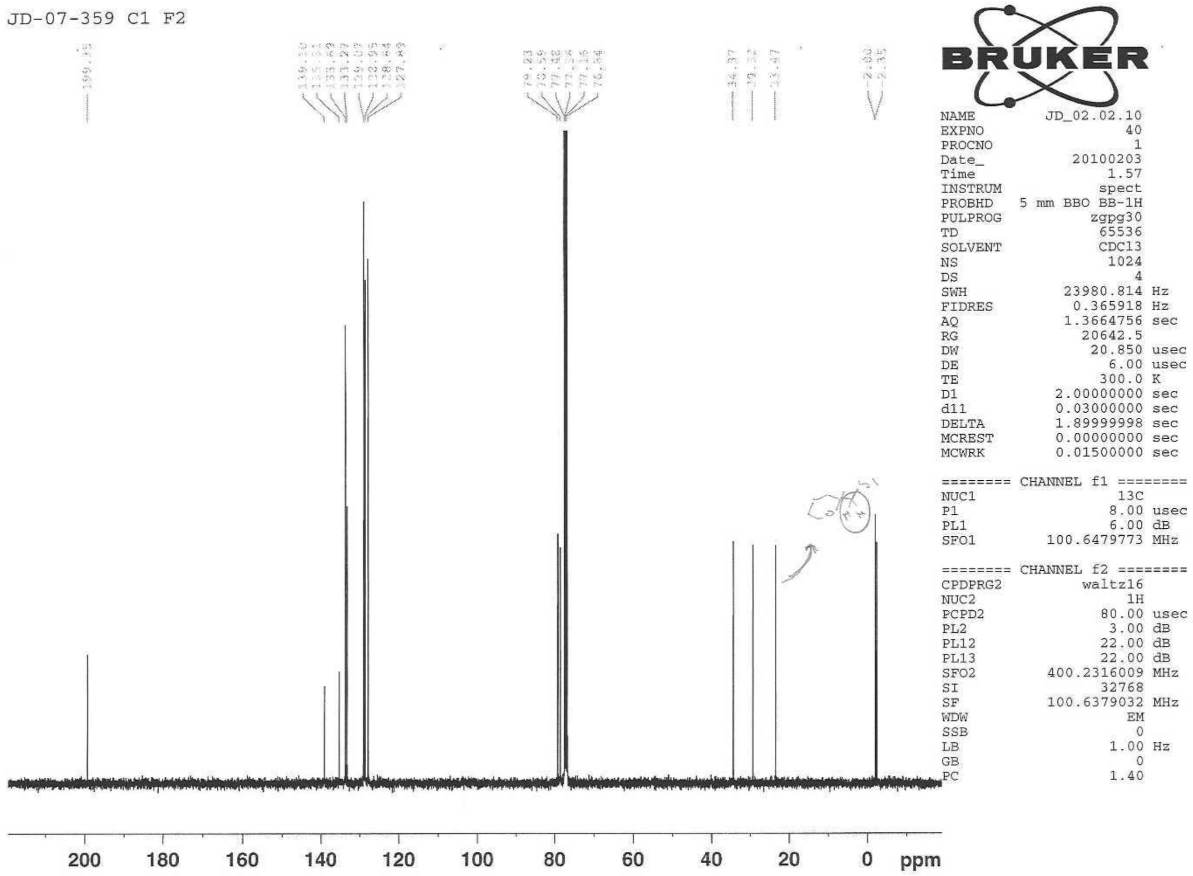

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TD                  65536
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NS                   1024
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SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                20642.5
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379032 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
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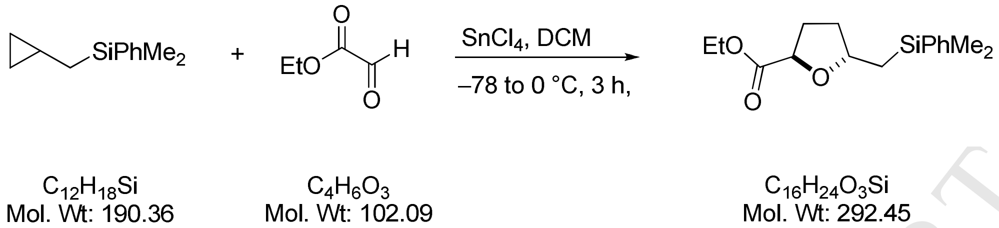
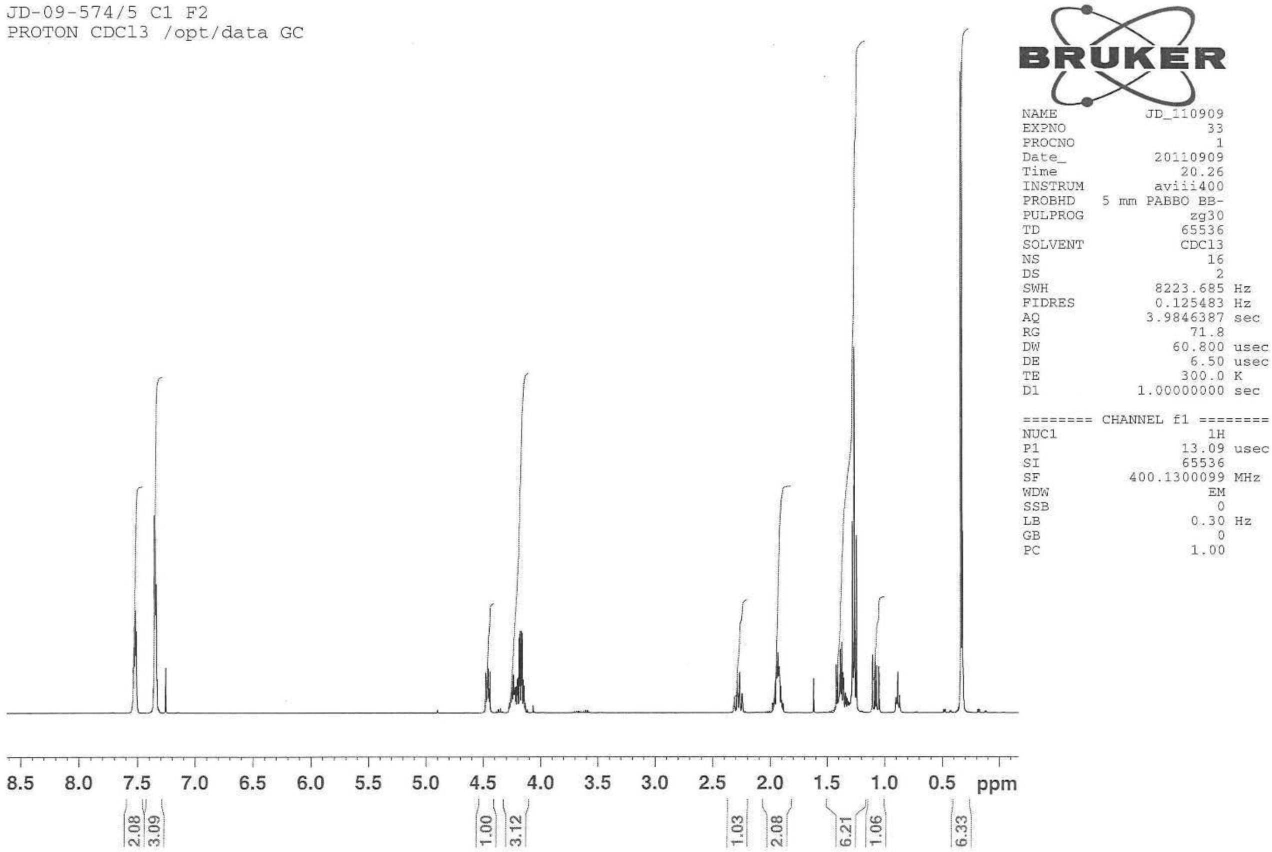
TABLE 5 ENTRY 10

(±)-Ethyl-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carboxylate



To a stirred solution of freshly distilled ethyl glyoxalate (0.23 g, 2.25 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.29 g, 1.50 mmol) in anhydrous DCM (15 mL) at −78 °C and under an atmosphere of argon was added dropwise, a solution of tin tetrachloride (0.39 g, 1.50 mmol) in anhydrous DCM (8 mL). The resulting mixture was allowed to warm to 0 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.47 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethylether : hexane] afforded the desired product as only the *trans* diastereoisomer (0.23 g, 0.79 mmol, 53%) as a colourless oil; R_f 0.46 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957 (C-H), 1749 (C-O), 1732 (C-O), 1427, 1180, 1091, 821 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.33 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$), 1.08 (1H, dd, 14.2 and 8.7, $SiC\underline{H}_aH_b$), 1.26 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$), 1.29-1.38 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.39 (1H, dd, *J* 14.2 and 5.7 $SiCH_a\underline{H}_b$), 1.90-1.97 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 2.25-2.31 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 4.14-4.26 (3H, m, overlapping signals $OC\underline{H}_2CH_3$ and CH C-2 THF), 4.46 (1H, dd, *J* 8.4 and 6.1, CH C-5 THF), 7.33-7.37 (3H, m, Ph), 7.50-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −2.0 ($SiCH_3$), 14.3 ($OCH_2\underline{C}H_3$), 23.4 ($SiCH_2$), 30.7 (CH_2, C-4 THF), 33.8 (CH_2, C-3 THF), 60.8 ($O\underline{C}H_2CH_3$), 76.1 (CH, C-5 THF), 78.8 (CH, C-2 THF), 127.9 (2 × *m*-CH, Ph), 129.1 (*p*-CH, Ph), 133.7 (2 × *o*-CH, Ph), 139.1 (C, Ph) 174.1(C=O); LRMS (EI^+, *m/z*): M^+ not visible, 277 ($[M-Me]^+$, 11%), 215 (13), 165 (12), 135 (100), 105 (13), 75 (18); HRMS (CI^+, *m/z*) 310.1824 $[M+NH_4]^+$, $C_{16}H_{28}O_3NSi$ requires 310.1833.

* The tin tetrachloride solution was prepared by adding a commercial 1 Mol solution of tin tetrachloride (3 mL) to anhydrous DCM (5 mL).



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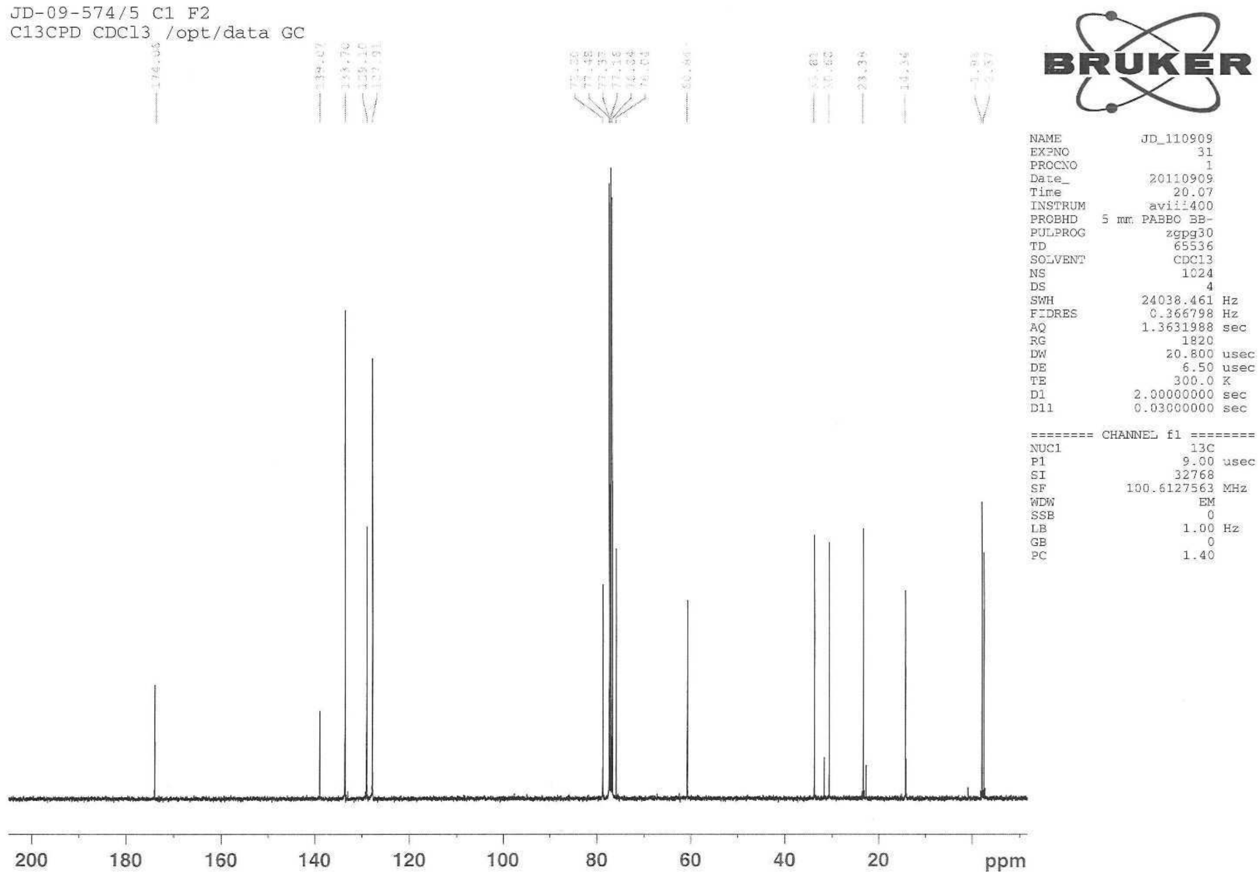

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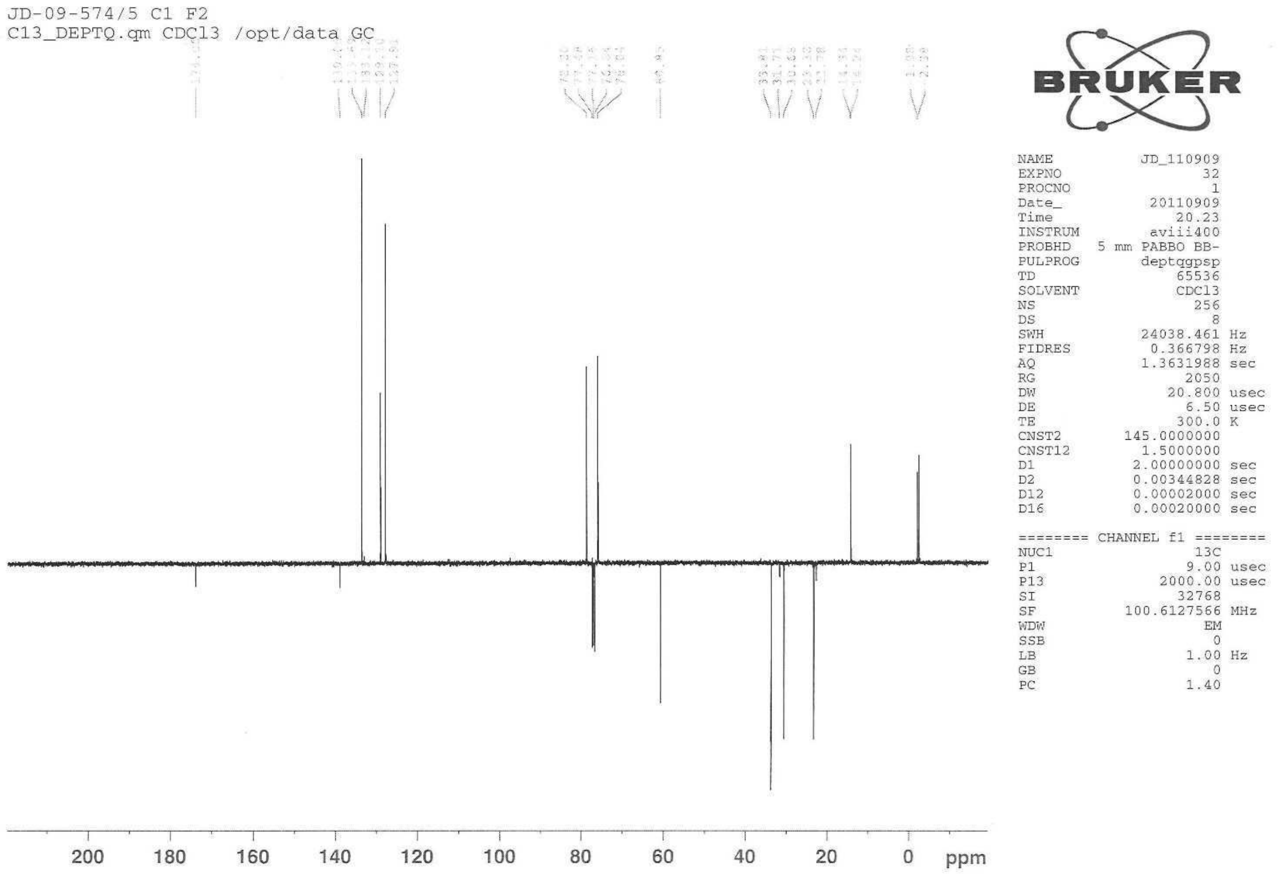
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WDW                      EM
SSB                       0
LB                     1.00 Hz
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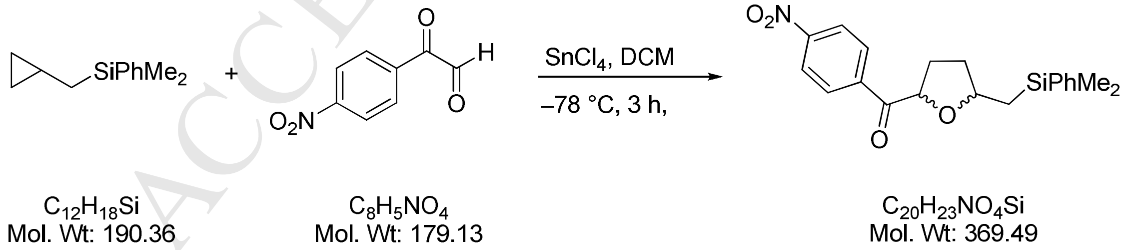
TABLE 5 ENTRY 11

(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-nitrophenyl)methanone



To a stirred solution of freshly distilled 4-nitrophenyl glyoxal (0.16 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried

($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a dark yellow oil (0.27 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.05 g, 0.14 mmol, 25%, *dr* (*trans* : *cis*) 1 : 2.6)[1] as a colourless oil; R_f 0.35 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2955, 2879, 1699 (C=O), 1524 (C-N), 1344 (C-N), 1219 (Si-C), 1112 (C-O), 825 (Si-C);

cis diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.26 (3H, m, SiMe), 0.28 (3H, s, SiMe), 1.10 (1H, dd, *J* 14.3 and 7.7, SiC$\underline{H}_a$H$_b$), 1.33 (1H, dd, *J* 14.3 and 6.5, SiCH$_a\underline{H}_b$), 1.39-1.52 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.94-2.05 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.10-2.19 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 2.36 (1H, app tdd, *J* 8.4, 4.6 and 3.5, CH$_a\underline{H}_b$ C-4 THF), 4.14 (1H, m, CH C-2 THF), 5.00 (1H, dd, *J* 8.6 and 4.7, CH C-5 THF), 7.30-7.34 (3H, m, Ph), 7.47-7.50 (2H, m, Ph), 8.15-8.28 (4H, m, $C_6\underline{H}_4NO_2$); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −2.1 ($SiCH_3$), 23.7 ($SiCH_2$), 28.5 (CH_2, C-4 THF), 33.8 (CH_2, C-3 THF), 80.0 (CH, C-2 THF), 80.5 (CH, C-5 THF), 123.7 (2 × *o*-CH, C_6H_4-NO_2) 127.9 (2 × *m*-CH, Ph), 129.2 (*p*-CH, Ph), 130.5 (2 × *m*-CH, C_6H_4-NO_2) 133.6 (2 × *o*-CH Ph), 138.8 (C, Ph), 140.3 (C, C_6H_4-NO_2), 150.4 (C, C_6H_4-NO_2), 197.2 (CO);

trans diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.29 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 1.12 (1H, dd, *J* 14.4 and 7.4, SiC$\underline{H}_a$H$_b$), 1.36 (1H, dd, *J* 14.4 and 6.9, SiCH$_a\underline{H}_b$), 1.39-1.52 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 2.01 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.20-2.27 (2H, m, CH_2 C-4 THF), 4.09 (1H, app dtd, *J* 8.4, 7.1 and 5.7, CH C-2 THF), 5.13 (1H, app t, *J* 7.2, CH C-5 THF), 7.31-7.36 (3H, m, Ar), 7.47-7.49 (2H, m, Ar), 8.10-8.28 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −2.1 ($SiCH_3$), 23.4 ($SiCH_2$), 28.3 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 78.9 (CH, C-2 THF), 79.9 (CH, C-5 THF), 123.7 (2 × *o*-CH, C_6H_4-NO_2) 127.9 (2 × *m*-CH, Ph), 129.2 (*p*-CH, Ph), 130.3 (2 × *m*-CH, C_6H_4-NO_2) 133.6 (2 × *o*-CH Ph), 138.8 (C, Ph), 140.3 (C, C_6H_4-NO_2), 150.4 (C, C_6H_4-NO_2), 198.1 (CO); LRMS (EI$^+$, *m/z*): M$^+$ not visible, ([M−Me]$^+$ 1%), 312 (8), 285 (8), 219 (14), 135 (100); HRMS (CI$^+$, *m/z*) 387.1741 [M+NH$_4$]$^+$, $C_{20}H_{27}N_2O_4Si$ requires 387.1735.

Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.13 (ppm) and 5.00 (ppm) *trans* and *cis* respectively.

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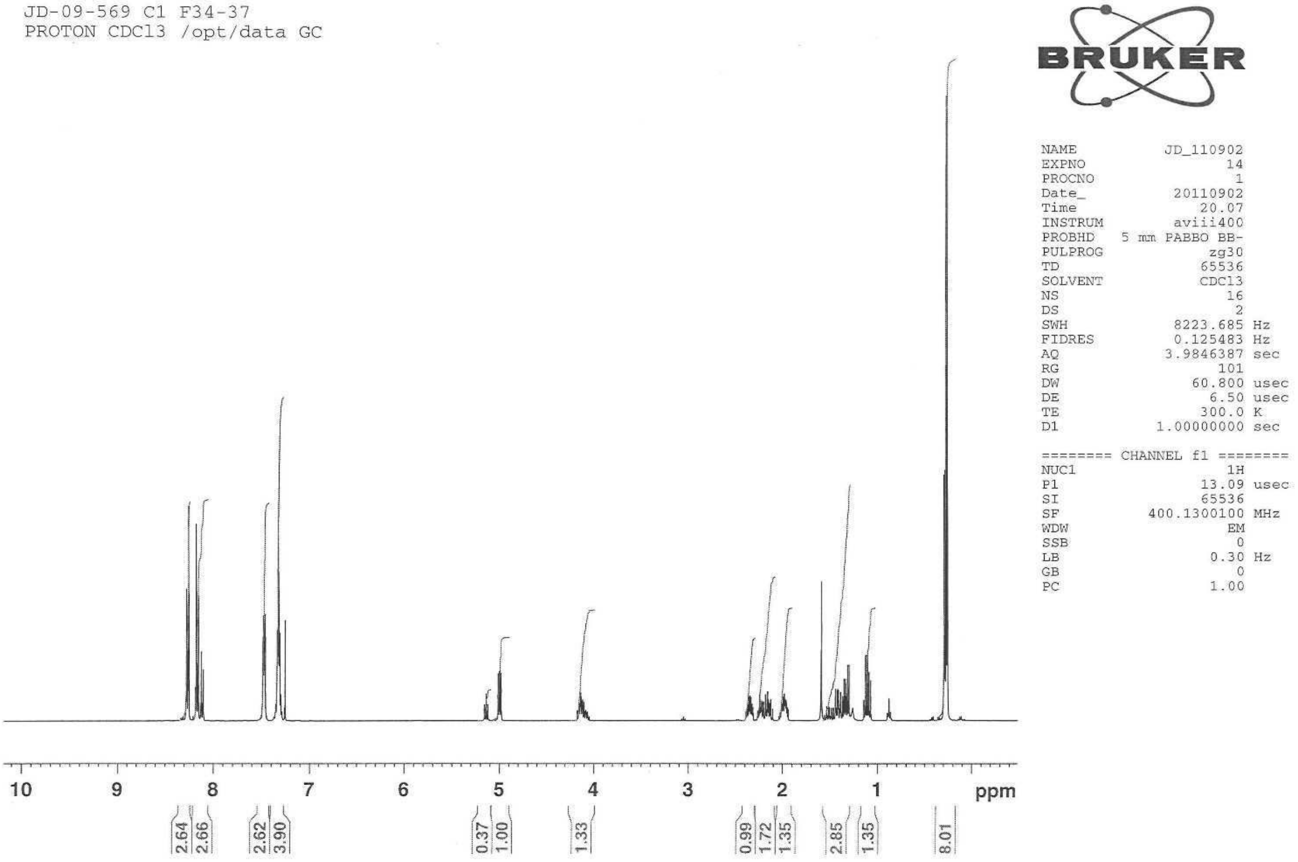
[1] 0.30 mmol of starting material was recoved (50%), therefore of the material that reacted 50% was converted to product



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D1            1.00000000 sec

======== CHANNEL f1 ========
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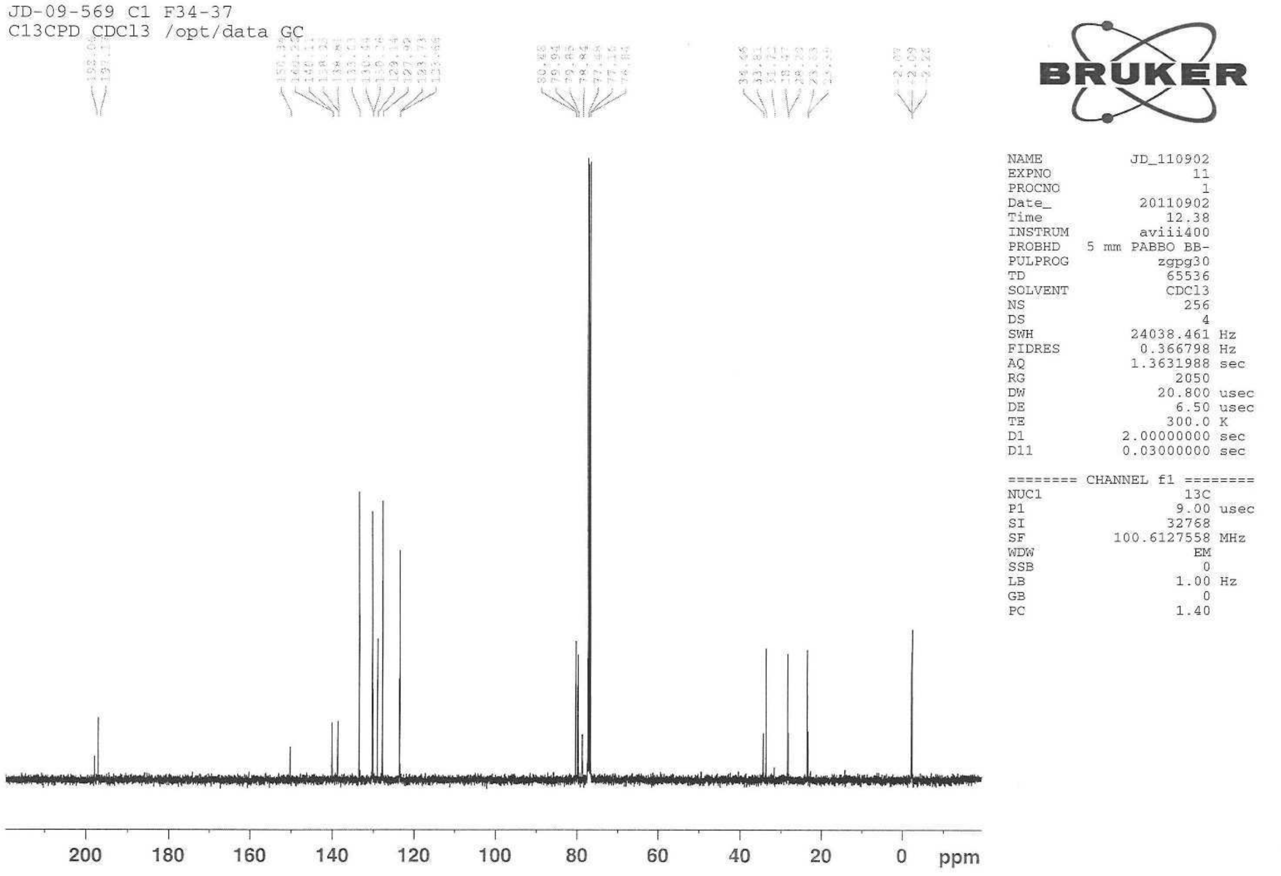

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AQ             1.3631988 sec
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TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
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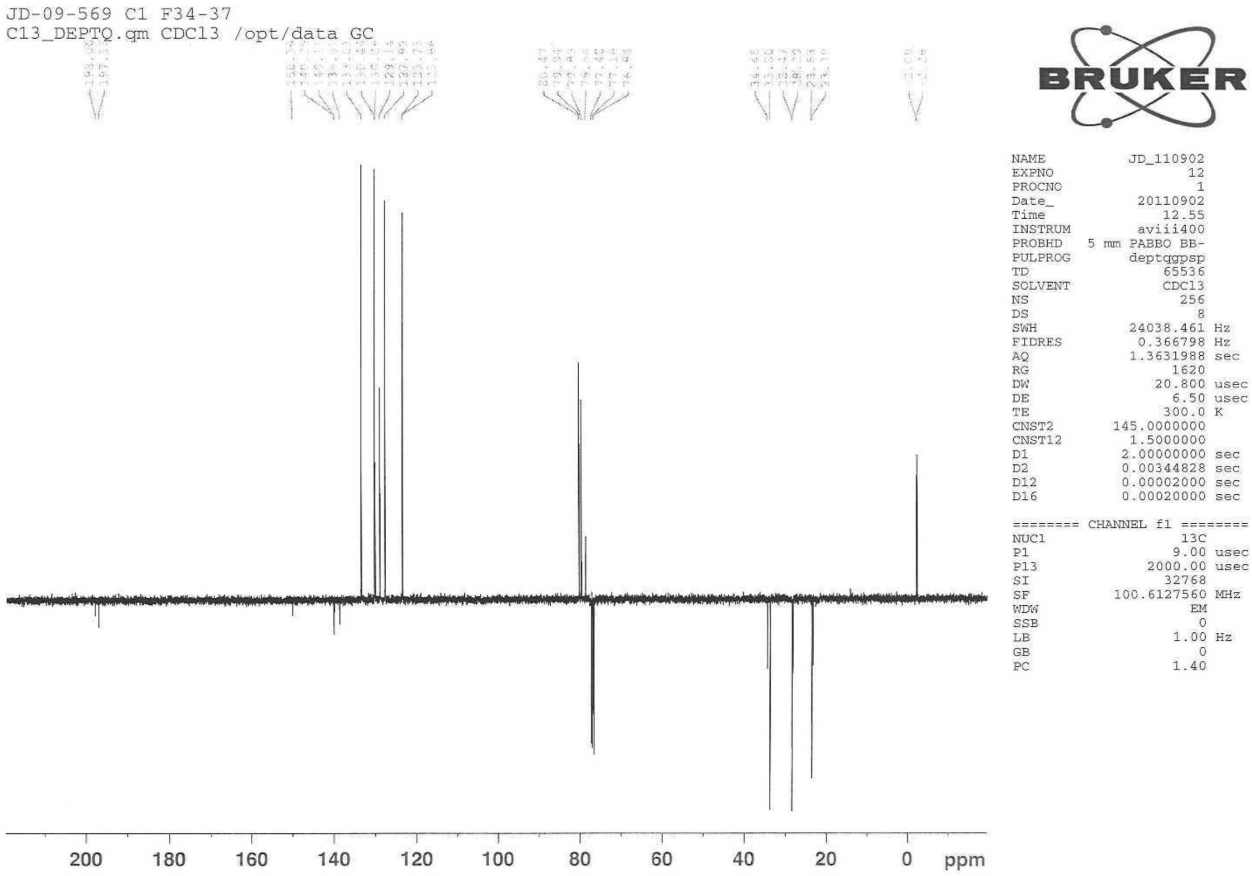

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RG                 1620
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DE                 6.50 usec
TE                300.0 K
CNST2       145.0000000
CNST12        1.5000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
D16          0.00020000 sec

======== CHANNEL f1 ========
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SI                32768
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WDW                  EM
SSB                   0
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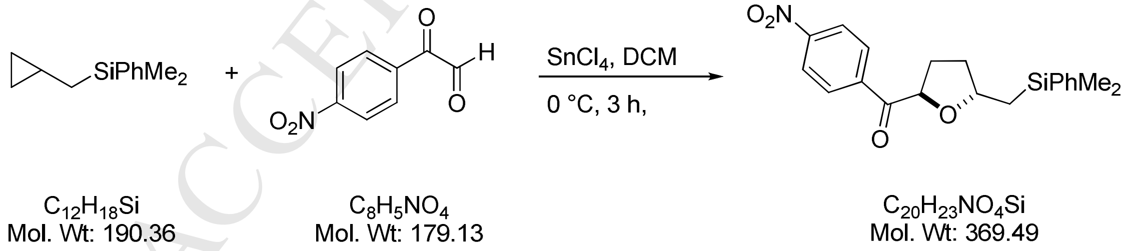
TABLE 5 ENTRY 12

(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-nitrophenyl)methanone



To a stirred solution of freshly distilled 4-nitrophenyl glyoxal (0.16 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.31 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane –

10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 8. mg, 0.02 mmol, 3%, *dr* (*trans* : *cis*) 1 : 0.2) as a colourless oil. Data is in agreement with that previously recorded.

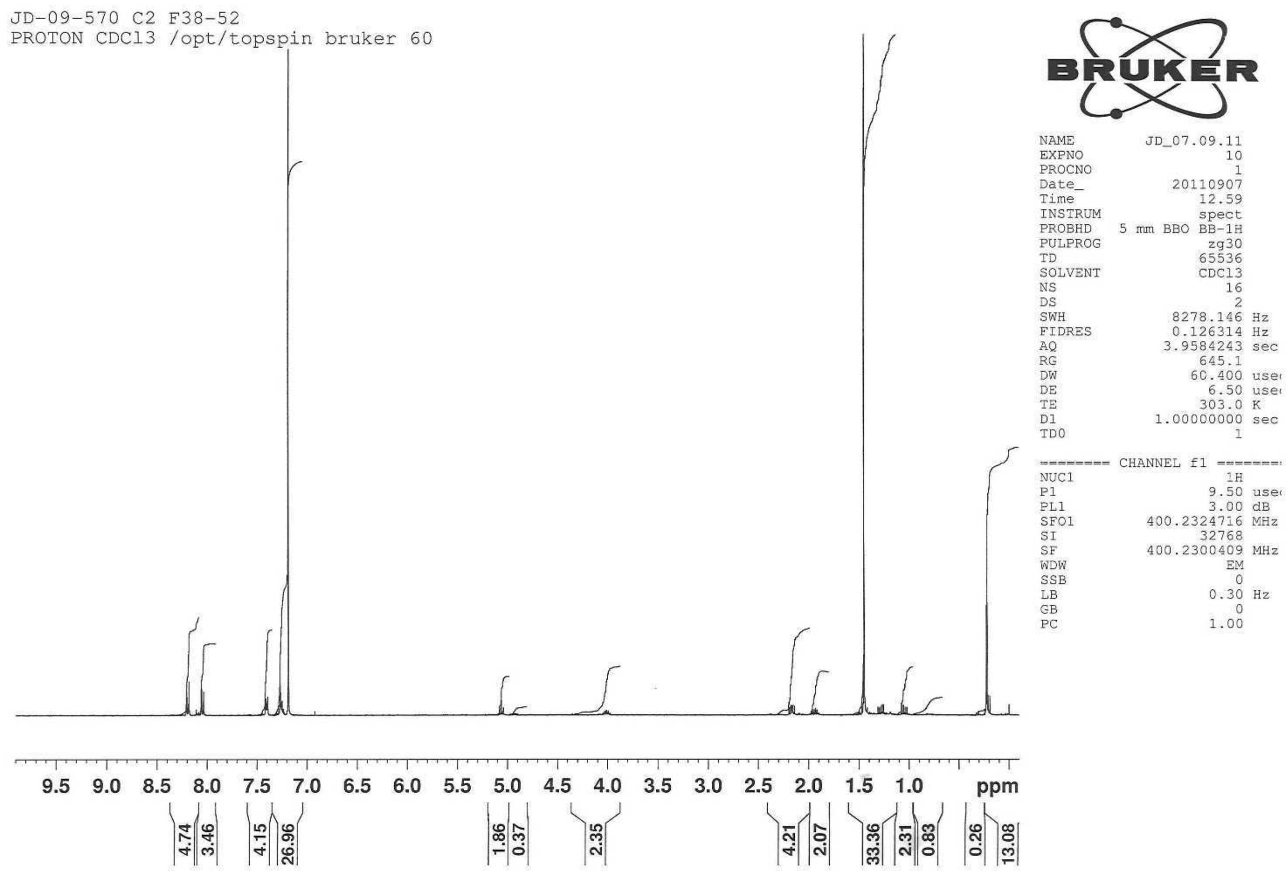
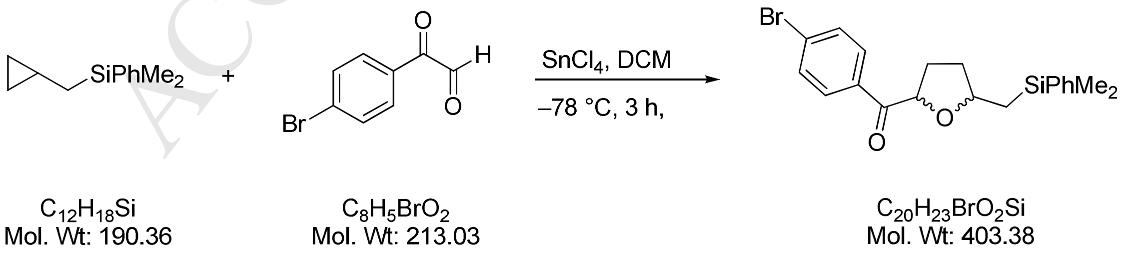


TABLE 5 ENTRY 13

(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-bromophenyl)methanone



To a stirred solution of freshly distilled 4-bromophenyl glyoxal (0.19 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (6.5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried

($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a dark yellow oil (0.29 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.12 g, 0.29 mmol, 55%, *dr* (*trans* : *cis*) 1 : 1.8)[2] as a colourless oil; R_f 0.50 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3089, 2955, 2879, 1690 (C=O), 1584, 1112, 1069, 835 (Si-C), 727;

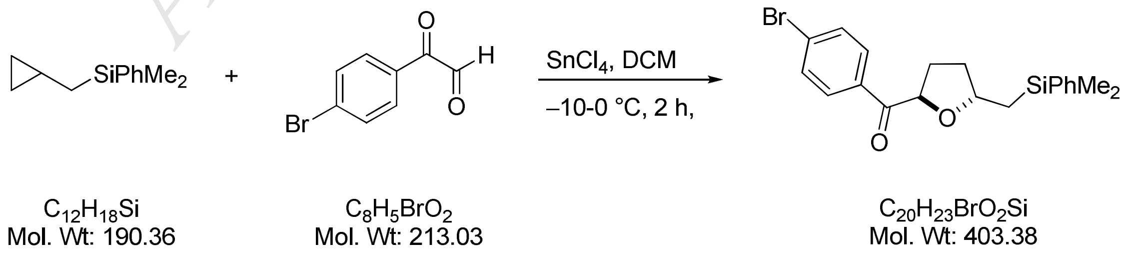
cis diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.29 (3H, m, SiMe), 0.31 (3H, s, SiMe), 1.15 (1H, dd, *J* 14.3 and 8.1, SiC$\underline{H}_a$H$_b$), 1.40 (1H, dd, *J* 14.3 and 6.2, SiCH$_a\underline{H}_b$), 1.41-1.48 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.92-2.00 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.09-2.33 (2H, m, CH_2 C-4 THF), 4.09-4.17 (1H, m, CH C-2 THF), 5.00 (1H, dd, *J* 8.7 and 4.9, CH C-5 THF), 7.31-7.39 (3H, m, SiPh), 7.49-7.52 (2H, m, SiPh), 7.57-7.60 (2H, m, Ar), 7.88-7.90 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 23.6 ($SiCH_2$), 28.7 (CH_2, C-4 THF), 33.7 (CH_2, C-3 THF), 79.6 (CH, C-2 THF), 80.0 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh) 128.3 (*ipso*-C, C_6H_4Br), 129.1 (*p*-CH, SiPh), 130.8 (2 × *m*-CH, C_6H_4Br), 131.8 (2 × *o*-CH, C_6H_4Br), 133.6 (2 × *o*-CH, SiPh), 134.3 (*p*-C, C_6H_4Br), 138.9 (C, SiPh), 197.4 (CO);

trans diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.32 (3H, s, $SiCH_3$), 0.32 (3H, s, $SiCH_3$), 1.12 (1H, dd, *J* 14.4 and 7.8, SiC$\underline{H}_a$H$_b$), 1.39 (1H, dd, *J* 14.4 and 6.6, SiCH$_a\underline{H}_b$), 1.48 (1H, app dq, *J* 12.1 and 8.8, C$\underline{H}_a$H$_b$ C-3 THF), 1.99 (1H, dddd, *J* 12.1, 8.3, 1.3 and 1.0, CH$_a\underline{H}_b$ C-3 THF), 2.20-2.28 (2H, m, CH_2 C-4 THF), 4.14 (1H, app ddd, *J* 14.4, 7.9 and 6.6, CH C-2 THF), 5.16 (1H, dd, *J* 8.0 and 6.6, CH C-5 THF), 7.31-7.39 (3H, m, SiPh), 7.49-7.52 (2H, m, SiPh), 7.57-7.60 (2H, m, Ar), 7.83-7.87 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 23.4 ($SiCH_2$), 28.7 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 78.6 (CH, C-2 THF), 79.3 (CH, C-5 THF), 127.9 (2 × *m*-CH, SiPh) 128.4 (*ipso*-C, C_6H_4Br), 129.1 (*p*-CH, SiPh), 130.6 (2 × *m*-CH, C_6H_4Br), 131.9 (2 × *o*-CH, C_6H_4Br), 133.6 (2 × *o*-CH, SiPh), 134.1 (*p*-C, C_6H_4Br), 139.0 (C, SiPh), 198.3 (CO); LRMS (EI^+, *m/z*): M^+ not visible, ($[M{-}Me]^+$ 2%), 347 (4), 319 (7), 239 (11), 219 (62), 183 (12), 155 (9), 135 (100), 105 (11), 75 (30); HRMS (CI^+, *m/z*) 420.0994 $[M+NH_4]^+$, $C_{20}H_{27}NO_2BrSi$ requires 420.0989.

Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.16 (ppm) and 5.00 (ppm) *trans* and *cis* respectively.

TABLE 5 ENTRY 14

(±)-2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-bromophenyl)methanone



To a stirred solution of freshly distilled 4-bromophenyl glyoxal (0.19 g, 0.90 mmol) and (cyclopropylmethyl)dimethylphenylsilane (0.11 g, 0.60 mmol) in anhydrous DCM (6.5 mL) at 0 °C and under an

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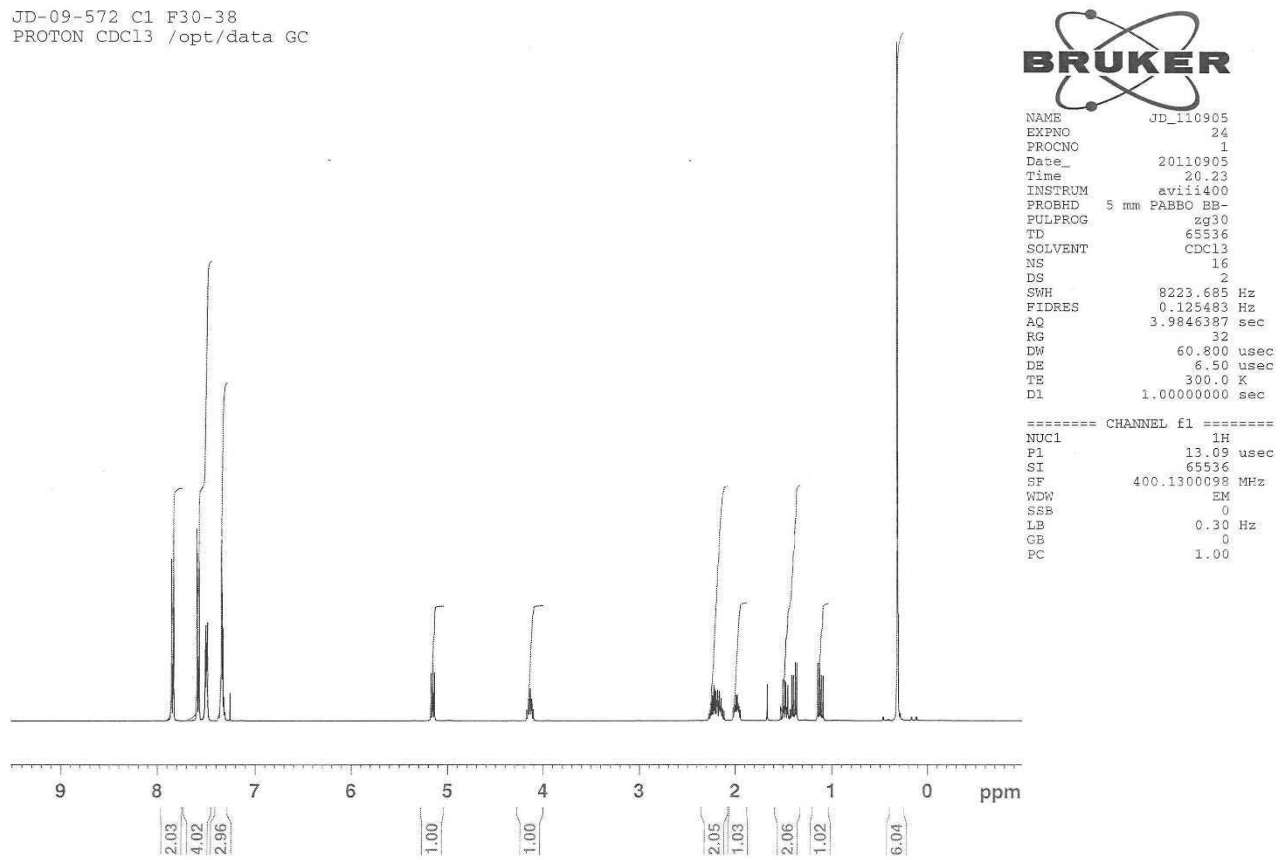
[2] 0.30 mmol of starting material was recoved (50%), therefore of the material that reacted 50% was converted to product

atmosphere of argon was added, dropwise, a 1 M solution of tin tetrachloride in DCM (0.50 mL, 0.50 mmol). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.24 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the *trans* diastereoisomers of the desired product (81 mg, 0.20 mmol, 34%) as a colourless oil. Data is in agreement with that previously recorded.



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SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                     32
DW                 60.800 usec
DE                   6.50 usec
TE                  300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.09 usec
SI                  65536
SF            400.1300098 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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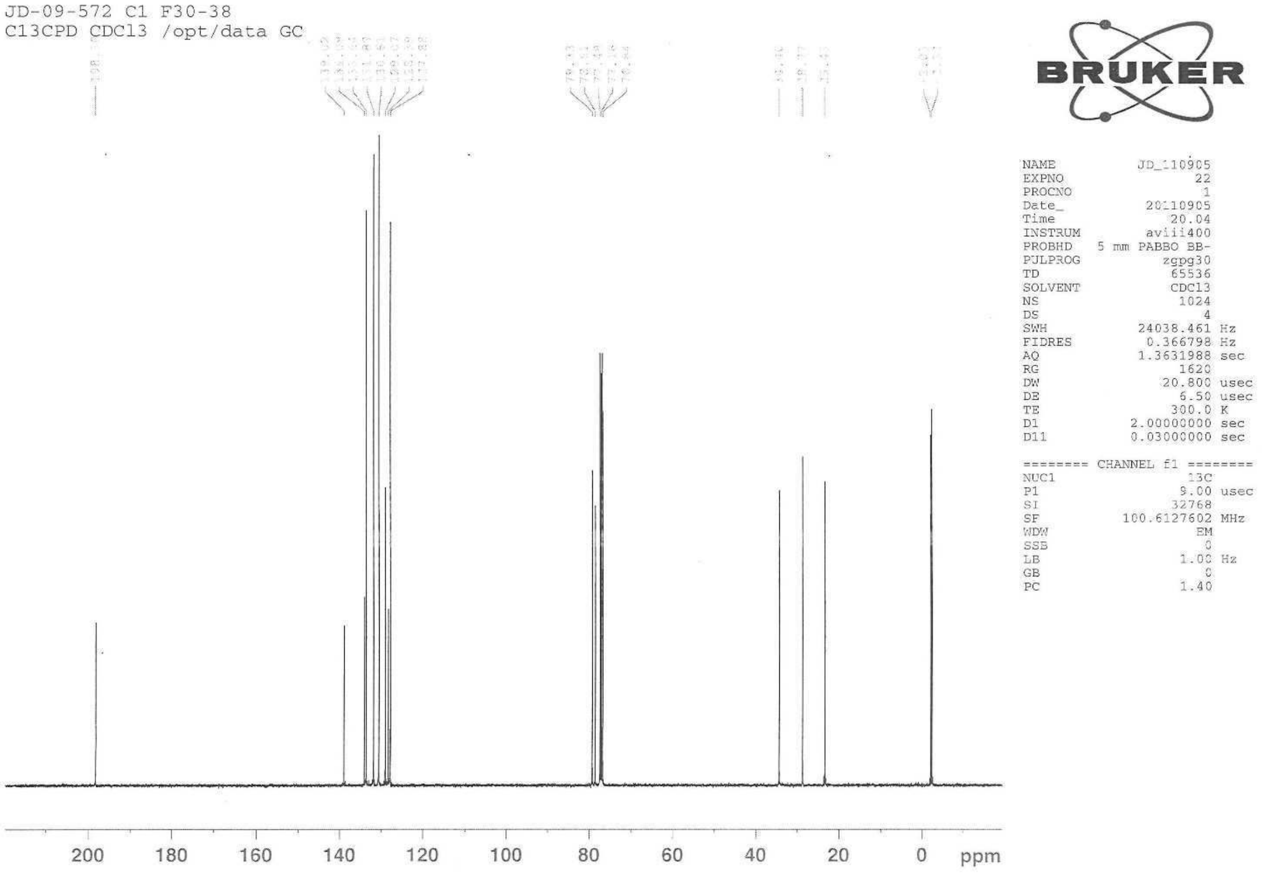

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JD-09-572 C1 F30-38
C13CPD CDCl3 /opt/data GC
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EXPNO                22
PROCNO                1
Date_          20110905
Time              20.04
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PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 1620
DW               20.800 usec
DE                 6.50 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.00 usec
SI                32768
SF          100.6127602 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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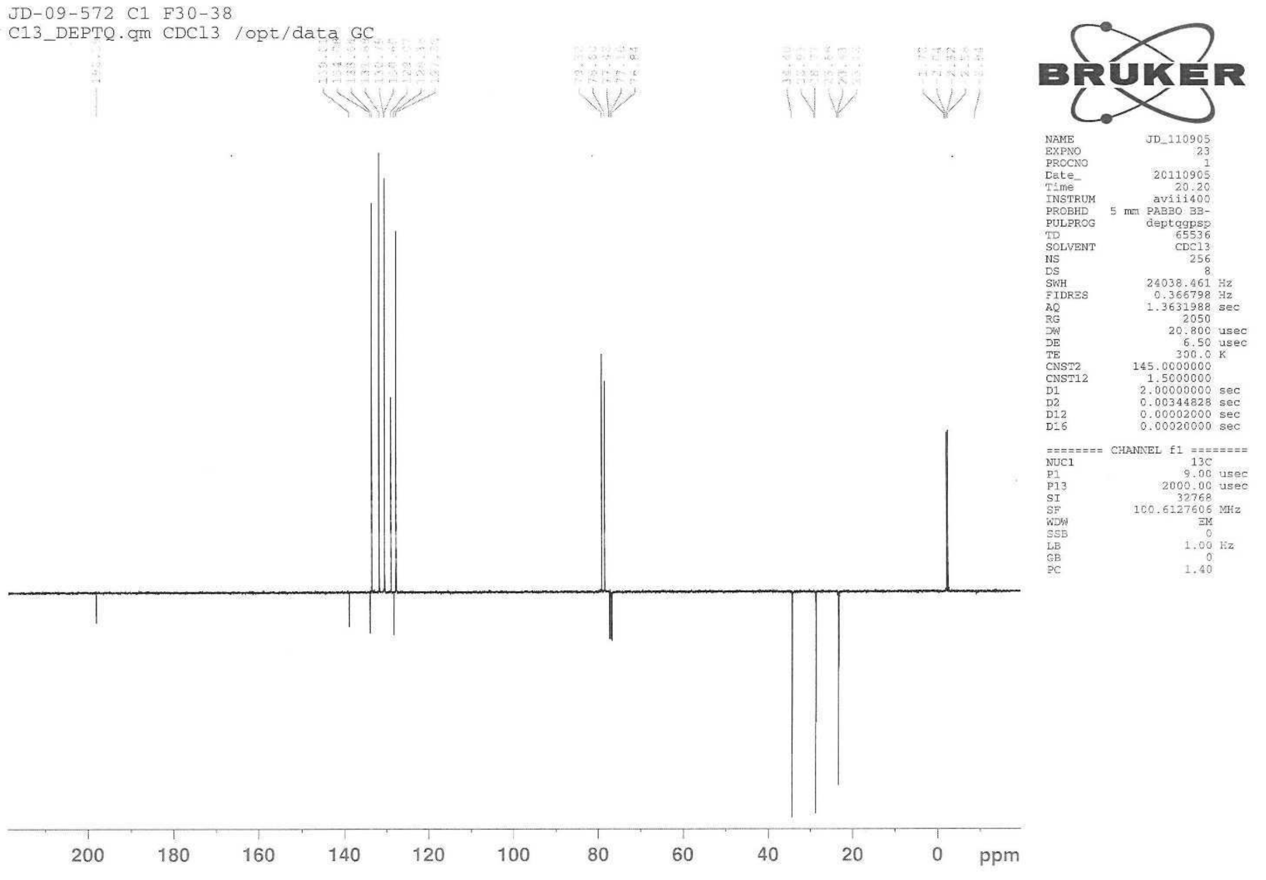

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JD-09-572 C1 F30-38
C13_DEPTQ.qm CDCl3 /opt/data GC
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EXPNO                23
PROCNO                1
Date_          20110905
Time              20.20
INSTRUM        aviii400
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PULPROG       deptqgpsp
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    8
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                 2050
DW               20.800 usec
DE                 6.50 usec
TE                300.0 K
CNST2       145.0000000
CNST12        1.5000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
D16          0.00020000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.00 usec
P13             2000.00 usec
SI                32768
SF          100.6127606 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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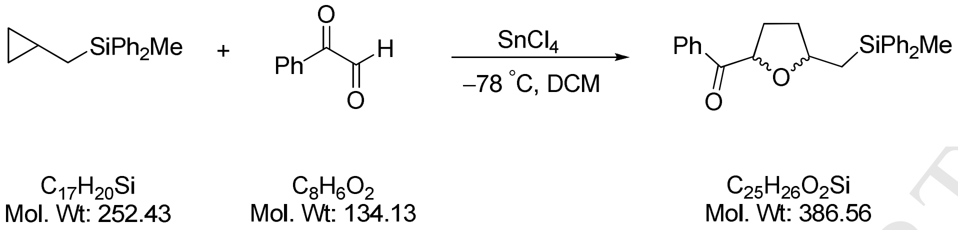
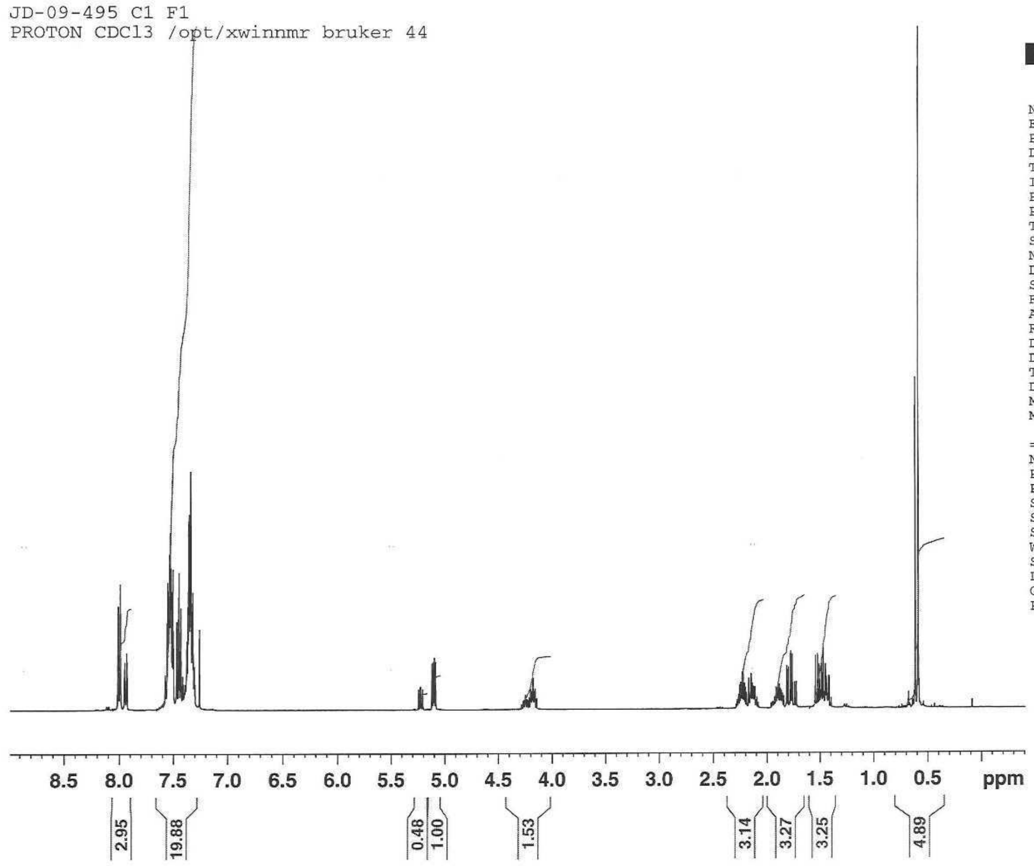
TABLE 5 ENTRY 15

(±)-(2-((Methyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)diphenylmethylsilane (0.15 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.5 mmol) in anhydrous DCM (2 mL). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.34 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.09 g, 0.24 mmol, 40%, *dr* (*trans* : *cis*) 0.49 : 1) as a colourless oil; R_f 0.27 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3068 2960, 1688, 1427, 1228, 1110, 873; *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.59 (3H, s, SiMe), 1.40-1.51 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.52 (1H, dd, *J* 14.4 and 8.2, $Si\underline{H}_aH_b$), 1.79 (1H, dd, *J* 14.4 and 5.9, $SiH_a\underline{H}_b$), 1.85-1.96 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.09-2.28 (2H, m, CH_2 C-4 THF), 4.18 (1H, app tt, *J* 8.7 and 5.7, CH C-2 THF), 5.11 (1H, dd, *J* 8.7 and 5.0, CH C-5 THF), 7.30-7.58 (13H, m, Ar), 8.00 (2H, app d, *J* 8.3, 2 × o-CH Ar); δ_C (100.6 MHz; $CDCl_3$) −3.3 (SiMe), 22.1 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 33.7 (CH_2, C-3 THF), 79.3 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.0 (4 × *m*-CH, Ar), 128.6 (2 × *m*-CH, Ar), 129.1 (2 × *o*-CH, Ar), 129.3 (2 × *p*-CH, Ar), 133.2 (*p*-CH, Ar), 134.5 (2 × *o*-CH, Ar), 134.6 (2 × *o*-CH, Ar), 135.6 (C, Ar), 137.0 (C, Ar), 199.2 (C=O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.62 (3H, s, SiMe), 1.40-1.51 (2H, m, overlapping signals $SiC\underline{H}_aH_b$ and $C\underline{H}_aH_b$, C-3 THF), 1.75 (1H, dd, *J* 14.4 and 6.3, $SiH_a\underline{H}_b$), 1.85-1.96 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.09-2.28 (2H, m, CH_2 C-4 THF), 4.25 (1H, app tt, *J* 8.0 and 5.8, CH C-2 THF), 5.23 (1H, dd, *J* 8.2 and 6.6, CH C-5 THF), 7.30-7.58 (13H, m, Ar), 7.94 (2H, app d, *J* 7.4, 2 × *o*-CH Ph) δ_C (100.6 MHz; $CDCl_3$) −3.4 (SiMe), 22.0 ($SiCH_2$), 29.1 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 78.4 (CH, C-2 THF), 79.3 (CH, C-5 THF), 128.0 (4 × *m*-CH, Ar), 128.6 (2 × *m*-CH, Ar), 129.0 (2 × *o*-CH, Ar), 129.3 (2 × *p*-CH, Ar), 133.2 (*p*-CH, Ar), 134.6 (2 × *o*-CH, Ar), 134.7 (2 × *o*-CH, Ar), 135.4 (C, Ar), 137.1 (C, Ar), 198.3 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 309 ([M−Ph]$^+$, 4%), 281 (11), 197 (100), 137 (19), 105 (21), 77 (13); HRMS (ESP, *m/z*) 404.2031 [M+NH$_4$]$^+$, $C_{25}H_{30}O_2NSi$ requires 404.2040. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.11 *cis* and 5.23 *trans*.



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JD-09-495 C1 F1
PROTON CDCl3 /opt/xwinnmr bruker 44
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EXPNO                  13
PROCNO                  1
Date_            20110109
Time                 8.35
INSTRUM             spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  143.7
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300119 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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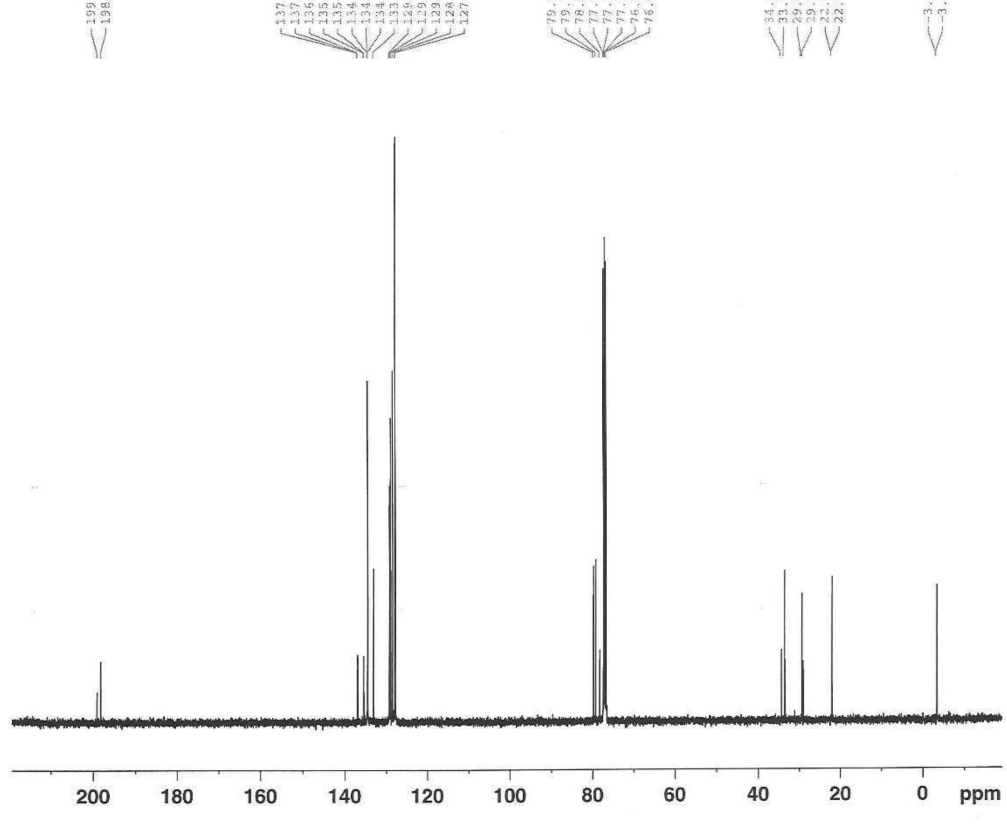

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JD-09-495 C1 F1
C13CPD CDCl3 /opt/xwinnmr bruker 44
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```
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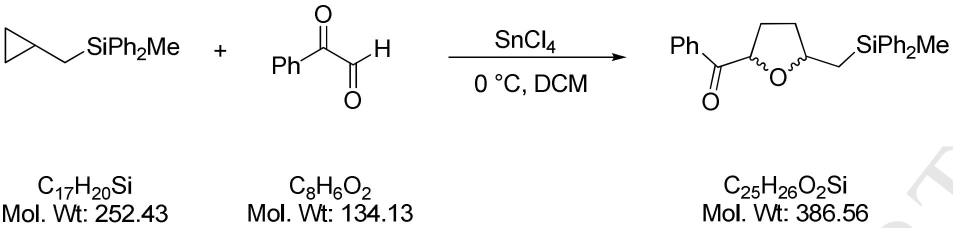
EXPNO                  10
PROCNO                  1
Date_            20110109
Time                 7.59
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                 9195.2
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379006 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

TABLE 5 ENTRY 16

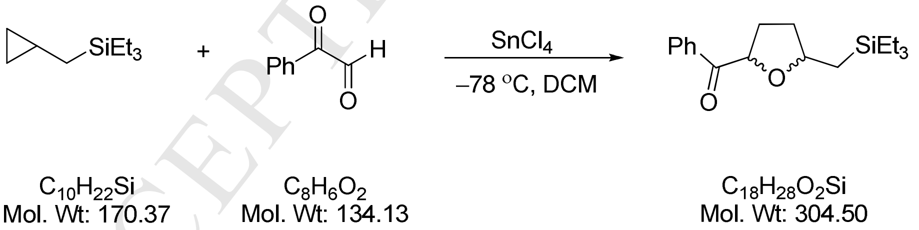
(±)-(2-((Methyldiphenylsilyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)triethylsilane (0.10 g, 0.60 mmol) in anhydrous DCM (5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.26 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 89.7 mg, 0.23 mmol, 38%, *dr* (*trans* : *cis*) 1 : 0.41) as a colourless oil. Data is in agreement with that previously recorded.

TABLE 5 ENTRY 17

(±)-Phenyl(2-((triethylsilyl)methyl)tetrahydrofuran-5-yl)methanone

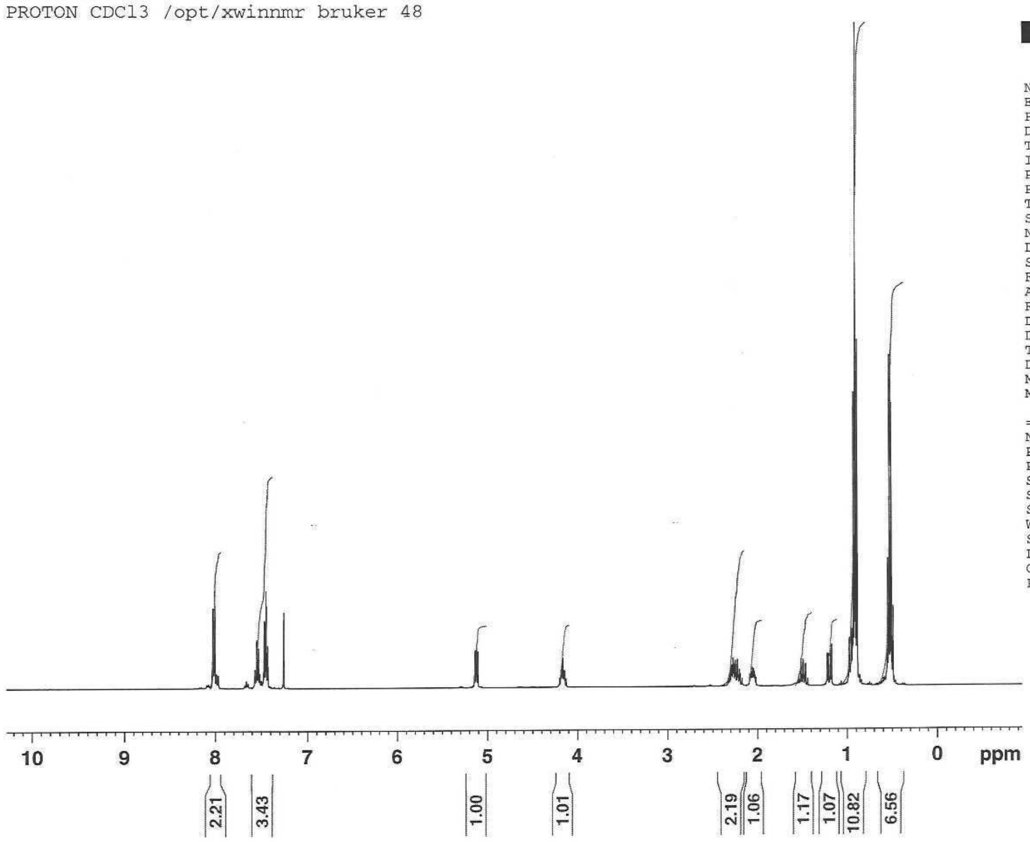


To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)triethylsilane (0.10 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.16 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded:

Product 1: the desired product as a mixture of *cis* and *trans* diastereoisomers (combined yield 26.0 mg, 0.09 mmol, 14%, *dr* (*trans* : *cis*) 0.88 : 1) as a colourless oil; R_f 0.45 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2909 (C-H), 2951, 2874, 1690 (C=O), 1449, 1228 (Si-C), 1180 (C-O), 1092, 1002; *cis* isomer: δ_H (400 MHz; $CDCl_3$) 0.53 (6H, q, *J* 7.9, 3 × CH_2), 0.91 (9H, t, *J* 7.9, 3 × CH_3), 0.95 (1H, dd, *J* 14.3 and 8.7, $\mathrm{SiC\underline{H}_aH_b}$), 1.20 (1H, dd, *J* 14.3 and 6.0, $\mathrm{SiCH_a\underline{H}_b}$), 1.49 (1H, dq, *J* 12.0 and 9.2, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 2.05 (1H, dddd, *J* 12.2 7.7 5.3 and 3.5, $\mathrm{CH_a\underline{H}_b}$ C-3 THF), 2.17-2.33 (2H, m, overlapping signals $\mathrm{C\underline{H}_2}$ C-4 THF), 4.17 (1H app tt, *J* 8.9 and 5.7,CH C-2 THF), 5.13 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.43-7.47 (2H, m, 2 × *m*-CH, Ph), 7.50-7.57 (1H, m, *p*-CH, Ph), 8.00-8.03 (2H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.2 ($SiCH_2$), 29.5 (CH_2, C-4 THF), 33.9 (CH_2, C-3 THF), 79.8 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.1 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.6 (C, Ph), 198.5 (C=O); *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.54 (6H, q, *J* 7.8, 3 × CH_2), 0.88 (1H, dd, *J* 14.1 and 8.4, $\mathrm{SiC\underline{H}_aH_b}$), 0.93 (9H, t, *J* 7.9, 3 × CH_3), 1.18 (1H, dd, *J* 14.1 and 6.1, $\mathrm{SiCH_a\underline{H}_b}$), 1.53 (1H, dq, *J* 11.6 and 8.7, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 2.06-2.13 (1H, m, $\mathrm{CH_a\underline{H}_b}$ C-3 THF), 2.41-2.22 (1H, m, $\mathrm{C\underline{H}_aH_b}$ C-4 THF) 2.28-2.36 (1H, m, $\mathrm{CH_a\underline{H}_b}$ C-4 THF), 4.19 (1H, app tt, *J* 8.5 and 5.7, CH C-2 THF), 5.29 (1H, dd, *J* 8.2 and 6.4, CH C-5 THF), 7.45 (2H, app t, *J* 7.5, *m*-CH, Ph), 7.53-7.57 (1H, m, *p*-CH, Ph), 7.98-8.00 (2H, m, *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.1 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 78.8 (CH, C-2 THF), 79.2 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C. Ph), 199.5 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 275 ($[M-Et]^+$, 36%), 233 (63), 199 (22), 163 (15), 115 (100), 105 (48), 77 (46), 59 (45); HRMS (ESP, *m/z*) 305.1924 $[M+H]^+$, $C_{18}H_{29}O_2Si$ requires 305.1931. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the C-5 protons of the THF ring, 5.13 *cis* and 5.29 *trans*.

Product 2: the desired product as the single *cis* diastereoisomer (13.0 mg, 0.04 mmol, 7%) as a colourless oil; R_f 0.45 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2910 (C-H), 2952, 2874, 1690 (C=O), 1450, 1226 (Si-C), 1175 (C-O), 1090, 1001; δ_H (400 MHz; $CDCl_3$) 0.53 (6H, q, *J* 7.9, 3 × CH_2), 0.91 (9H, t, *J* 7.9, 3 × CH_3), 0.95 (1H, dd, *J* 14.3 and 8.7, $\mathrm{SiC\underline{H}_aH_b}$), 1.20 (1H, dd, *J* 14.3 and 6.0, $\mathrm{SiCH_a\underline{H}_b}$), 1.49 (1H, dq, *J* 12.0 and 9.2, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 2.05 (1H, dddd, *J* 12.2 7.7 5.3 and 3.5, $\mathrm{CH_a\underline{H}_b}$ C-3 THF), 2.17-2.33 (2H, m, overlapping signals $\mathrm{C\underline{H}_2}$ C-4 THF), 4.17 (1H, app tt, *J* 8.9 and 5.7, CH C-2 THF), 5.13 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.43-7.47 (2H, m, 2 × *m*-CH, Ph), 7.50-7.57 (1H, m, *p*-CH, Ph), 8.00-8.03 (2H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.2 ($SiCH_2$), 29.5 (CH_2, C-4 THF), 33.9 (CH_2, C-3 THF), 79.8 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.1 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.6 (C, Ph), 198.5 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 275 ($[M-Et]^+$, 7%), 233 (66), 199 (24), 163 (15), 115 (100), 105 (50), 77 (46), 59 (45); HRMS (ESP, *m/z*) 305.1935 $[M+H]^+$, $C_{18}H_{29}O_2Si$ requires 305.1931.

JD-09-496 C1 F2
PROTON CDCl3 /opt/xwinnmr bruker 48



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PROCNO                  1
Date_            20110109
Time                22.31
INSTRUM             spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  228.1
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300119 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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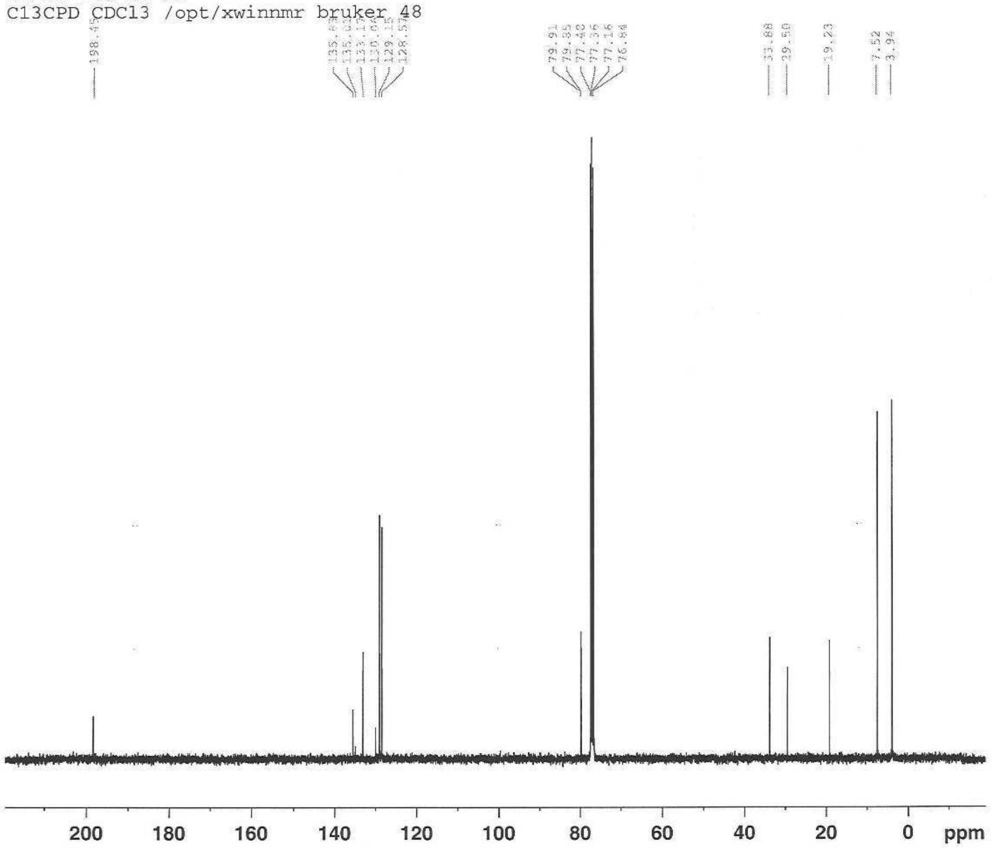
JD-09-496 C1 F2
C13CPD CDCl3 /opt/xwinnmr bruker 48



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EXPNO                  50
PROCNO                  1
Date_            20110109
Time                21.55
INSTRUM             spect
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PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                 7298.2
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6378984 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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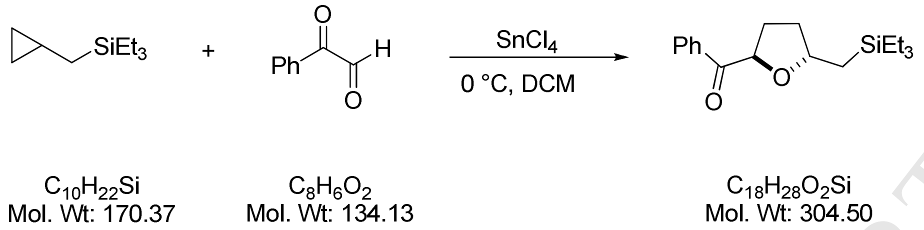
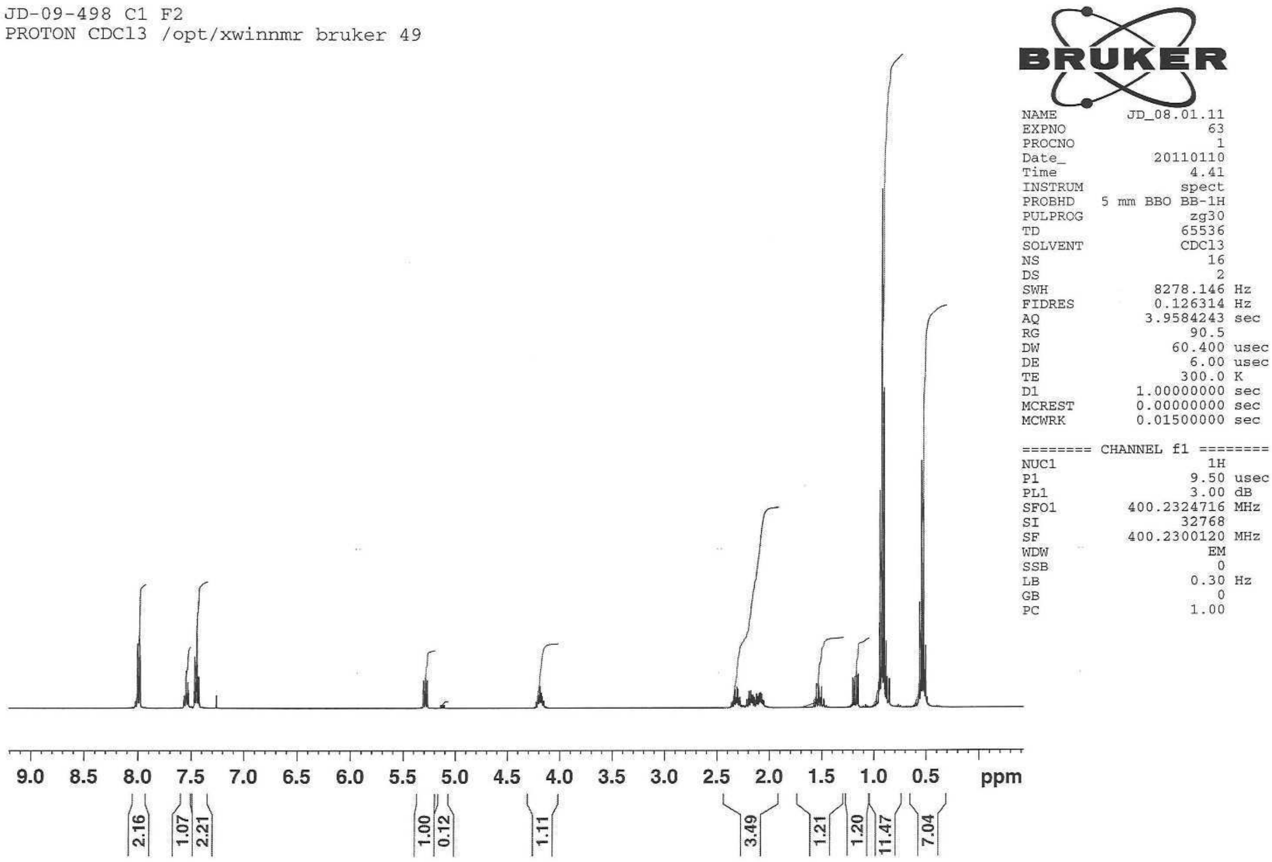
TABLE 5 ENTRY 18

(±)-Phenyl(2-((triethylsilyl)methyl)tetrahydrofuran-5-yl)methanone



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and (cyclopropylmethyl)triethylsilane (0.10 g, 0.60 mmol) in anhydrous DCM (5 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at 0 °C and monitored by TLC. After 2 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.16 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.10 g, 0.32 mmol, 53%, *dr* (*trans* : *cis*) 1 : 0.1) as a colourless oil; *trans* isomer: R_f 0.45 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2952, 2909 (C-H), 2874, 1690 (C=O), 1449, 1229, 1180, 1016, 877; δ_H (400 MHz; $CDCl_3$) 0.54 (6H, q, *J* 7.8, 3 × CH_2), 0.88 (1H, dd, *J* 14.1 and 8.4, SiC$\underline{H}_aH_b$), 0.93 (9H, t, *J* 7.9, 3 × CH_3), 1.18 (1H, dd, *J* 14.1 and 6.1, SiC$H_a\underline{H}_b$), 1.53 (1H, dq, *J* 11.6 and 8.7, C$\underline{H}_aH_b$ C-3 THF), 2.06-2.13 (1H, m, C$H_a\underline{H}_b$ C-3 THF), 2.41-2.22 (1H, m, C$\underline{H}_aH_b$ C-4 THF) 2.28-2.36 (1H, m, C$H_a\underline{H}_b$ C-4 THF), 4.19 (1H, app tt, *J* 8.5 and 5.7, CH C-2 THF), 5.29 (1H, dd, *J* 8.2 and 6.4,CH C-5 THF), 7.45 (2H, app t, *J* 7.5, *m*-CH Ph), 7.53-7.57 (1H, m, *p*-CH Ph), 7.98-8.00 (2H, m, *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 3.9 (3 × CH_2), 7.5 (3 × CH_3), 19.1 ($SiCH_2$), 29.4 (CH_2, C-4 THF), 34.5 (CH_2, C-3 THF), 78.8 (CH, C-2 THF), 79.2 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 129.0 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 275 ([M−Et]$^+$, 11%), 233 (75), 199 (29), 163 (16), 115 (100), 105 (38), 87 (76), 77 (36), 59 (36); HRMS (ESP, *m/z*) 305.1925 [M+H]$^+$, $C_{18}H_{29}O_2Si$ requires 305.1931.



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JD-09-498 C1 F2
PROTON CDCl3 /opt/xwinnmr bruker 49
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SOLVENT             CDCl3
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DS                      2
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FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   90.5
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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PL1                  3.00 dB
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WDW                    EM
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LB                   0.30 Hz
GB                      0
PC                   1.00
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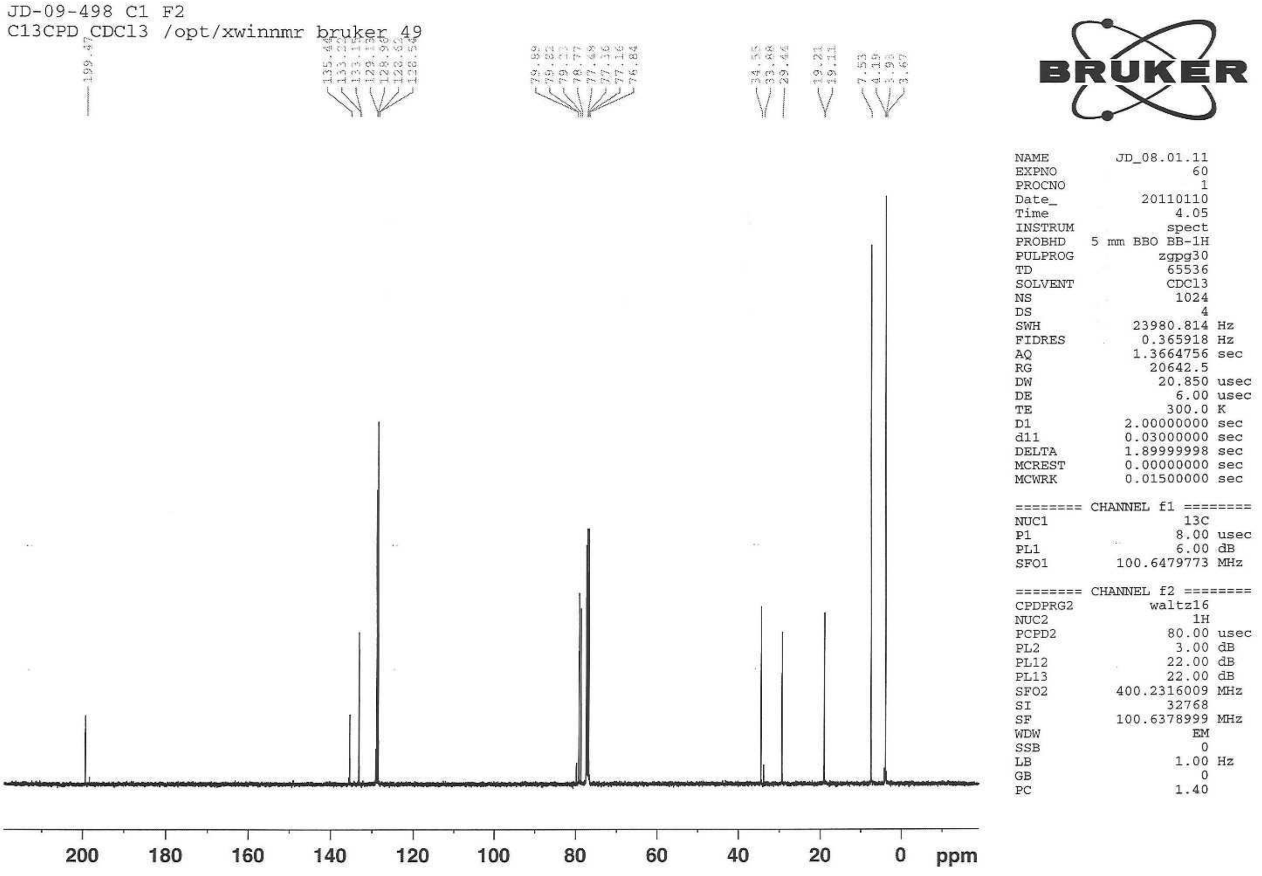

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JD-09-498 C1 F2
C13CPD CDCl3 /opt/xwinnmr bruker 49
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TD                  65536
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NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                20642.5
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6378999 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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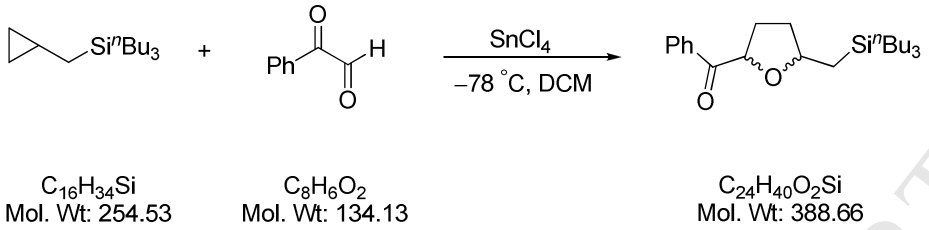
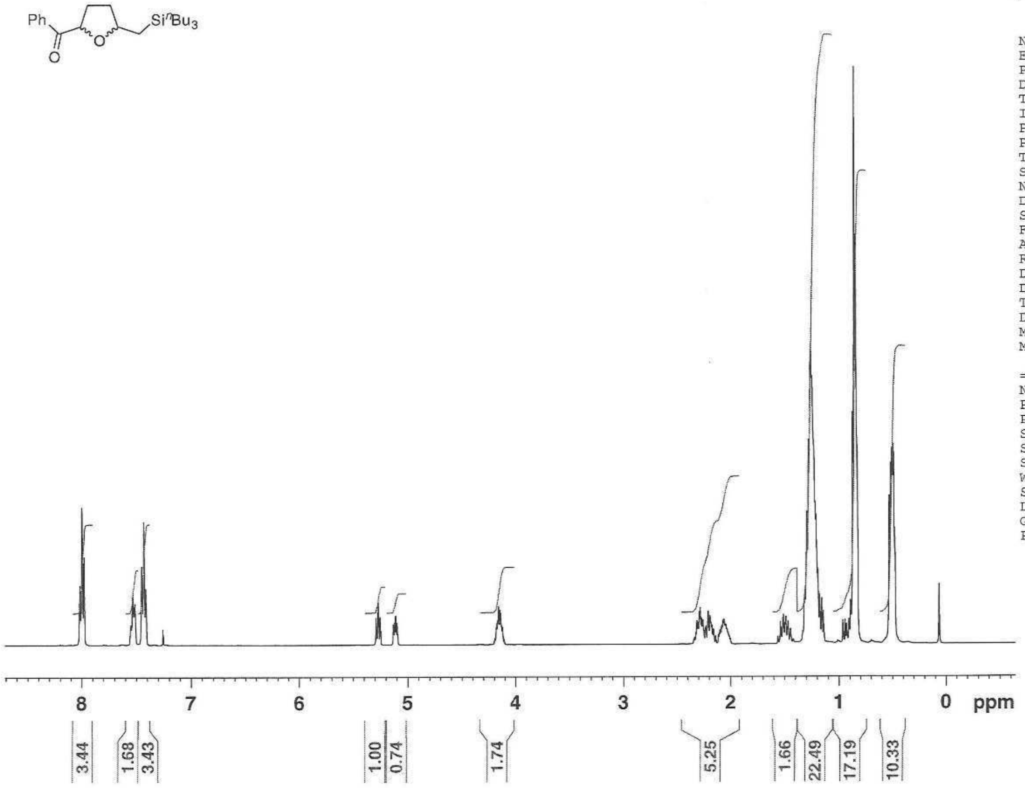
TABLE 5 ENTRY 19

(±)-Phenyl(2-((tri-*n*-butylsilyl)methyl)tetrahydrofuran-5-yl)methanone



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of (cyclopropylmethyl)tri-*n*-butylsilane (0.15 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of wet acetone (5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.25 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as an inseparable mixture of *cis* and *trans* diastereoisomers (combined yield 0.09 g, 0.26 mmol, 43%, *dr* (*trans* : *cis*) 1.35 : 1) as a colourless oil; R_f 0.63 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2920 (C-H), 1691 (C=O), 1449 (C-H), 1228 (Si-C), 1180 (C-O), 1080 (C-O); *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.48-0.53 (6H, m, $Si(CH_2)_3$), 0.83-0.97 (10H, m, overlapping signals $SiC\underline{H}_aH_b$ and 3 × CH_3), 1.14-1.34 (13H, m, overlapping signals $SiCH_a\underline{H}_b$ and 6 × CH_2), 1.42-1.56 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 2.01-2.12 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.14-2.35 (2H, m, CH_2 C-4 THF), 4.11-4.20 (1H, m, CH C-2 THF), 5.27 (1H, dd, *J* 8.2 and 6.5, CH C-5 THF), 7.42-7.45 (2H, m, 2 × *m*-CH, Ph), 7.51-7.56 (1H, m, *p*-CH, Ph), 7.98-8.02 (1H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 12.7 ($Si(CH_2)_3$), 13.9 (3 × CH_3), 20.1 ($SiCH_2$), 26.2 (3 × CH_2 Bu), 26.9 (3 × CH_2 Bu), 29.2 (CH_2, THF), 34.5 (CH_2, THF), 78.8 (CH, C-2 THF), 79.1 (CH, C-5 THF), 128.6 (2 × *m*-CH, Ph), 128.9 (2 × *o*-CH, Ph), 133.2 (*p*-CH, Ph), 135.4 (C, Ph), 199.3 (CO); *cis* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.48-0.53 (6H, m, $Si(CH_2)_3$), 0.83-0.97 (11H, m, overlapping signals $SiCH_2$ and 3 × CH_3), 1.14-1.34 (12H, m, 6 × CH_2), 1.42-1.56 (1H, m,$C\underline{H}_aH_b$ C-3 THF), 2.01-2.12 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.14-2.35 (2H, m, CH_2 C-4 THF), 4.11-4.20 (1H, m, CH C-2 THF), 5.12 (1H, dd, *J* 8.6 and 5.1, CH C-5 THF), 7.42-7.45 (2H, m, 2 × *m*-CH, Ph), 7.51-7.56 (1H, m, *p*-CH, Ph), 7.98-8.02 (1H, m, 2 × *o*-CH, Ph); δ_C (100.6 MHz; $CDCl_3$) 12.7 ($Si(CH_2)_3$), 13.9 (3 × CH_3), 20.2 ($SiCH_2$), 26.2 (3 × CH_2 Bu), 26.9 (3 × CH_2 Bu), 29.3 (CH_2, THF), 33.8 (CH_2, THF), 79.7 (CH, C-2 THF), 79.9 (CH, C-5 THF), 128.5 (2 × *m*-CH, Ph), 129.1 (2 × *o*-CH, Ph), 133.1 (*p*-CH, Ph), 135.5 (C, Ph), 198.2 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, ([M−^{n}Bu]$^+$ 36%), 289 (100), 199 (9), 171 (68), 143 (26), 105 (32), 77 (20); HRMS (CI$^+$, *m/z*) 389.2870 [M+H]$^+$, $C_{24}H_{41}O_2Si$ requires 389.2870. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.27 (ppm) and 5.12 (ppm) *trans* and *cis* respectively.

phenyl(5-((tributylsilyl)methyl)tetrahydrofuran-2-yl)methanone



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PROCNO                  1
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SOLVENT             CDCl3
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DS                      2
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FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   28.5
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
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PC                   1.00
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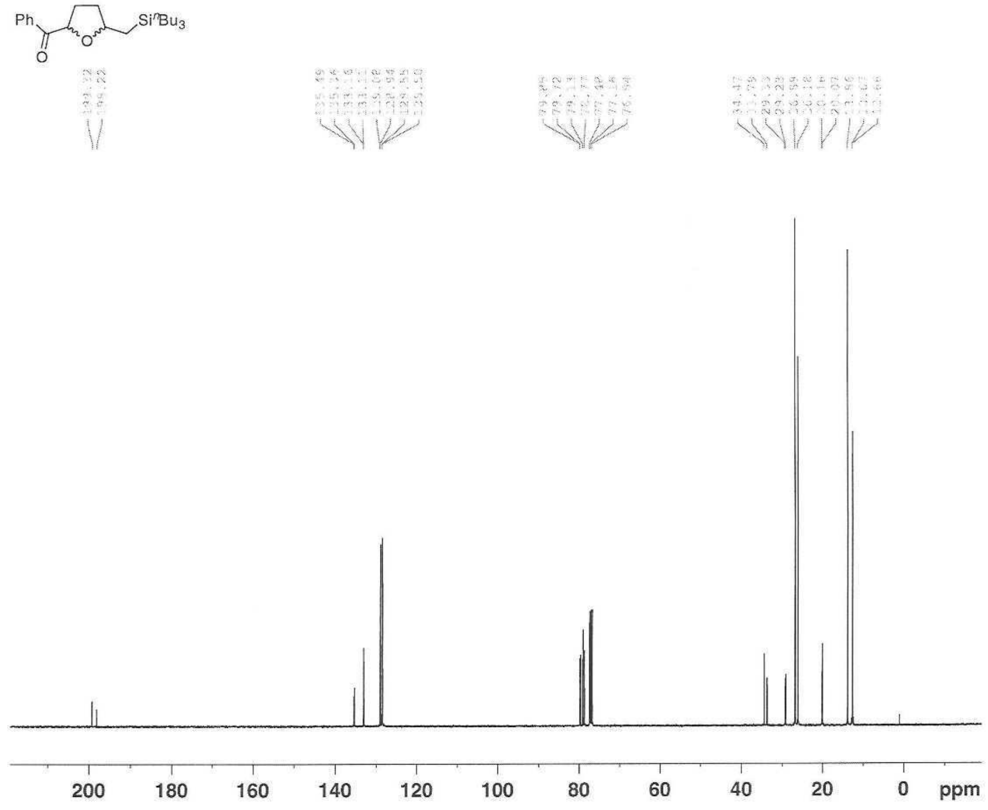
phenyl(5-((tributylsilyl)methyl)tetrahydrofuran-2-yl)methanone



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PROCNO                  1
Date_            20100130
Time                 3.50
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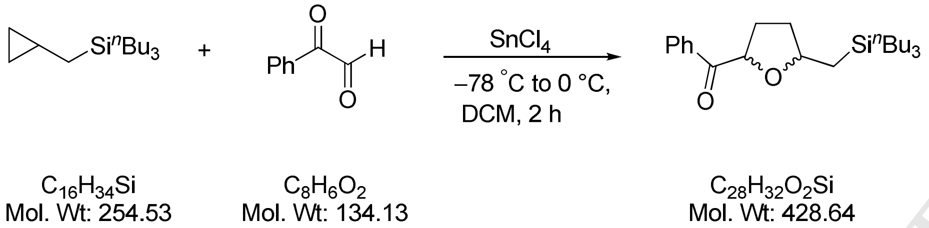
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379064 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

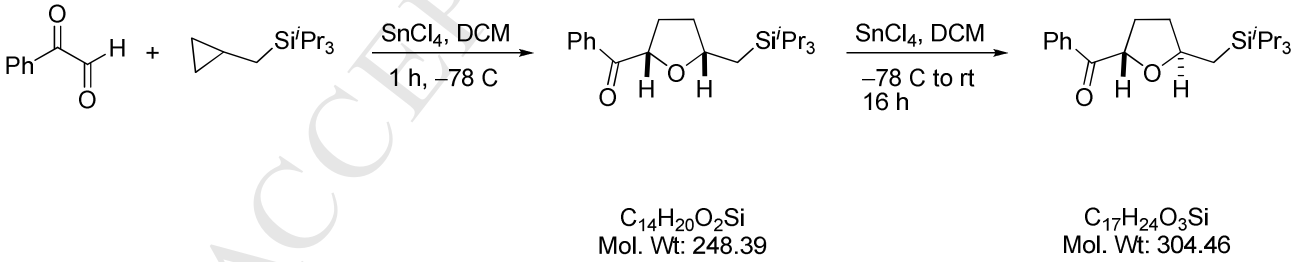
TABLE 5 ENTRY 20

(±)-Phenyl(2-((tri-*n*-butylsilyl)methyl)tetrahydrofuran-5-yl)methanone



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.9 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of (cyclopropylmethyl)tri-*n*-butylsilane (0.15 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 1 h the reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The reaction was quenched by the addition of H_2O (10 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.29 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : cyclohexane] afforded an inseparable mixture of diastereoisomers of the desired product (combined yield 0.08 g, 0.19 mmol, 31%, *dr* (*trans* : *cis*) 11 : 1) as a colourless oil. Data is in agreement with that previously recorded.

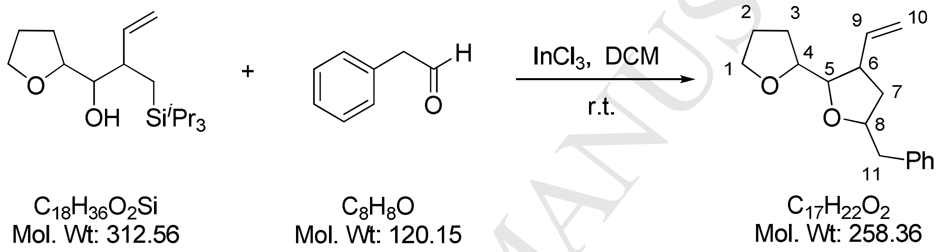
Interconversion of the *cis* diastereoisomer to the *trans* diastereoismer of (±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone



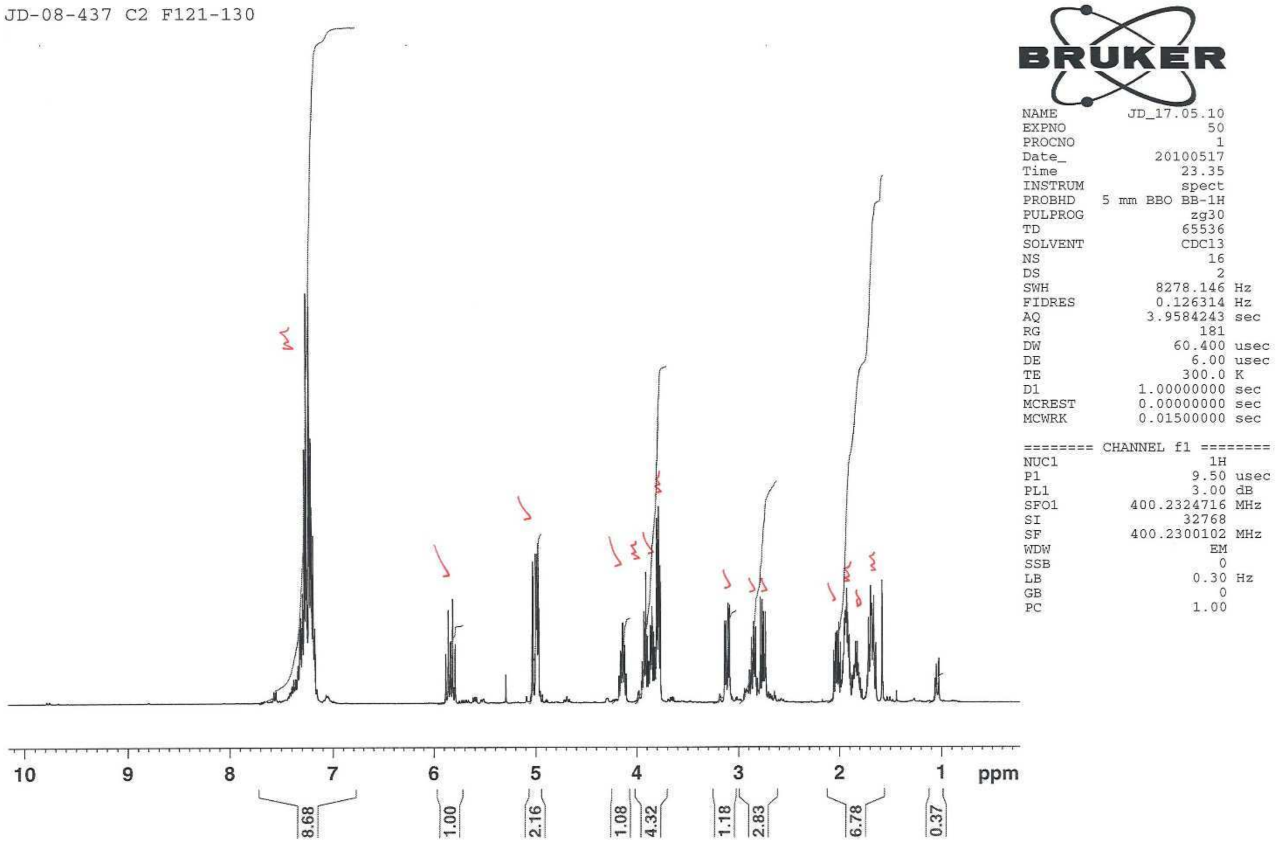
To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 1.5 mmol) and (Cyclopropylmethyl)triisopropylsilane (0.13 g, 0.60 mmol) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was stirred at −78 °C and monitored by TLC. After 1 h the reaction was quenched by the addition of acetone/water (5 : 1, 5 mL), allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether:hexane] afforded (±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (0.128 g, 0.37 mmol, 62%, *cis*/*trans* 2.4 : 1) .

To a stirred solution of (±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (0.128 g, 0.37 mmol, 62%, *cis*/*trans* 2.4 : 1) (obtained from the previous reaction) in anhydrous DCM (5 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.13 g, 0.06 mL, 0.50 mmol) in anhydrous DCM (2 mL). The reaction was allowed to warm to room temperature and after 16 h quenched by the addition of water (5 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded (±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (0.101 g, 0.29 mmol, 86%, *cis*/*trans* 0.04 : 1) .

5-benzyl-3-vinyloctahydro-2,2'-bifuran



To a solution of phenylacetaldehyde (70.0 mg, 0.60 mmol) in DCM (2 mL) was added in a single portion indium trichloride (45.0 mg, 0.20 mmol) and the resulting mixture was stirred for 1 h at room temperature. After this time a solution of 1-(tetrahydrofuran-2-yl)-2-((triisopropylsilyl)methyl)but-3-en-1-ol (35.0 mg, 0.11 mmol) in DCM (1 mL) was added and the reaction mixture stirred at room temperature for 16 h. The reaction was quenched by the addition of H_2O (5 mL) and the organic layer separated. The aqueous layer was extracted with DCM (3 × 10 mL) and the combined organic layers were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a colourless oil (0.10 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] followed by flash column chromatography [silica gel, gradient elution 100% DCM – 5% diethyl ether : DCM] afforded the desired product containing trace impurities (15.0 mg, 0.05 mmol, 40%) as a colourless oil; R_f 0.30 [20% diethylether : hexane]; ν_{max}(film)/cm^{-1} 3063, 2974, 2940, 2865, 1641, 1603, 1497, 1454, 1067, 1028, 947, 912; δ_H (600 MHz; $CDCl_3$); 1.65-1.72 (2H, m, overlapping signals C-3 and C-7), 1.79-186 (1H, m, C-2), 1.91-1.97 (2H, m, overlapping signals C-2 and C-3), 2.02 (1H, ddd, *J* 12.2 7.7 and 6.4, C-7), 2.76 (1H, dd, *J* 13.4 and 7.6, C-11 CH_2Ph), 2.82-2.88 (1H, m, C-6), 3.11 (1H, dd, *J* 13.4 and 5.6, C-11 CH_2Ph), 3.77-3.81 (2H, m, overlapping signals C-5 and C-1), 3.84-3.87 (1H, m, C-4), 3.92 (1H, dt, *J* 8.1 and 6.7, C-1), 4.14 (1H, dddd, *J* 8.6 7.6 6.4 and 5.6, CH C-8), 4.98-5.03 (2H, m, $CH=C\underline{H_2}$), 5.83 (1H, app dt, *J* 17.0 and 9.8 $C\underline{H}=CH_2$); δ_C (100.6 MHz; $CDCl_3$) 26.3 (CH_2, C-2), 28.2 (CH_2, C-3), 38.3 (CH_2, C-7), 42.5 (CH_2, C-11), 47.0 (CH, C-6), 68.8 (CH_2, C-1), 79.0 (CH, C-4), 80.4 (CH, C-8), 84.2 (CH, C-5), 115.7 (CH_2, C-10), 126.3 (CH, *p*-CH, Ar), 128.4 (2 × CH, *o*-CH Ar), 129.4 (2 × CH, *m*-CH Ar), 138.6 (CH, C-9), 139.0 (C, Ar); LRMS (EI$^+$, *m/z*): 258 (M$^+$, 3%), 167 ([M$^+$−Bn], 6), 123 (71), 117 (68), 104 (24), 91 (Bn, 100), 71 (THF, 34); HRMS (EI$^+$, *m/z*) 258.1614 [M]$^+$, $C_{17}H_{22}O_2$ requires 258.1614.



JD-08-437 C2 F121-130

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FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                      181
DW                   60.400 usec
DE                     6.00 usec
TE                    300.0 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

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PL1                    3.00 dB
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PC                     1.00
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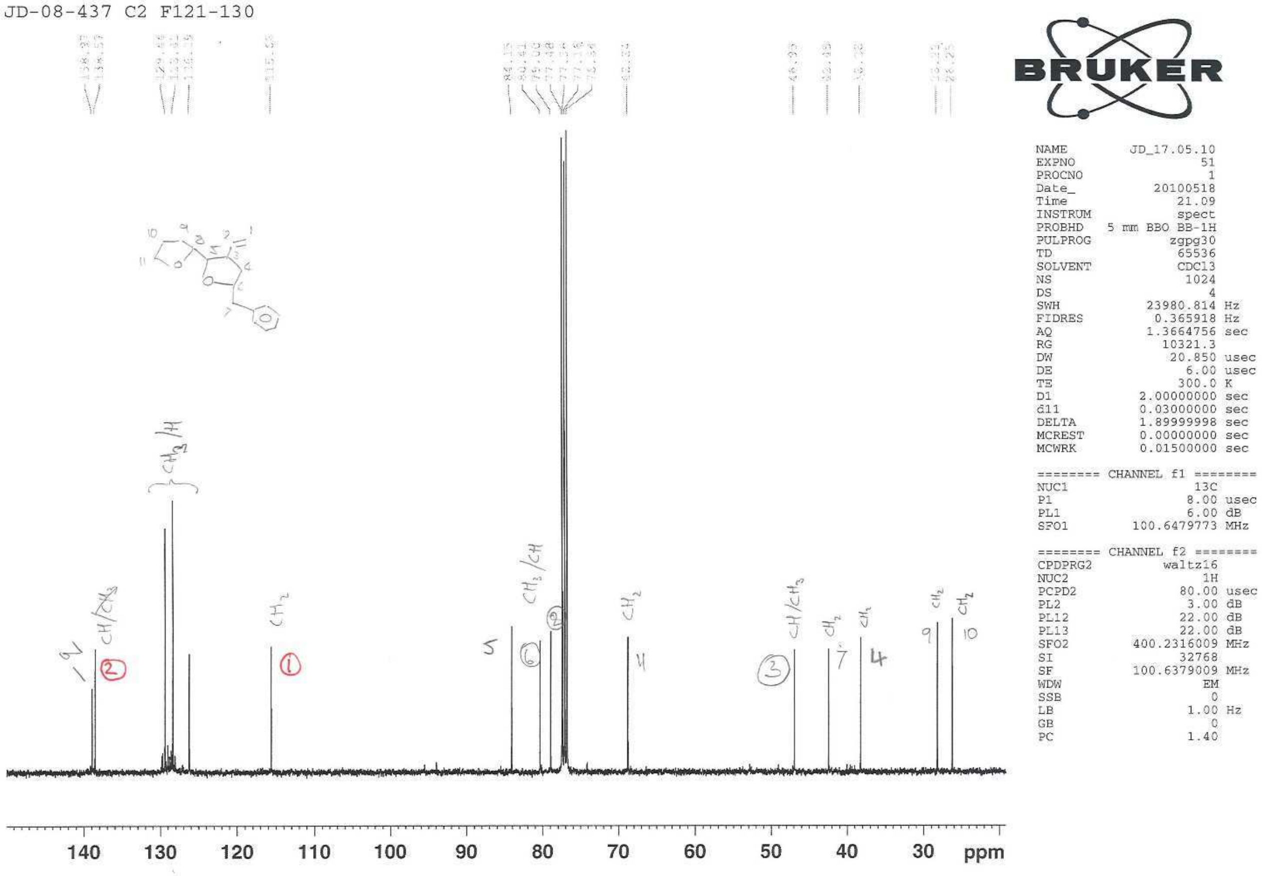

JD-08-437 C2 F121-130

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NS                     1024
DS                        4
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FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                  10321.3
DW                   20.850 usec
DE                     6.00 usec
TE                    300.0 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.00 usec
PL1                    6.00 dB
SFO1            100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    3.00 dB
PL12                  22.00 dB
PL13                  22.00 dB
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SSB                       0
LB                     1.00 Hz
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PC                     1.40
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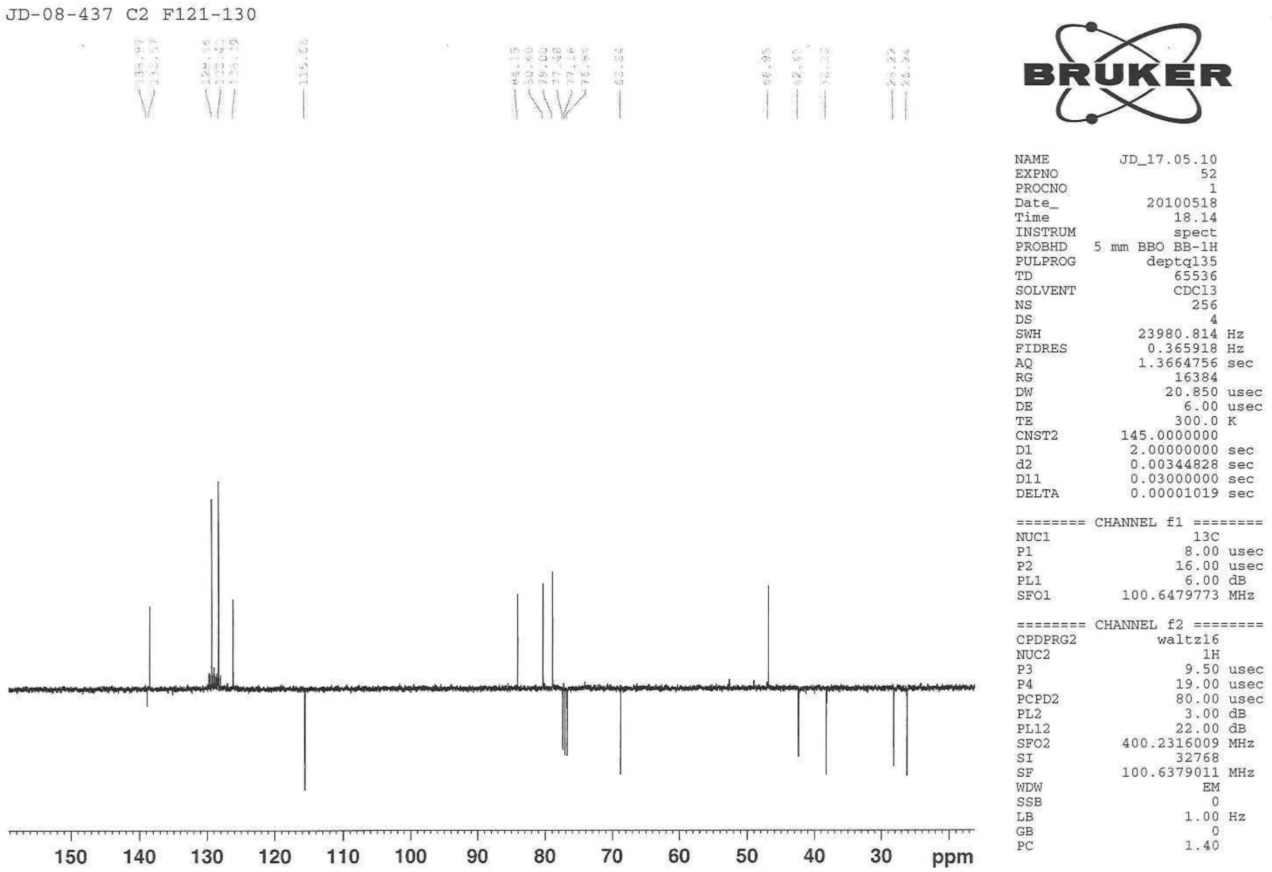
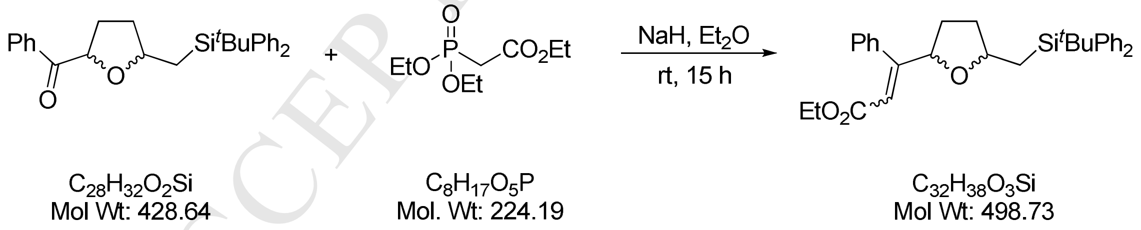


Ethyl 3-(2-((tert-butyldiphenylsilyl)methyl)tetrahydrofuran-3-yl)-3-phenylacrylate (16a)

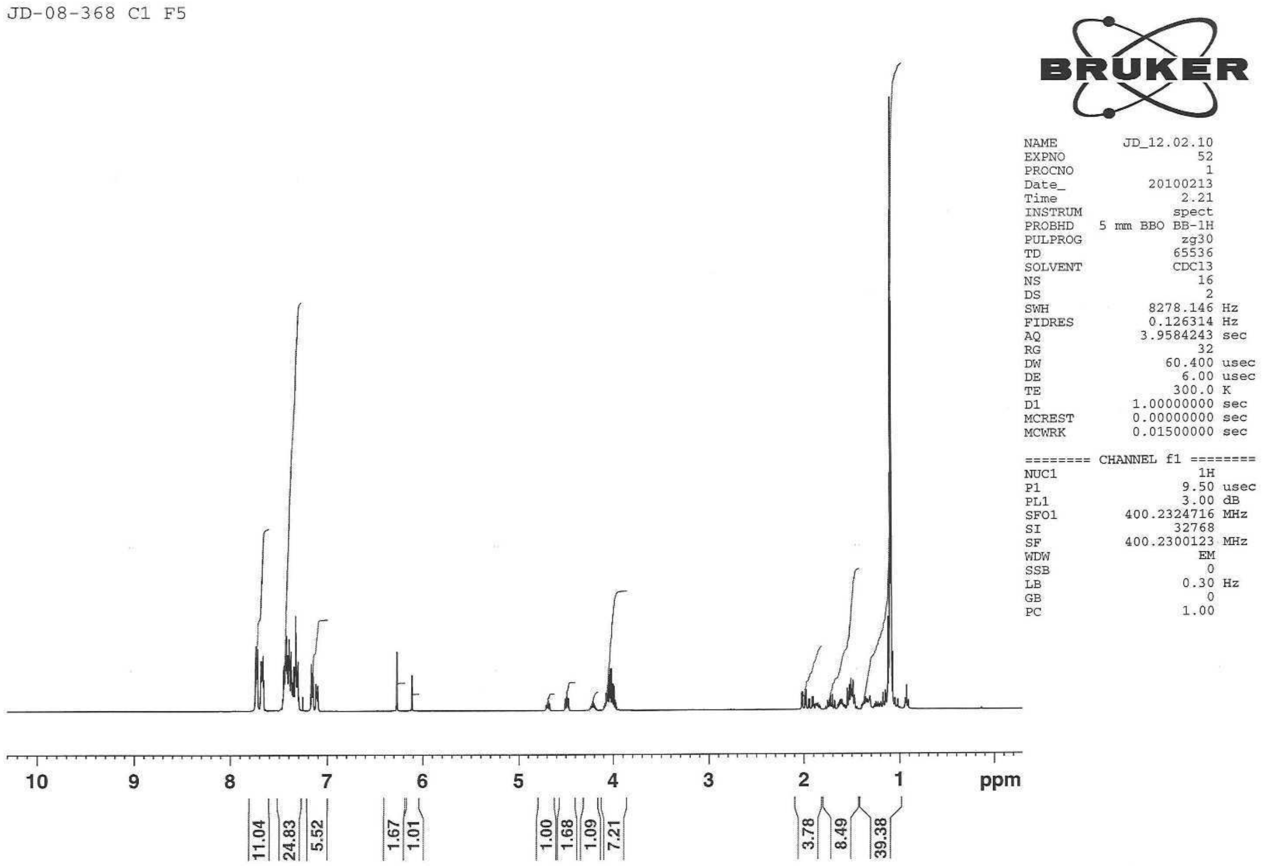


A 60% dispersion of sodium hydride in mineral oil (0.08 g, 2.00 mmol) was washed with petroleum ether (3 × 2 mL), dried under reduced pressure and placed under an atmosphere of argon. Diethyl ether (3 mL) was added and to the resulting suspension was added dropwise over 1 min a solution of triethyl phosphonoacetate (0.38 g, 0.34 mL, 1.70 mmol) in diethyl ether (3 mL) at −5 °C. The solution was allowed to warm to room temperature, stirred for a further 15 min followed by the dropwise addition of a solution of (5-((tert-butyldiphenylsilyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (0.73 g, 1.70 mmol, 1 : 2.1 mixture of *trans*/*cis* diastereoisomers) in diethyl ether (3 mL). The resulting yellow solution was stirred for 15 h at 25 °C and monitored by TLC. The reaction was quenched with water (10 mL) and the organic layer separated. The aqueous layer further extracted with diethyl ether (3 × 10 mL). The etherate fractions were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a cloudy colourless oil (0.92 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20%

diethyl ether : hexane] afforded two products both as inseparable mixtures of diastereoisomers of the desired compound (combined yield 0.74 g, 1.38 mmol, 87%, product ratio 1.6 : 1) as a colourless oils;

Product 1: (0.45 g, 0.90 mmol, 53%, *dr* 3 : 1), Colourless oil; R_f 0.38 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2931, 2856, 1712 (C=O), 1625, 1427, 1268, 1172 (C-O), 1105, 1027, 877, 820; Major diastereoisomer: δ_H (400 MHz; $CDCl_3$); 0.93-1.09 (10H, m, overlapping signals 3 × CH_3 and $C\underline{H}_aH_b$ C-3 THF), 1.17-1.60 (1H, m, overlapping signals $CH_a\underline{H}_b$ C-3 THF),1.26 (1H, dd, *J* 14.5 and 9.9, $SiC\underline{H}_aH_b$), 1.31 (3H, t, *J* 7.1 $OCH_2C\underline{H}_3$), 1.70 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.83 (1H, dd, *J* 14.4 and 4.1, $SiCH_a\underline{H}_b$), 2.17 (1H, app dq, *J* 12.7 and 8.5, $CH_a\underline{H}_b$ C-4 THF), 3.96-4.03 (1H, m, CH C-2 THF), 4.21 (2H, q, *J* 7.1, $OC\underline{H}_2CH_3$), 5.66 (1H, app t, *J* 7.7, CH, C-5 THF), 5.90 (1H, d, *J* 0.8, C=CH), 7.58-7.67 (4H, m, Ar), 7.31-7.49 (11H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.3 ($OCH_2\underline{C}H_3$), 17.6 ($SiCH_2$), 18.3 (3 × C, ^{t}Bu), 27.8 (3 × CH_3, ^{t}Bu), 32.3 (CH_2, C-4 THF), 33.5 (CH_2, C-3 THF), 60.2 ($O\underline{C}H_2CH_3$), 75.6 (CH, C-5 THF), 78.4 (CH, C-2 THF), 119.6 ($\underline{C}$H=C), 127.5 (CH, Ar), 127.6 (CH, Ar), 127.7 (CH, Ar), 128.2 (CH, Ar), 128.8 (CH, Ar), 129.2 (CH, Ar), 129.2 (CH, Ar), 134.0 (C, Ar), 134.8 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 139.2 (C, Ar), 160.4 ($\underline{C}$=CH), 165.9 (C=O); Minor diastereoisomer: δ_H (400 MHz; $CDCl_3$) 1.04 (9H, s, 3 × CH_3), 1.17-1.60 (4H, m, overlapping signals CH_2 C-3 THF and $C\underline{H}_aH_b$ C-4 THF and $SiC\underline{H}_aH_b$), 1.32 (3H, t, *J* 7.1, $OCH_2C\underline{H}_3$), 1.87 (1H, dd, *J* 14.4 and 4.1, $SiCH_a\underline{H}_b$), 2.30 (1H, app dtd, *J* 12.5 7.2 and 1.9, $CH_a\underline{H}_b$ C-4 THF), 3.81-3.88 (1H, m, CH C-2 THF), 4.20 (2H, q, *J* 7.1, $OC\underline{H}_2CH_3$), 5.81 (1H, d, *J* 1.0, C=CH), 5.91 (1H, app t, *J* 7.7, CH C-5 THF), 7.31-7.49 (11H, m, Ar), 7.58-7.67 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.3 ($OCH_2\underline{C}H_3$), 18.1 ($SiCH_2$), 18.3 (3 × C, ^{t}Bu), 27.8 (3 × CH_3, ^{t}Bu), 33.1 (CH_2, C-4 THF), 34.6 (CH_2, C-3 THF), 60.2 ($O\underline{C}H_2CH_3$), 75.8 (CH, C-5 THF), 78.4 (CH, C-2 THF), 119.3 ($\underline{C}$H=C), 127.6 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 128.0 (CH, Ar), 128.7 (CH, Ar), 129.1 (CH, Ar), 129.2 (CH, Ar), 134.0 (C, Ar), 134.8 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 139.1 (C, Ar), 161.9 (C=CH), 165.9 (C=O); LRMS (EI$^+$, *m/z*): 498 ([M]$^+$, 3%), 441(100), 199 (42), 181 (18), 135 (39), 105 (12); HRMS (ESP$^+$, *m/z*) 499.2656 [M+H]$^+$, $C_{32}H_{39}O_3Si$ requires 499.2663.

Product 2 : (0.29 g, 0.58 mmol, 34%, *dr* 1.7 : 1), Colourless oil; R_f 0.29 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2931, 2858, 1722 (C=O), 1648, 1427, 1223, 1155 (C-O), 1103, 1050, 819; Major diastereoisomer: δ_H (400 MHz; $CDCl_3$) 1.02-1.18 (13H, m, overlapping signals 3 × CH_3, $OCH_2C\underline{H}_3$ and $C\underline{H}_aH_b$ C-3 THF), 1.17-1.40 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 1.47-1.55 (1H, m, $SiC\underline{H}_aH_b$), 1.57-1.78 (2H, m, $C\underline{H}_aH_b$ C-4 THF), 2.00 (1H, dd, *J* 14.4 and 4.4, $SiCH_a\underline{H}_b$), 3.97-4.10 (3H, m, overlapping signals $OC\underline{H}_2CH_3$ and CH C-2 THF), 4.49 (1H, dd, *J* 6.0 and 1.5, CH C-5 THF), 6.27 (1H, d, *J* 1.5, C=CH),7.10-7.17 (2H, m, Ar), 7.30-7.46 (9H, m, Ar), 7.66-7.74 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.0 ($OCH_2\underline{C}H_3$), 18.0 ($SiCH_2$), 18.5 (3 × C, ^{t}Bu), 27.9 (3 × CH_3, ^{t}Bu), 31.5 (CH_2, C-4 THF), 32.7 (CH_2, C-3 THF), 59.8 ($O\underline{C}H_2CH_3$), 78.6 (CH, C-2 THF), 81.0 (CH, C-5 THF), 116.0 (C=$\underline{C}$H), 127.6 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 128.7 (CH, Ar), 127.8 (CH, Ar), 129.3 (CH, Ar), 129.3 (CH, Ar), 134.0 (C, Ar), 134.6 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 138.0 (C, Ar), 159.3 (C=CH), 166.4 (C=O); Minor diastereoisomer: 1.02-1.18 (12H, m, overlapping signals 3 × CH_3 and $OCH_2C\underline{H}_3$), 1.17-1.40 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.47-1.55 (3H, m, overlapping signals $C\underline{H}_aH_b$ C-4 THF, $CH_a\underline{H}_b$ C-3 THF and $SiC\underline{H}_aH_b$), 1.83-1.89 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 1.93 (1H, dd, *J* 14.5 and 4.7, $SiCH_a\underline{H}_b$), 3.97-4.10 (2H, m, $OC\underline{H}_2CH_3$ overlapping signals with other diastereomer), 4.22 (1H, app tt, *J* 9.1 and 4.6, CH C-2 THF), 4.69 (1H, app tt, *J* 7.8 and 1.4, CH C-5 THF), 6.11 (1H, d, *J* 1.5, C=CH), 7.10-7.17 (2H, m, Ar), 7.30-7.46 (9H, m, Ar), 7.66-7.74 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 14.0 ($OCH_2\underline{C}H_3$), 18.2 ($SiCH_2$), 18.5 (3 × C, ^{t}Bu), 27.9 (6 × CH_3, ^{t}Bu), 32.5 (CH_2, C-4 THF), 34.4 (CH_2, C-3 THF), 59.8 ($O\underline{C}H_2CH_3$), 78.2 (CH, C-2 THF), 81.1 (CH, C-5 THF), 114.9 (C=CH), 127.5 (CH, Ar), 127.6 (CH, Ar), 127.7 (CH, Ar), 127.7 (CH, Ar), 127.9 (CH, Ar), 129.1 (CH, Ar), 129.2 (CH, Ar), 134.0 (C, Ar), 134.8 (C, Ar), 136.1 (CH, Ar), 136.2 (CH, Ar), 137.8 (C, Ar), 159.6 ($\underline{C}$=CH), 166.3 (C=O); LRMS (EI$^+$, *m/z*): 498 ([M]$^+$, 3%), 441(100), 199 (42), 181 (18), 135 (39), 105 (12); HRMS (ESP$^+$, *m/z*) 516.2918 [M+NH]$^+$, $C_{32}H_{42}O_3NSi$ requires 516.2928.



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SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                     32
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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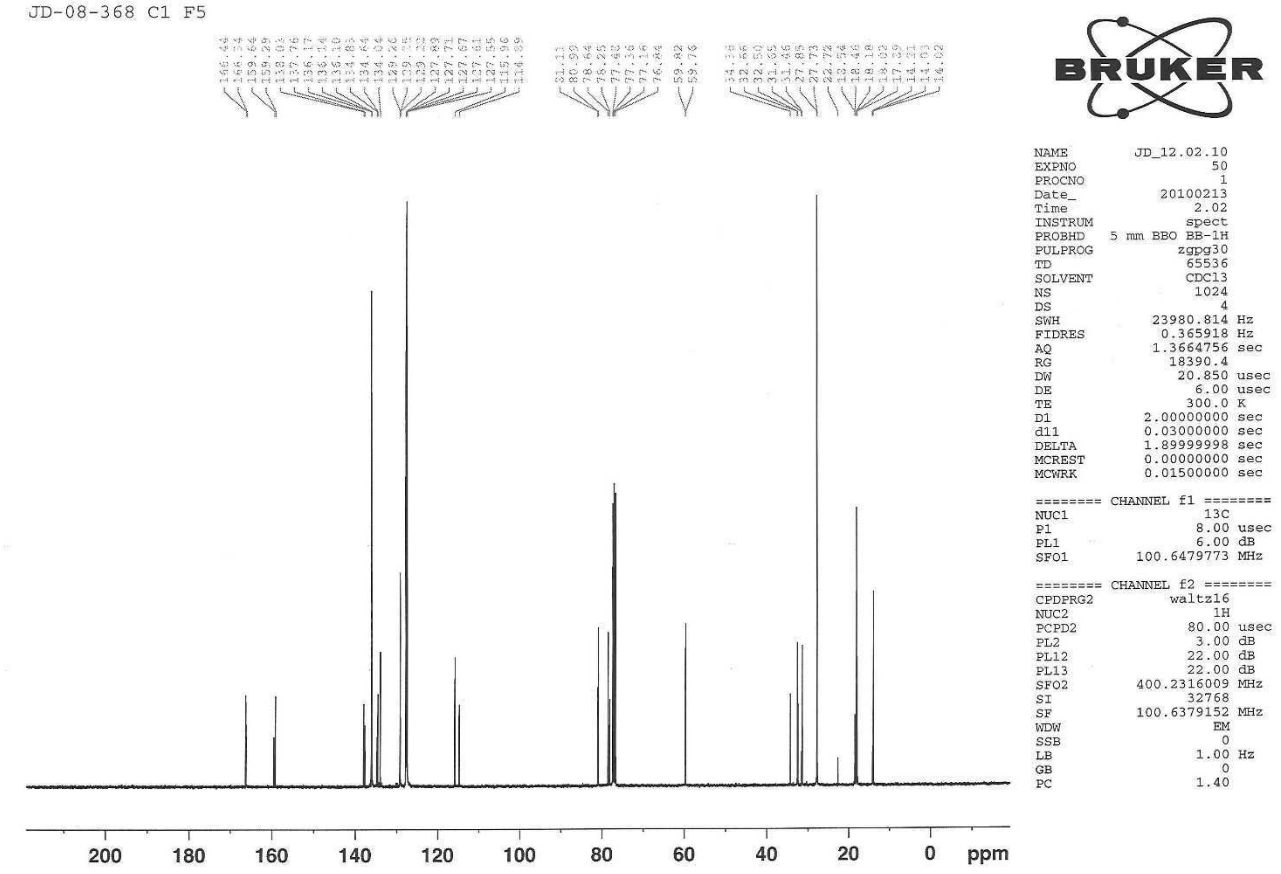

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TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ           1.3664756 sec
RG                 18390.4
DW              20.850 usec
DE                6.00 usec
TE                 300.0 K
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d11         0.03000000 sec
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MCREST      0.00000000 sec
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======== CHANNEL f1 ========
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PL1                6.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
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PCPD2            80.00 usec
PL2                3.00 dB
PL12              22.00 dB
PL13              22.00 dB
SFO2        400.2316009 MHz
SI                   32768
SF          100.6379152 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.40
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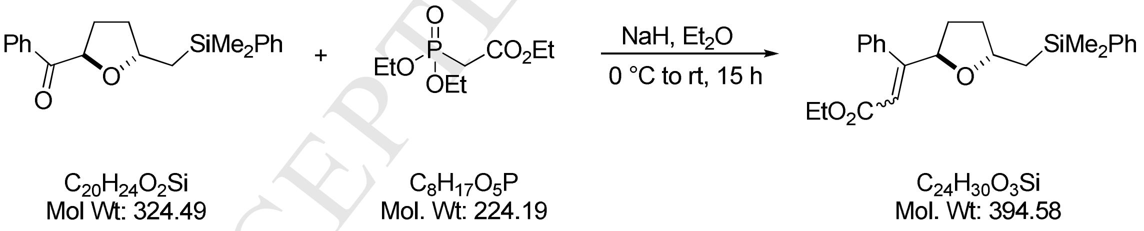
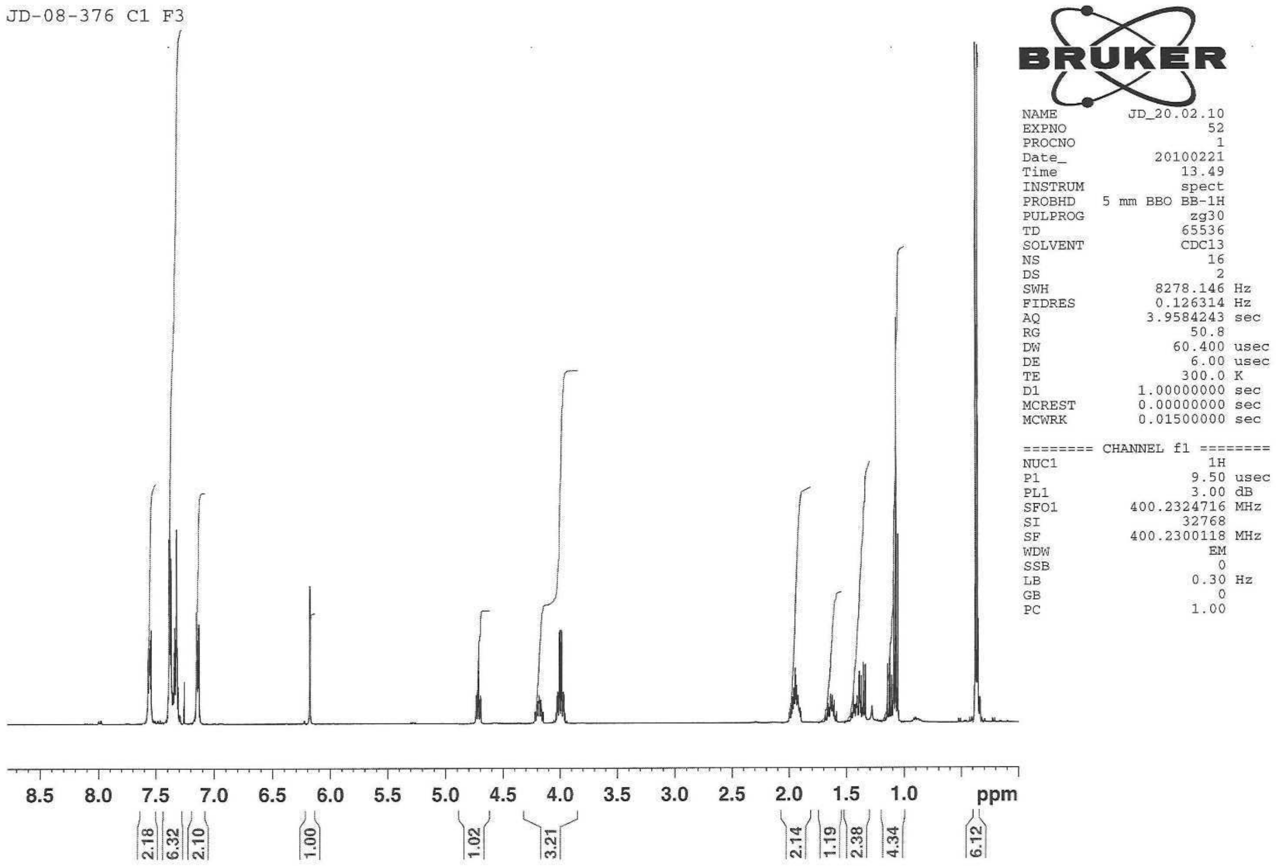
(±)-Ethyl 3-(2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)-3-phenylacrylate (16b)



A 60% dispersion of sodium hydride in mineral oil (0.02 g, 0.50 mmol) was washed with *n*-hexane (2 × 1 mL), dried under reduced pressure and placed under an atmosphere of argon. Diethyl ether (1 mL) was added and the suspension cooled to 0 °C followed by the dropwise addition of triethyl phosphonoacetate (0.10 g, 0.08 mL, 0.45 mmol). The solution was allowed to warm to room temperature, stirred for a further 15 min followed by the dropwise addition of a solution of (±-5-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (0.13 g, 0.40 mmol, only *trans* diastereoisomer) in diethyl ether (1.5 mL). The resulting yellow solution was stirred for 15 h at 25 °C and monitored by TLC. After this time, the reaction was quenched with water (10 mL) and the organic layer separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a colourless oil (0.18 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded two diastereoisomers of the title compound (combined yield 0.15 g, 0.38 mmol, 96%) as colourless oils:

Major diastereoisomer: (0.08 g, 0.20 mmol, 51%); R_f 0.29 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957 (C-H), 1724 (C=O), 16.26 (C=C), 1220 (Si-C), 1154 (C-O), 1095 (C-O), 823 (Si-C); δ_H (400 MHz; CDCl$_3$) 0.36 (3H, s, SiCH$_3$), 0.38 (3H, s, SiCH$_3$), 1.08 (3H, t, *J* 7.1, OCH$_2$C$\underline{H}_3$), 1.12 (1H, dd, *J* 14.2 and 7.8, SiC$\underline{H}_a$H$_b$), 1.37 (1H, dd, *J* 14.2 and 6.6, SiCH$_a\underline{H}_b$), 1.37-1.46 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.59-1.69 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 1.90-2.00 (2H, m, overlapping signals C-3 and C-4 THF), 4.00 (2H, qd, *J* 7.1 and 2.3, OC$\underline{H}_2$CH$_3$), 4.19 (1H, dtd, *J* 7.8 6.6 and 1.3, CH C-2 THF), 4.72 (1H, ddd, *J* 8.1, 6.9 and 1.4, CH C-5 THF), 6.18 (1H, d, *J* 1.5, C=C(H)CO$_2$Et), 7.13-7.17 (2H, m, Ar), 7.29-7.40 (6H, m, Ar), 7.53-7.58 (2H, m, Ar); δ_C (100.6 MHz; CDCl$_3$) −2.3 (SiCH$_3$), −1.9 (SiCH$_3$), 14.1 (OCH$_2\underline{C}$H$_3$), 24.0 (SiCH$_2$), 32.0 (CH$_2$, C-4 THF), 34.9 (CH$_2$, C-3 THF), 59.9 (O$\underline{C}$H$_2$CH$_3$), 78.3 (CH, C-2 THF), 81.3 (CH, C-5 THF), 115.0 (C=$\underline{C}$(H)CO$_2$Et), 127.6 (2 × *o*-CH, Ar), 127.8 (*p*-CH, Ar), 127.9 (2 × *m*-CH, Ar), 128.0 (2 × *m*-CH, Ar), 129.1 (*p*-CH, Ar), 133.7 (2 × *o*-CH, Ar), 137.9 (C, Ar), 139.1 (C, Ar), 159.8 ($\underline{C}$=C(H)CO$_2$Et), 166.5 (C=C(H)$\underline{C}$O$_2$Et); LRMS (EI$^+$, *m/z*): 394 (M$^+$, 6%), 349 ([M−OEt]$^+$, 4), 307 (6), 275 (5), 175 (11), 135 (100) 77 (5); HRMS (ESP, *m/z*) 412.2302 [M+NH$_4$]$^+$, C$_{24}$H$_{34}$O$_3$NSi requires 412.2302.

Minor diastereoisomer: (0.07 g, 0.18 mmol, 45%); R_f 0.49 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957 (C-H), 1711 (C=O), 1626 (C=C), 1267 (Si-C), 1169 (C-O), 1027 (C-O), 823 (Si-C); δ_H (400 MHz; CDCl$_3$) 0.24 (3H, s, SiCH$_3$), 0.26 (3H, s, SiCH$_3$), 1.05 (1H, dd, *J* 14.3 and 7.7, SiC$\underline{H}_a$H$_b$), 1.26 (1H, dd, *J* 14.3 and 6.5, SiCH$_a\underline{H}_b$), 1.30 (3H, t, *J* 7.1, OCH$_2$C$\underline{H}_3$), 1.44 (1H, dddd, *J* 11.6 10.9 8.9 and7.6, C$\underline{H}_a$H$_b$ C-3 THF), 1.70 (1H, dddd, *J* 12.3 10.9 9.1 and 7.5, C$\underline{H}_a$H$_b$ C-4 THF), 1.84 (1H, dddd, 11.6 7.5 5.3 and 2.0, CH$_a\underline{H}_b$ C-3 THF), 2.38 (1H, dtd, *J* 12.3 7.2 and 2.0, CH$_a\underline{H}_b$ C-4 THF), 3.80 (1H, dddd, *J* 8.9 7.7 6.5 and 5.4, CH C-2 THF), 4.18 (2H, q, *J* 7.1, OC$\underline{H}_2$CH$_3$), 5.86 (1H, dd, *J* 9.1 and 7.0, CH C-5 THF), 7.27-7.38 (8H, m, Ar), 7.45-7.47 (2H, m, *o*-CH SiPh); δ_C (100.6 MHz; CDCl$_3$) −2.4 (SiCH$_3$), −1.9 (SiCH$_3$), 14.4 (OCH$_2\underline{C}$H$_3$), 23.9 (SiCH$_2$), 33.0 (CH$_2$, C-4 THF), 35.3(CH$_2$, C-3 THF), 60.3 (O$\underline{C}$H$_2$CH$_3$), 76.3 (CH, C-5 THF), 78.1 (CH, C-2 THF), 119.4 (C=$\underline{C}$(H)CO$_2$Et), 127.8 (2 × *m*-CH, Ar), 127.8 (2 × *m*-CH, Ar), 128.1 (*p*-CH, Ar), 128.8 (2 × *o*-CH, Ar), 129.0 (*p*-CH, Ar), 133.7 (2 × *o*-CH, Ar), 139.3 (C Ar), 139.3 (C Ar), 161.9 ($\underline{C}$=C(H)CO$_2$Et), 166.1 (C=C(H)$\underline{C}$O$_2$Et); LRMS (EI$^+$, *m/z*): 394 (M$^+$, 6%), 349 ([M−OEt]$^+$, 4), 307 (6), 275 (5), 175 (11), 135 (100) 77 (5); HRMS (ESP, *m/z*) 395.2036 [M+H]$^+$, C$_{24}$H$_{31}$O$_3$Si requires 395.2037.



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TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                     50.8
DW                   60.400 usec
DE                     6.00 usec
TE                    300.0 K
D1               1.00000000 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                     9.50 usec
PL1                    3.00 dB
SFO1            400.2324716 MHz
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PC                     1.00
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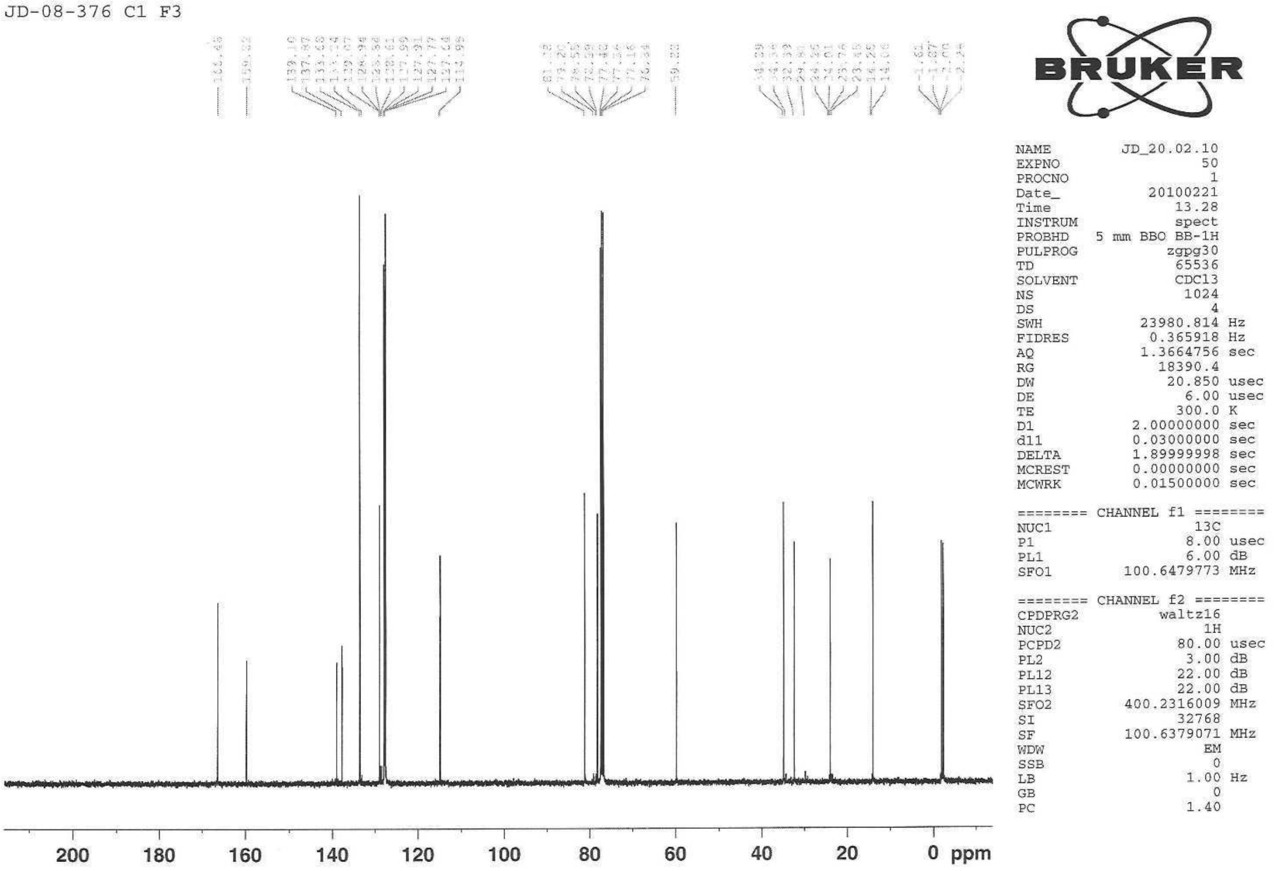

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TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379071 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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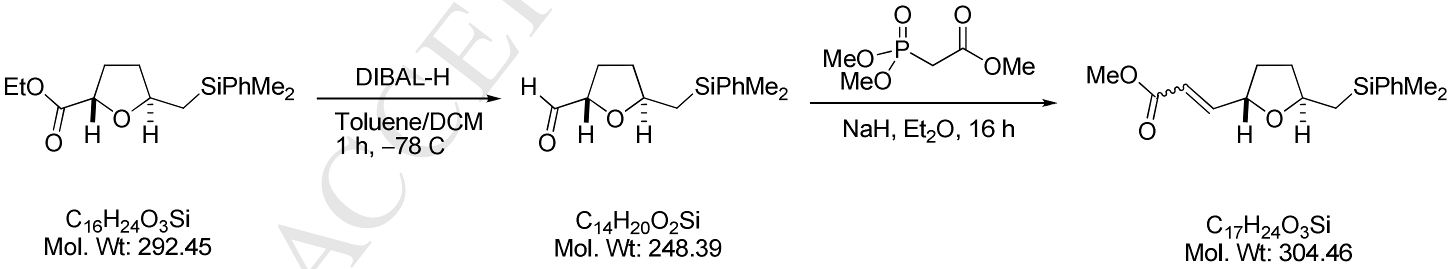
Methyl 3-(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)acrylate (19)

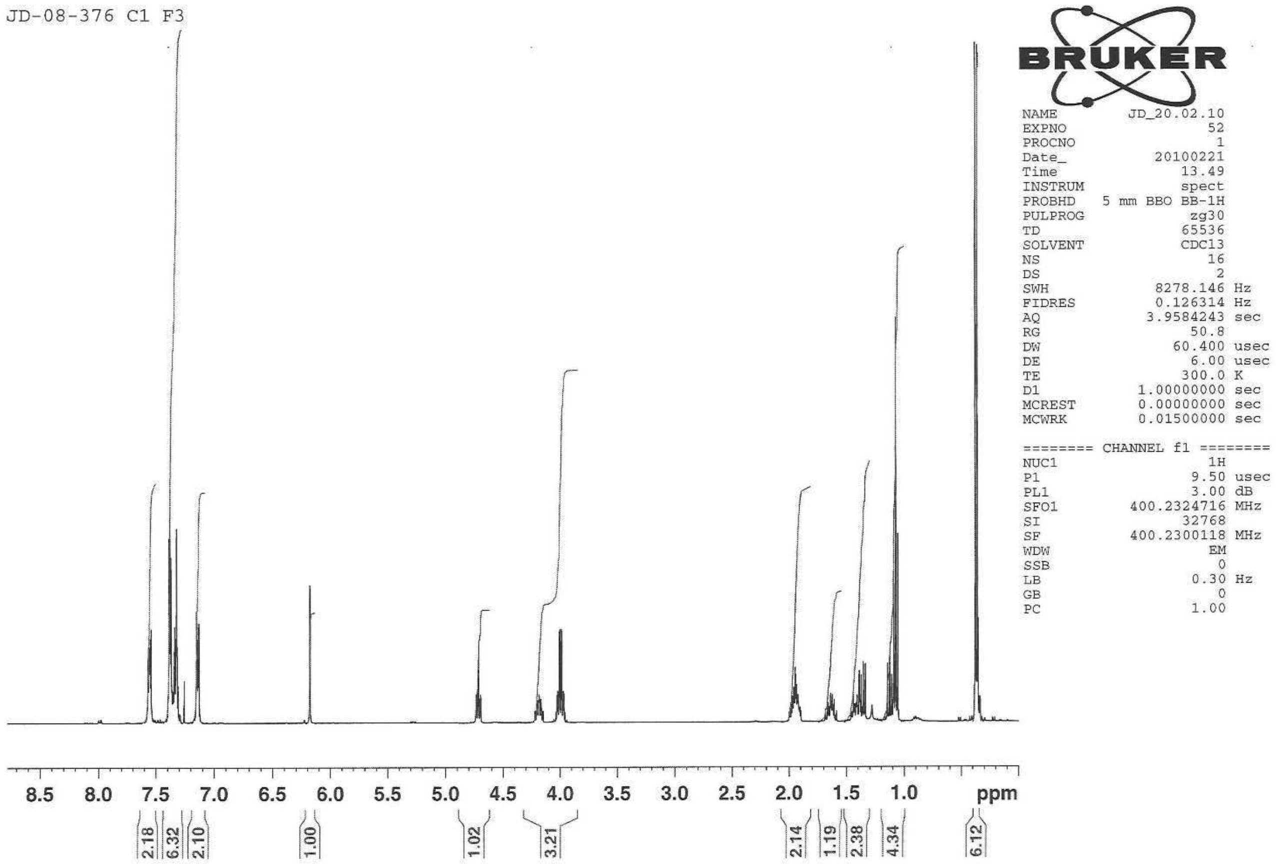


To a stirred solution of (±)-ethyl 2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carboxylate (0.38 g, 1.30 mmol) in anhydrous DCM (18 mL) under an atmosphenre of nitrogen was added a 1M solution of DIBAL-H (2.6 mL, 2.6 mmol) in toluene at -78 °C. The resulting solution was stirred at -78 C for 1 h and monitored by TLC. The reaction was quenched by adding sat. aq. NH_4Cl (10 mL) and allowed to walm to room temperature. Rochelle's salts (10 mL, sat. aq.) were added and the reaction stirred for 30 min at room temperature. The mixture was diluted with DCM (20 mL) and the organic phase separated. The aqueous phase was extracted with DCM (2 × 20 mL) and the combined organic phase was washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated under reduced pressure to give

2-(dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carbaldehyde as a colourless oil (0.25 g, 1.01 mmol, 78%); R_f 0.16 [20% diethyl ether : hexane]; δ_H (400 MHz; $CDCl_3$) 0.34 (s, $SiCH_3$), 0.36 (s, $SiCH_3$), 1.11 (1H, dd, *J* 14.2 and 8.1, $SiC\underline{H}_aH_b$), 1.21-1.46 (3H, m, $SiCH_a\underline{H}_b$ and CH_2 C-3 THF), 1.79-2.21 (2H, m, CH_2 C-4 THF), 4.04-4.11 (1H, m, CH C-2 THF), 4.25-4.30 (1H, m, CH C-5 THF), 7.33-7.38 (3H, m, Ar), 7.52-7.56 (2H, m, Ar), 9.61 (1H, d, *J* 1.7, CHO); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 23.4 ($SiCH_2$), 27.6 (CH_2, C-4 THF), 34.0 (CH_2, C-3 THF), 79.2 (CH, C-2 THF), 82.0 (CH, C-5 THF), 128.0 (2 × *m*-CH, SiPh), 129.2 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 138.8 (C, SiPh), 203.5 (CO); LRMS (EI^+, *m/z*): M^+ not visible, 233 ($[M−Me]^+$ 1%), 219 (19), 191 (9), 135 (100), 105 (11), 75 (15). The impure product was used immediately in the next reaction without further purification:

A 60% dispersion of sodium hydride in mineral oil (0.024 g, 1.00 mmol) was washed with *n*-hexane (2 × 1 mL), dried under reduced pressure and placed under an atmosphere of argon. Diethyl ether (3 mL) was added followed by the dropwise addition of a solution of trimethyl phosphonoacetate (0.20 g, 0.16 mL, 1.10 mmol) in anhydrous diethyl ether (5 mL). The solution was stirred at room temperature for further 15 min followed by the dropwise addition of a solution of 2-(dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-carbaldehyde (0.25 g, 1.01 mmol, only *trans* diastereoisomer) in anhydrous diethyl ether (4 mL). The resulting yellow solution was stirred for 16 h at 25 °C and monitored by TLC. After this time, the reaction was quenched with water (10 mL) and the organic layer separated. The aqueous layer was extracted with diethyl ether (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a yellow oil (0.26 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 15% diethyl ether : hexane] afforded the *cis* and *trans* diastereoisomers of the title compound (combined yield 0.164 g, 0.54 mmol, 53%) as colourless oils:

Trans diastereoisomer: (0.13 g, 0.43 mmol, 44%); R_f 0.35 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3069, 2957, 1722 (C=O), 1659 (C=C), 1261, 1164 (C-O), 1112 (C-O), 819 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.33 (3H, s, $SiCH_3$), 0.34 (3H, s, $SiCH_3$), 1.08 (1H, dd, *J* 14.2 and 7.9, $SiC\underline{H}_aH_b$), 1.32 (1H, dd, *J* 14.2 and 6.5, $SiCH_a\underline{H}_b$), 1.39-1.49 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.59-1.68 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.93-2.00 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.16 (1H, dtd, *J* 12.1 7.6 and 3.4, $CH_a\underline{H}_b$ C-4 THF), 3.73 (3H, s, OCH_3), 4.08-4.15 (1H, m, CH C-2 THF), 4.57 (1H, app tdd, *J* 7.2 4.9 and 1.4, CH C-5 THF), 5.99 (1H, dd, *J* 15.6 and 1.4, $HC=C(\underline{H})CO_2Me$), 6.89 (1H, dd, *J* 15.6 and 4.9, $\underline{H}C=C(H)CO_2Me$), 7.34-7.36 (3H, m, SiPh), 7.51-7.54 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −1.9 ($SiCH_3$), 23.9 ($SiCH_2$), 32.5 (CH_2, C-4 THF), 34.8 (CH_2, C-3 THF), 51.6 (OCH_3), 76.7 (CH, C-5 THF), 77.7 (CH, C-2 THF), 119.2 ($HC=\underline{C}(H)CO_2Me$), 127.9 (2 × *m*-CH, SiPh), 129.1 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.1 (C, SiPh), 149.6 ($H\underline{C}=C(H)CO_2Me$), 167.2 ($HC=C(H)\underline{C}O_2Me$); LRMS ($EI^+$, *m/z*): M^+ not visible, 289 ($[M-Me]^+$, 22%), 227 (26), 185 (32), 151 (37), 135 (100), 121 (17); HRMS (ESP, *m/z*) 327.1381 $[M+Na]^+$, $C_{17}H_{24}O_3Si$ requires 327.1387.



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SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   50.8
DW                 60.400 usec
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TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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P1                   9.50 usec
PL1                  3.00 dB
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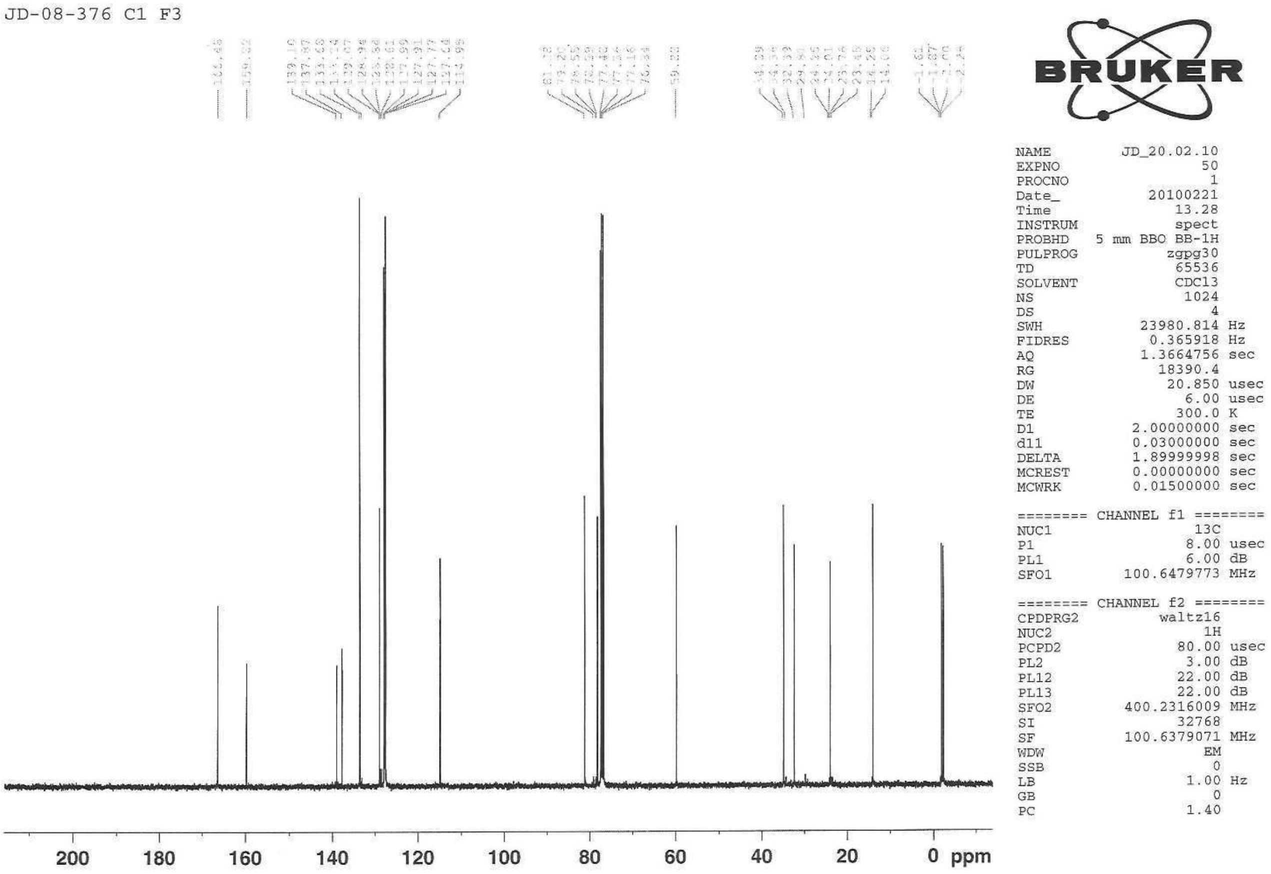

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TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
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SI                  32768
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LB                   1.00 Hz
GB                      0
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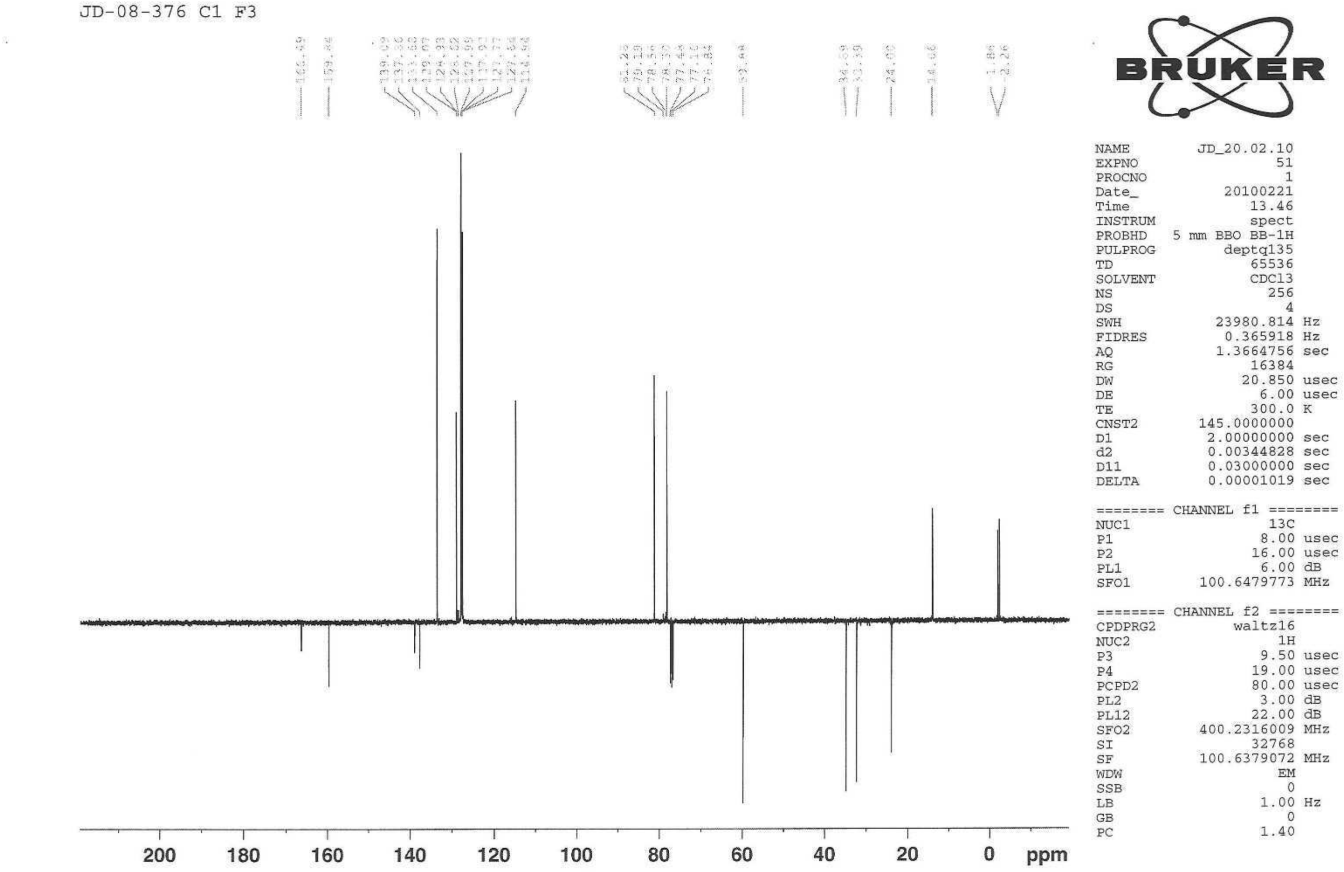

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TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
D11           0.03000000 sec
DELTA         0.00001019 sec

======== CHANNEL f1 ========
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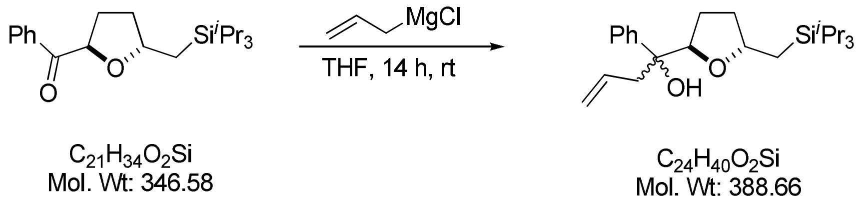
P1                  8.00 usec
P2                 16.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  9.50 usec
P4                 19.00 usec
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379072 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Cis diastereoisomer: (0.034 g, 0.11 mmol, 11%); R_f 0.48 [20% diethyl ether : hexane]; v_{max}(film)/cm^{-1} 3069, 2952, 1720 (C=O), 1646 (C=C), 1176 (C-O), 1112, 1025 (C-O), 818 (Si-C); δ_H (400 MHz; $CDCl_3$) 0.32 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.09 (1H, dd, *J* 14.3 and 8.6, $SiC\underline{H}_aH_b$), 1.34 (1H, dd, *J* 14.3 and 6.0, $SiCH_a\underline{H}_b$), 1.37-159 (2H, m, overlapping signals $C\underline{H}_aH_b$ C-3 THF and $C\underline{H}_aH_b$ C-4 THF), 1.90-1.97 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.37 (1H, dtd, *J* 12.2 7.3 and 2.4, $CH_a\underline{H}_b$ C-4 THF), 3.70 (3H, s, OCH_3), 4.01 (1H, tt, *J* 8.5 and 5.7, CH C-2 THF), 5.39 (1H, app q, *J* 7.4, CH C-5 THF), 5.73 (1H, dd, *J* 11.6 and 1.3, $HC=C(\underline{H})CO_2Me$), 6.27 (1H, dd, *J* 11.6 and 7.4, $\underline{H}C=C(H)CO_2Me$), 7.34-7.36 (3H, m, SiPh), 7.51-7.54 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −1.9 ($SiCH_3$), 23.7 ($SiCH_2$), 33.2 (CH_2, C-4 THF), 34.9 (CH_2, C-3 THF), 51.4 (OCH_3), 74.9 (CH, C-5 THF), 77.6 (CH, C-2 THF), 118.3 ($HC=\underline{C}(H)CO_2Me$), 127.9 (2 × *m*-CH, SiPh), 129.1 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.2 (C, SiPh), 152.9 ($H\underline{C}=C(H)CO_2Me$), 166.5 ($HC=C(H)\underline{C}O_2Me$); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 289 ([M-Me]$^+$, 22%), 227 (26), 185 (32), 151 (37), 135 (100), 121 (17); HRMS (ESP, *m/z*) 327.1382 [M+Na]$^+$, $C_{17}H_{24}O_3Si$ requires 327.1387.

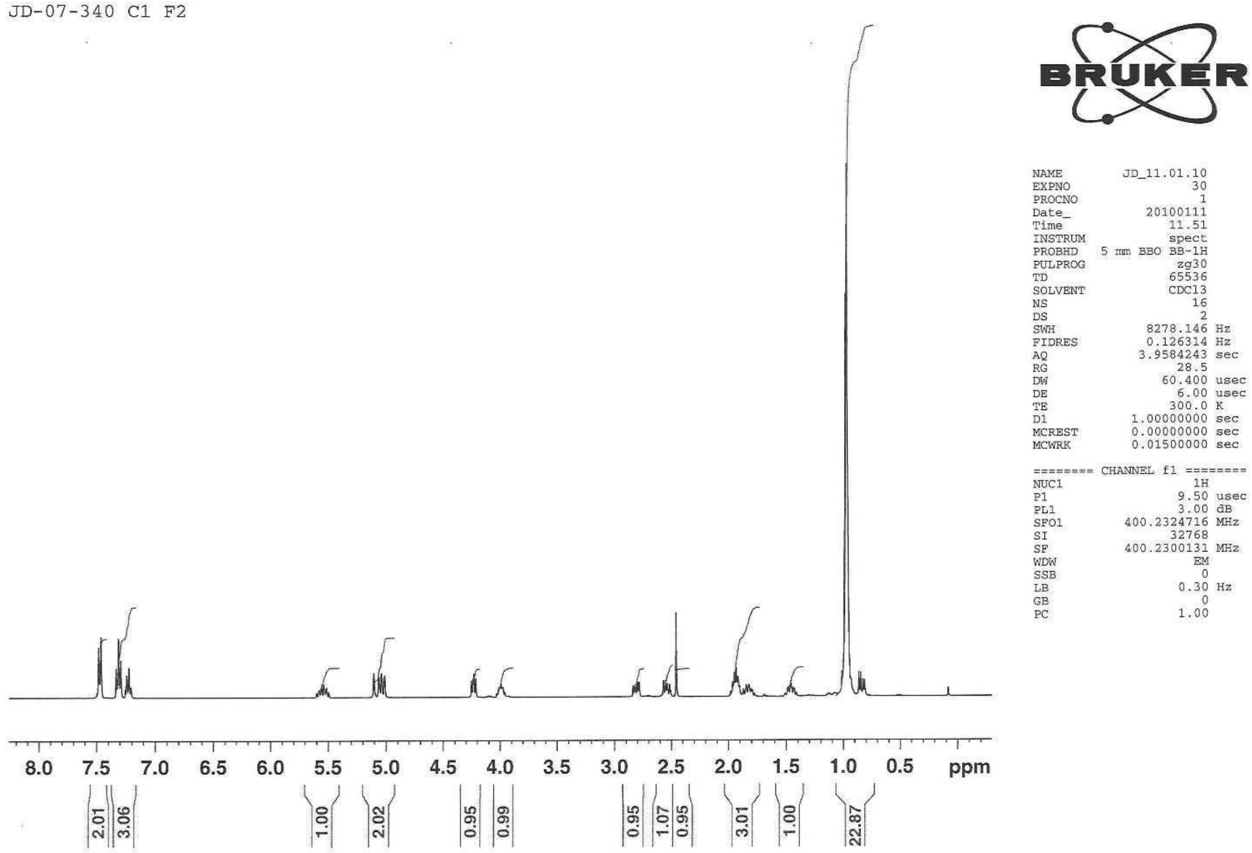
(±)-1-Phenyl-1-(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)but-3-en-1-ol (20)



To a stirred solution of phenyl(5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)methanone (0.18 g, 0.52 mmol) in THF (3.5 mL) at 0 °C was added a solution of allylmagnesium chloride (2 M solution in THF, 0.32 mL, 0.64 mmol). The mixture was stirred at 0 °C for 1 h then warmed to room temperature and stirred for a further 14 h. The mixture was cooled to 0 °C, quenched with 10% *w*/*v* aqueous ammonium chloride solution (10 mL), warmed to room temperature and partioned between H_2O and diethyl ether. The organic phase was separated and the aqueous phase extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.22 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] afforded two diastereoisomers of the title compound (combined yield 0.17 g, 0.44 mmol, 85%) as colourless oils:

Major diastereoisomer: (0.12 g, 0.31 mmol, 60%); R_f 0.54 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3556 (O-H), 2941, 2864, 1640 (C=C), 1463, 1446, 1183, 1066, 881; δ_H (400 MHz; $CDCl_3$) 0.85 (1H, dd, *J* 14.4 and 6.3, $\mathrm{SiC\underline{H}_aH_b}$), 0.94-1.02 (22H, m, overlapping signals $\mathrm{{}^i\underline{Pr}_3SiCH_a\underline{H}_b}$), 1.41-1.51 (1H, m, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 1.78-1.88 (1H, m, $\mathrm{C\underline{H}_aH_b}$ C-4 THF), 1.90-1.99 (2H, m, overlapping signals $\mathrm{CH_a\underline{H}_b}$ C-3 and $\mathrm{CH_a\underline{H}_b}$ C-4 THF), 2.46 (1H, s, OH), 2.54 (1H, dd, *J* 13.9 and 8.0, $\mathrm{C\underline{H}_aH_bCH{=}CH_2}$), 2.81 (1H, dd, *J* 13.9 and 6.5 $\mathrm{CH_a\underline{H}_bCH{=}CH_2}$), 3.96-4.03 (1H, m, CH C-2 THF), 4.24 (1H, dd, *J* 8.9 and 6.0, CH C-5 THF), 5.03 (1H, dd, *J* 10.2 and 1.0, $\mathrm{CH{=}CH_{\mathit{trans}}\underline{H}_{\mathit{cis}}}$), 5.08 (1H, br d, *J* 17.2, $\mathrm{CH{=}C\underline{H}_{\mathit{trans}}H_{\mathit{cis}}}$), 5.55 (1H, dddd, *J* 17.2 10.1 7.8 and 6.6, $\mathrm{C\underline{H}{=}CH_{\mathit{trans}}H_{\mathit{cis}}}$), 7.23 (1H, br t, *J* 7.0, *p*-CH Ph), 7.32 (2H, br t, *J* 7.5, 2 × *m*-CH Ph), 7.48 (2H, br d, *J* 8.0, 2 × *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^{i}Pr$_3$), 17.5 ($SiCH_2$), 18.9 (3 × CH_3 Si^{i}Pr$_3$), 18.9 (3 × CH_3 Si^{i}Pr$_3$), 27.6 (CH_2, C-4 THF), 36.3 (CH_2, C-3 THF), 43.3 ($\mathrm{\underline{C}H_2CH{=}CH_2}$), 76.9 (COH), 78.3 (CH, C-2 THF), 84.4 (CH, C-5 THF), 118.9 ($\mathrm{CH{=}C\underline{H}_2}$), 126.3 (2 × *o*-CH, Ph), 126.7 (*p*-CH, Ph), 127.8 (2 × *m*-CH, Ph), 133.5 ($\mathrm{C\underline{H}{=}CH_2}$), 143.9 (C, Ph); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 345 ([M−^{i}Pr]$^+$, 27%), 303 (25), 261 (13), 241 (31), 157 (100), 131 (80), 115 (58), 105 (63), 103 (70), 87 (27), 75 (43); HRMS (ESP, *m/z*) 406.3131 [M+NH$_4$]$^+$, $C_{24}H_{44}O_2NSi$ requires 406.3136.

Minor diastereoisomer: (0.05 g, 0.13 mmol, 25%); R_f 0.68 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3560 (O-H), 2941, 2864, 1640 (C=C), 1463, 1447, 1179, 1066, 881; δ_H (400 MHz; $CDCl_3$) 0.93 (1H, dd, *J* 14.4 and 6.3, $\mathrm{SiC\underline{H}_aH_b}$), 1.05-1.13 (22H, m, overlapping signals $\mathrm{{}^i\underline{Pr}_3SiCH_a\underline{H}_b}$), 1.35-1.48 (2H, m, C-3/4 THF), 1.63-1.73 (2H, m, C-3/4 THF), 1.93-2.03 (1H, m, C-3/4 THF), 2.41 (1H, s, OH), 2.69 (1H, dd, *J* 14.3 and 6.6, $\mathrm{C\underline{H}_aH_bCH{=}CH_2}$), 2.81 (1H, dd, *J* 14.3 and 7.8 $\mathrm{CH_a\underline{H}_bCH{=}CH_2}$), 4.21-4.28 (2H, m, overlapping signals CH C-2 THF and CH C-5 THF), 4.95-5.04 (2H, m, overlapping signals $\mathrm{CH{=}C\underline{H}_{\mathit{trans}}\underline{H}_{\mathit{cis}}}$), 5.58 (1H, dddd, *J* 17.0 10.2 7.8 and 6.6, $\mathrm{C\underline{H}{=}CH_{\mathit{trans}}H_{\mathit{cis}}}$), 7.22 (1H, br t, *J* 7.2, *p*-CH Ph), 7.32 (2H, br dd, *J* 8.1 and 7.2, 2 × *m*-CH Ph), 7.38 (2H, br d, *J* 8.1, 2 × *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH Si^{i}Pr$_3$), 17.6 ($SiCH_2$), 19.0 (6 × CH_3 Si^{i}Pr$_3$), 27.7 (CH_2, THF), 36.4 (CH_2, THF), 45.8 ($\mathrm{\underline{C}H_2CH{=}CH_2}$), 76.7 (COH), 79.8 (CH, C-2 THF), 84.4 (CH, C-5 THF), 118.1 ($\mathrm{CH{=}C\underline{H}_2}$), 125.3 (2 × *o*-CH, Ph), 126.6 (*p*-CH, Ph), 128.1 (2 × *m*-CH, Ph), 134.1 ($\mathrm{C\underline{H}{=}CH_2}$), 142.8 (C, Ph); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 345 ([M−^{i}Pr]$^+$, 20%), 303 (28), 261 (35), 241 (26), 157 (100), 131 (89), 115 (78), 105 (85), 103 (91), 75 (68); HRMS (ESP, *m/z*) 406.3130 [M+NH$_4$]$^+$, $C_{24}H_{44}O_2NSi$ requires 406.3136.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FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 28.5
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
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SI 32768
SF 400.2300131 MHz
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LB 0.30 Hz
GB 0
PC 1.00
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7.5
7.0
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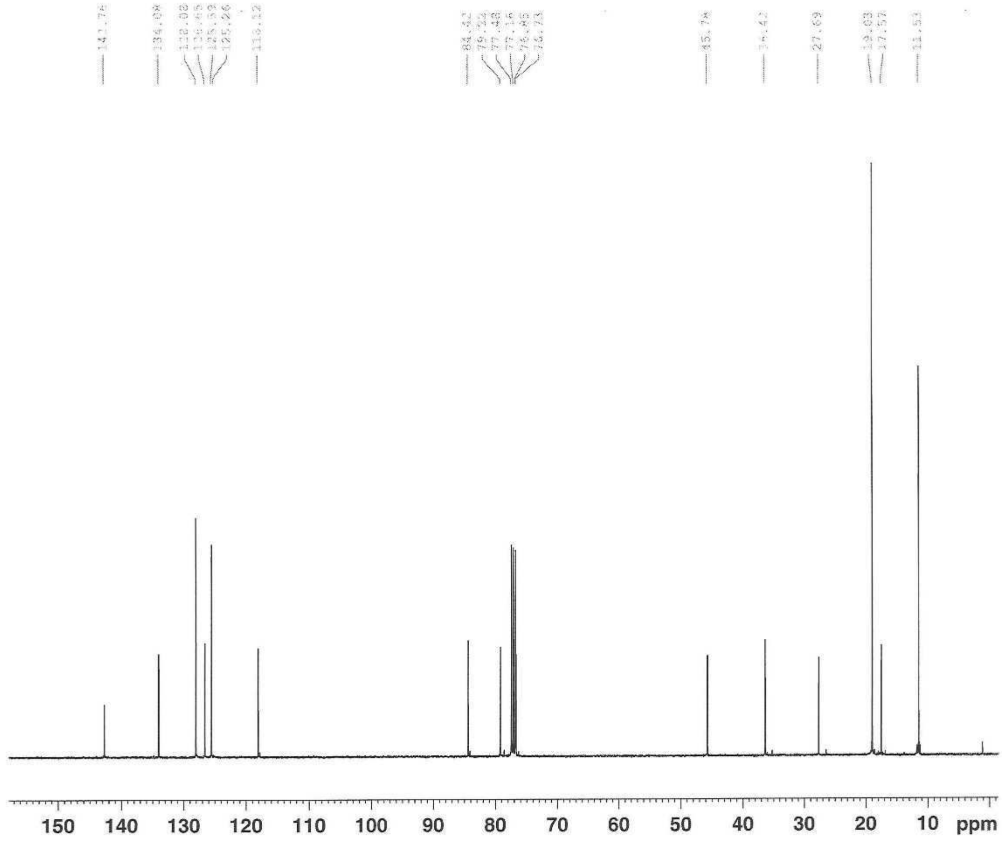
JD-07-340 C1 F1



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SOLVENT              CDCl3
NS                    1024
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SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                  9195.2
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
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DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

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======== CHANNEL f2 ========
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NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379035 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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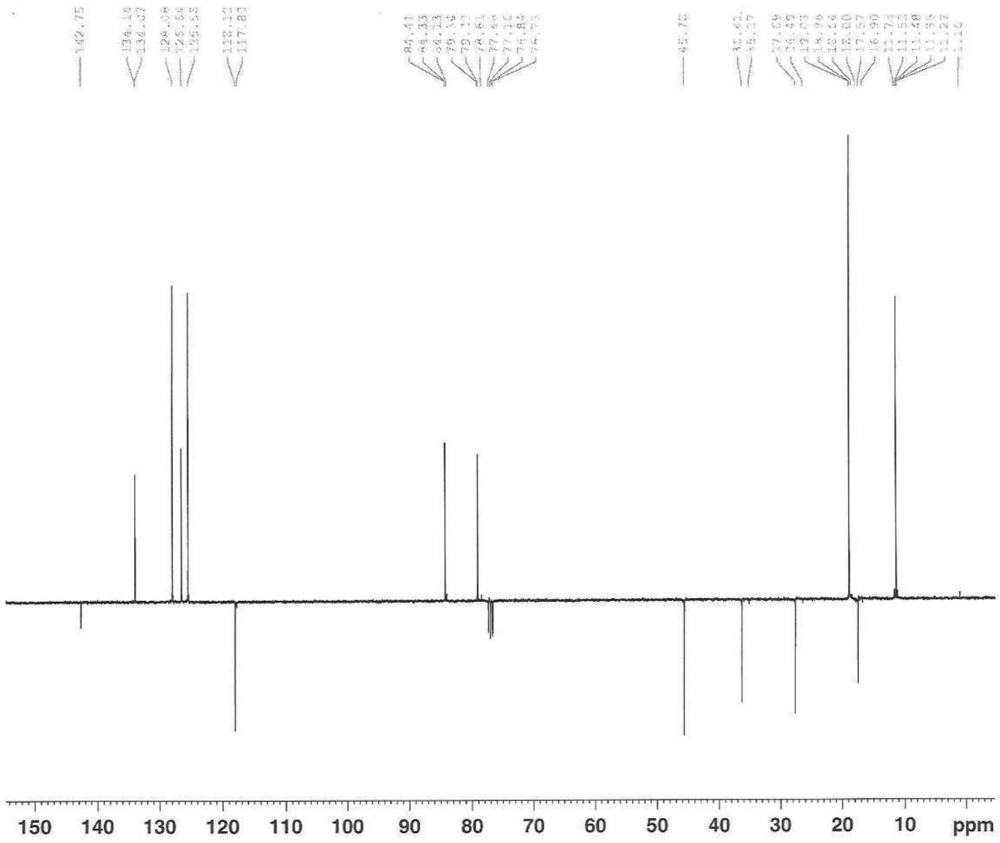
JD-07-340 C1 F1



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TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
D11             0.03000000 sec
DELTA           0.00001019 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
P2                   16.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                    1H
P3                    9.50 usec
P4                   19.00 usec
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379040 MHz
WDW                     EM
SSB                      0
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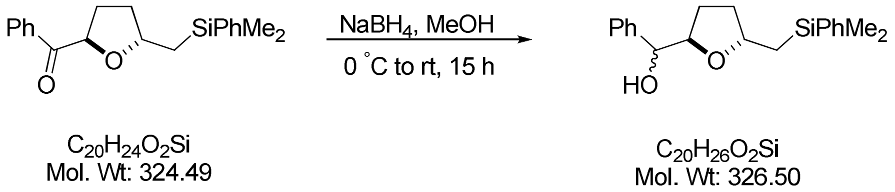
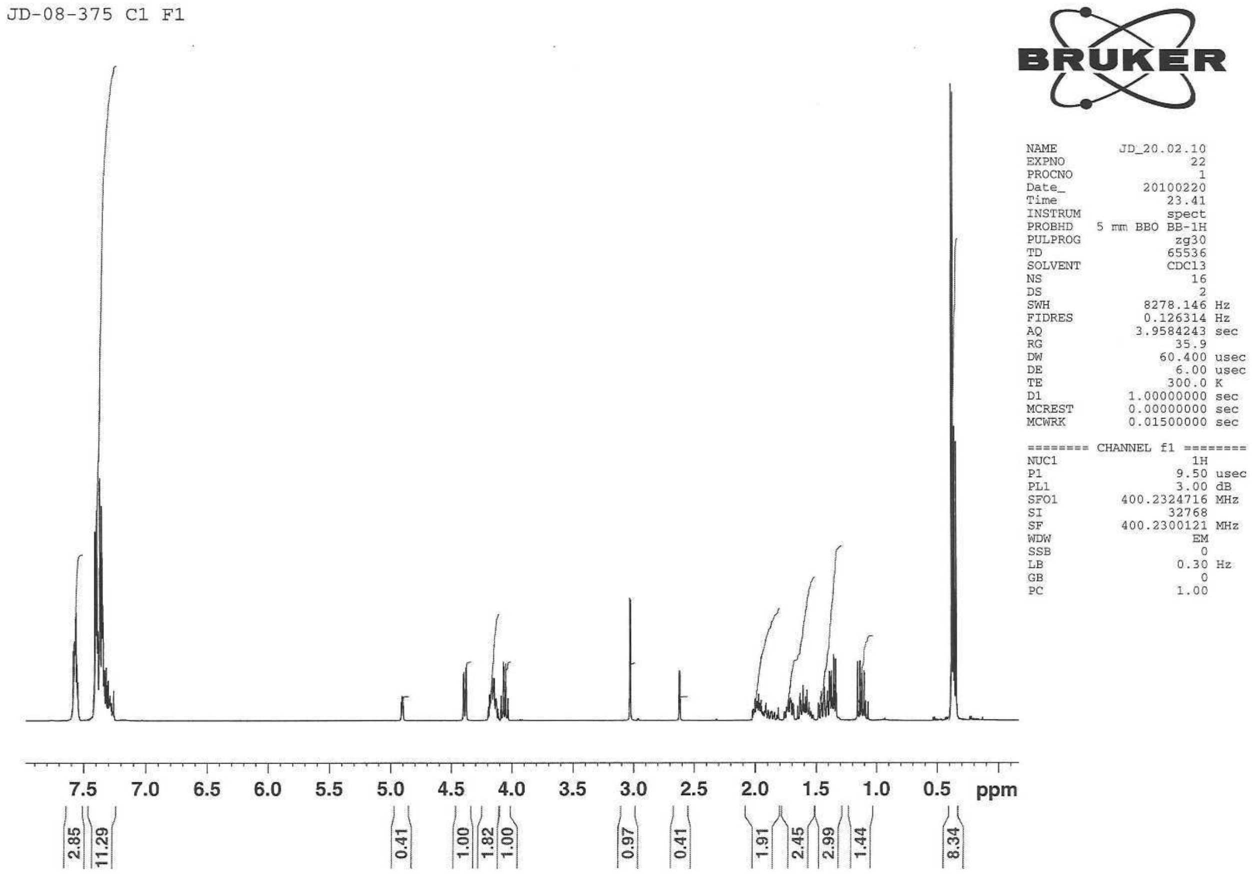
(±)-(2-((Dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanol (21a)



The following procedure was carried out on a range of scales from 0.2 mmol to 2 mmol: To a stirred solution of 2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanone (0.13 g, 0.40 mmol) in HPLC grade methanol (3.0 mL) at 0 °C was added in one portion $NaBH_4$ (0.02 g, 0.52 mmol). The mixture was stirred at 0 °C until effervescense had ceased then warmed to room temperature and stirred for a further 2 h. The reaction was quenched by the addition of acetic acid (10 drops), concentrated to approximately one quarter of the volume under reduced pressure and partitioned between dichloromethane (10 mL) and water (10 mL). The organic phase was separated and the aqueous phase extracted with dichloromenthane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude product (0.11 g) as a cloudy colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 30% diethylether : hexane] afforded title compound as an inseparable mixture of the two diastereoisomers (combined yield 0.11 g, 0.34 mmol, 85%, *dr* 2.5 : 1) as colourless oils; R_f 0.36 [30% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3440 (O-H), 2955, 2864, 1452, 1248, 1194, 1026, 833; Major Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.38 (3H, s, $SiCH_3$), 0.39 (3H, s, $SiCH_3$), 1.13 (1H, dd, *J* 14.2 and 7.6, $SiC\underline{H}_aH_b$), 1.12 (1H, dd, *J* 14.2 and 6.6, $SiCH_a\underline{H}_b$), 1.37-1.66 (2H, m, $C\underline{H}_aH_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 1.73 (1H, dddd, *J* 12.5, 8.2, 7.3 and 2.9, $CH_a\underline{H}_b$ C-4 THF), 1.81-2.02 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 3.03 (1H, d, *J* 2.2, OH), 4.06 (1H, q, *J* 7.4, CH C-5 THF), 4.12-4.20 (1H, m, CH C-2 THF), 4.39 (1H, dd, *J* 7,7 and 2.2, $\underline{H}$COH), 7.25-7.42 (8H, m, Ar), 7.54-7.59 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −2.0 ($SiCH_3$), 23.7 ($SiCH_2$), 28.6 (CH_2, C-4 THF), 35.2 (CH_2, C-3 THF), 77.3 (COH), 77.5 (CH, C-2 THF), 82.7 (CH, C-5 THF), 127.2 (CH, Ar), 127.9 (CH, Ar), 127.9 (CH, Ar), 128.4 (CH, Ar), 129.1 (CH, Ar), 133.6 (CH, Ar), 139.1 (C, Ar), 140.5(C, Ar); Minor Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.35 (3H, s, $SiCH_3$), 0.36 (3H, s, $SiCH_3$), 1.10 (1H, dd, *J* 14.2 and 8.2, $SiC\underline{H}_aH_b$), 1.36 (1H, dd, *J* 14.2 and 6.3, $SiCH_a\underline{H}_b$), 1.37-1.66 (2H, m, $C\underline{H}_aH_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 1.81-2.02 (2H, m, $CH_a\underline{H}_b$ C-3 and $CH_a\underline{H}_b$ C-4 THF), 2.62 (1H, d, *J* 2.5, OH), 4.12-4.20 (2H, m, CH C-2 THF and CH C-5 THF), 4.91(1H, br t, *J* 3.1, $\underline{H}$COH), 7.25-7.42 (8H, m, Ar), 7.54-7.59 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), -2.0 ($SiCH_3$), 24.2 ($SiCH_2$), 25.7 (CH_2, C-4 THF), 35.0 (CH_2, C-3 THF), 74.2 (COH), 78.5 (CH, C-2 THF), 82.0 (CH, C-5 THF),126.1 (CH, Ar), 127.3 (CH, Ar), 128.0 (CH, Ar), 128.2 (CH, Ar), 129.0 (CH, Ar), 133.6 (CH, Ar), 139.1 (C, Ar), 140.5(C, Ar); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 219 ([M−BnOH]$^+$, 12%), 135 (100), 107 (7), 75 (13); HRMS (ESP, *m/z*) 344.2039 [M+NH_4]$^+$, $C_{20}H_{30}O_2NSi$ requires 344.2040. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the $\underline{H}$COH proton at 4.39 (major diastereoisomer) and 4.91 ppm (minor diastereoisomer).



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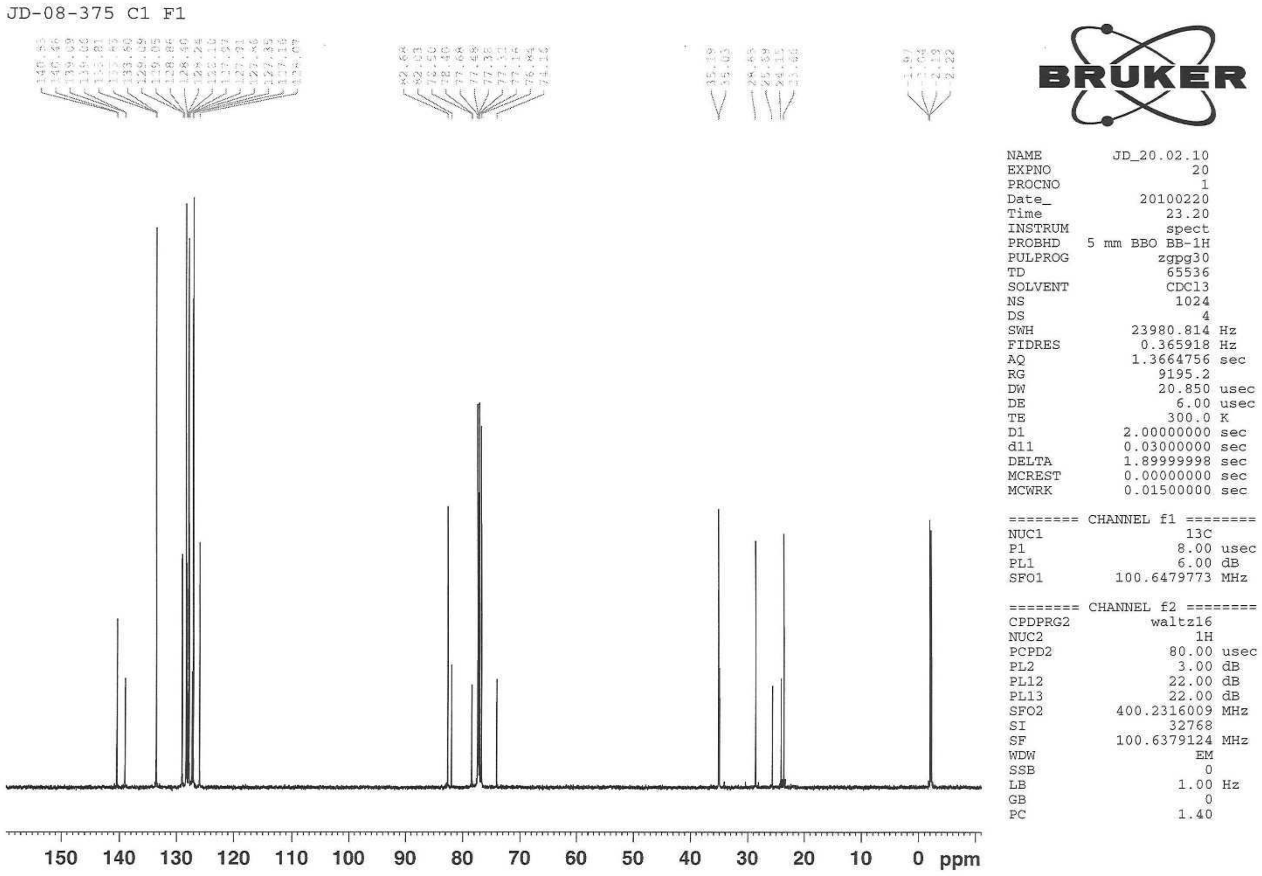

JD-08-375 C1 F1

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RG                9195.2
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TE                 300.0 K
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DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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PL1                 6.00 dB
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PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
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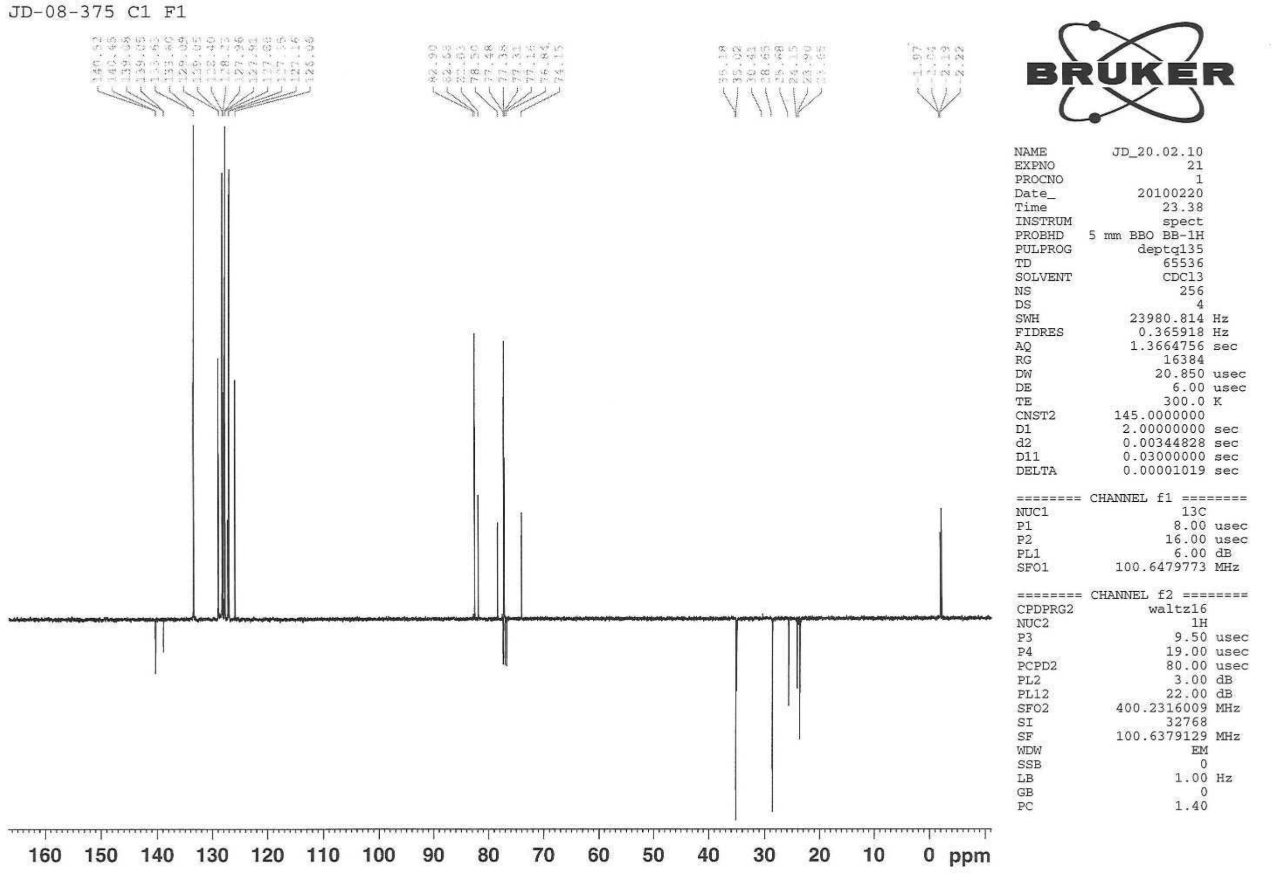
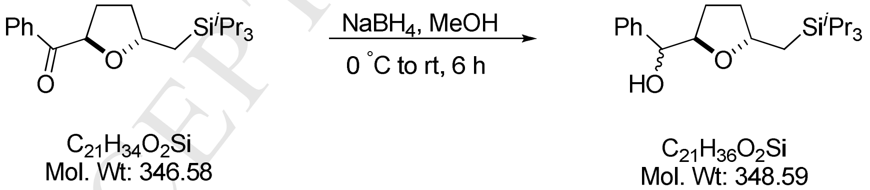
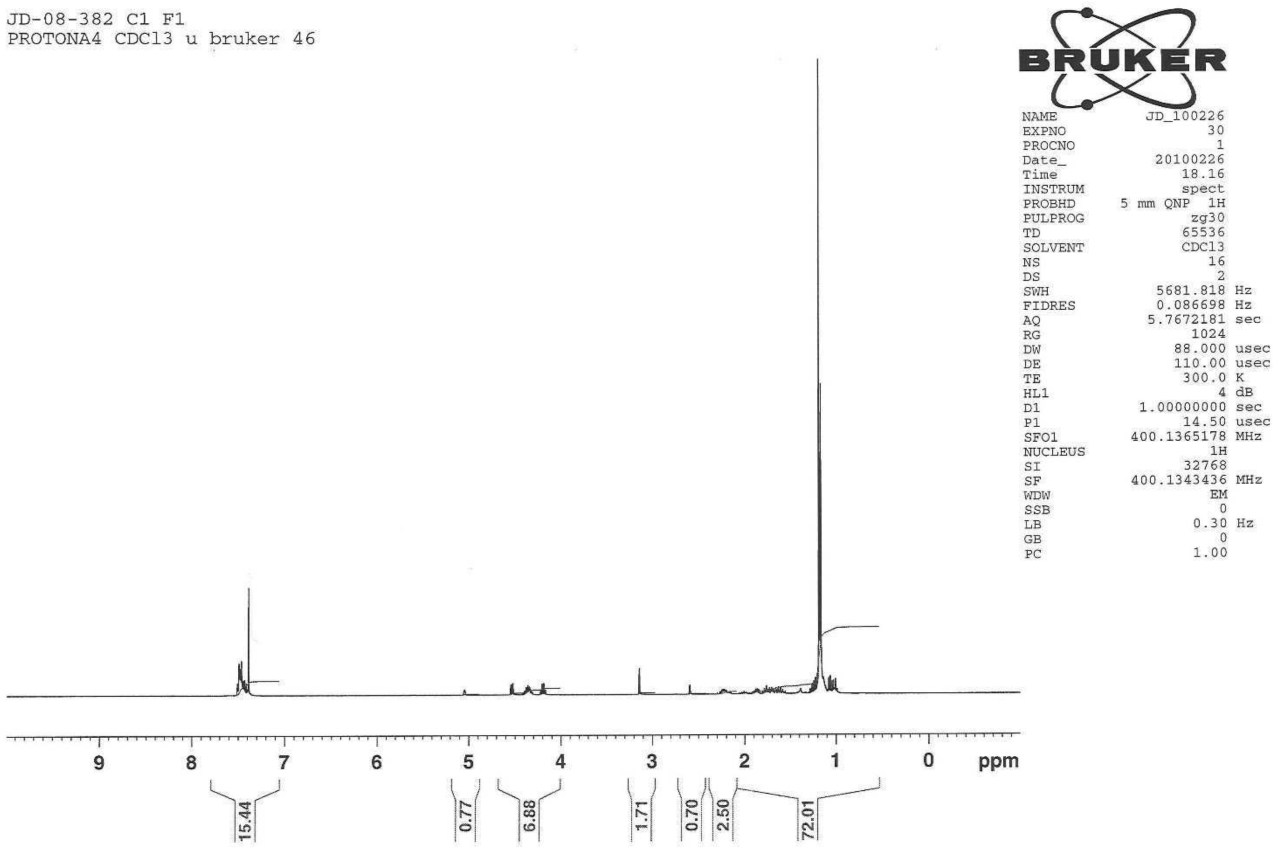


(±)-Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanol (21b)



To a stirred solution of phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanone (0.40 g, 1.16 mmol) in HPLC grade methanol (7.0 mL) at 0 °C was added in one portion NaBH$_4$ (0.11 g, 2.90 mmol). The mixture was stirred at 0 °C until effervescence had ceased then warmed to room temperature and stirred for a further 15 h. The reaction was quenched by the addition of acetic acid (0.1 mL), concentrated to approximately one quarter of the volume under reduced pressure and partitioned between dichloromethane (10 mL) and water (10 mL). The organic phase was separated and the aqueous phase extracted with dichloromenthane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried (MgSO$_4$), filtered and concentrated *in vacuo* to give the crude product (0.33 g) as a cloudy colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] afforded title compound as an inseparable mixture of the two diastereoisomers (combined yield 0.31 g, 0.89 mmol, 77 %, dr 2.6 : 1) as a colourless oil; R_f 0.29 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3426 (O-H), 2940, 2864, 1462, 1195, 1027, 881; Major Diastereoisomer: δ_H (400 MHz; CDCl$_3$) 0.94 (1H, dd, *J* 14.5 and 6.8, SiC$\underline{H_a}$H$_b$), 1.03-1.12 (21H, m, overlapping signals Si$^i\underline{Pr}_3$), 1.12 (1H, dd, *J* 14.5 and 7.4, SiCH$_a\underline{H_b}$), 1.42-1.79 (3H, m, CH$_2$ C-3 and C$\underline{H_a}$H$_b$C-4 THF), 2.03-2.15 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 3.06 (1H, d, *J* 1.6, OH), 4.08 (1H, q, *J* 7.4, C-5 THF), 4.19-4.29 (1H, m, overlapping signals C-2 THF), 4.42 (1H, dd, *J* 7.9 and 1.6, $\underline{H}$COH), 7.24-7.39 (5H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH Si^iPr_3), 17.7 ($SiCH_2$), 19.0 (6 × CH_3 Si^iPr_3), 28.8 (CH_2, C-4 THF), 36.1 (CH_2, C-3 THF), 77.5 (COH), 77.6 (CH, C-2 THF), 83.0 (CH, C-5 THF), 127.2 (2 × *o*-CH, Ph), 128.0 (*p*-CH, Ph), 128.4 (2 × *m*-CH, Ph), 140.4 (C, Ph); Minor Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.92 (1H, dd, *J* 14.4 and 7.9, $SiC\underline{H}_aH_b$), 1.03-1.12 (22H, m, overlapping signals $^i\underline{Pr}_3SiCH_a\underline{H}_b$), 1.42-179 (2H, m, overlapping signals $C\underline{H}_aH_b$ C-3 and $C\underline{H}_aH_b$ C-4 THF), 1.89 (1H, dddd, *J* 12.2, 10.8, 9.1 and 7.6, $CH_a\underline{H}_b$ C-3 THF), 2.03-2.15 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 2.59 (1H, d, *J* 2.5, OH), 4.19-4.29 (2H, m, overlapping signals C-5 and C-2 THF), 4.91 (1H, dd appearing as br t, *J* 2.5, $\underline{H}$COH), 7.24-7.39 (5H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^iPr_3), 17.1 (CH_2, $^iPr_3SiCH_2$), 19.0 (6 × CH_3 Si^iPr_3), 26.0 (CH_2, C-4 THF), 35.7 (CH_2, C-3 THF), 74.3 (COH), 78.7 (CH, C-2 THF), 82.2 (CH, C-5 THF), 126.1 (2 × *o*-CH, Ph), 127.4 (*p*-CH, Ph), 128.3 (2 × *m*-CH, Ph), 140.5 (C, Ph); LRMS (EI^+, *m/z*): M^+ not visible, 305 ($[M-{}^iPr]^+$, 9%), 287 (3), 263 (6), 241 (24), 157 (100), 131 (68), 103 (86), 75 (50); HRMS (ESP, *m/z*) 366.2822 $[M+NH_4]^+$, $C_{21}H_{40}O_2NSi$ requires 366.2823. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the $\underline{H}$COH proton at 4.42 (major diastereoisomer) and 4.91 ppm (minor diastereoisomer).



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PROCNO 1
Date_ 20100226
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TE 300.0 K
HL1 4 dB
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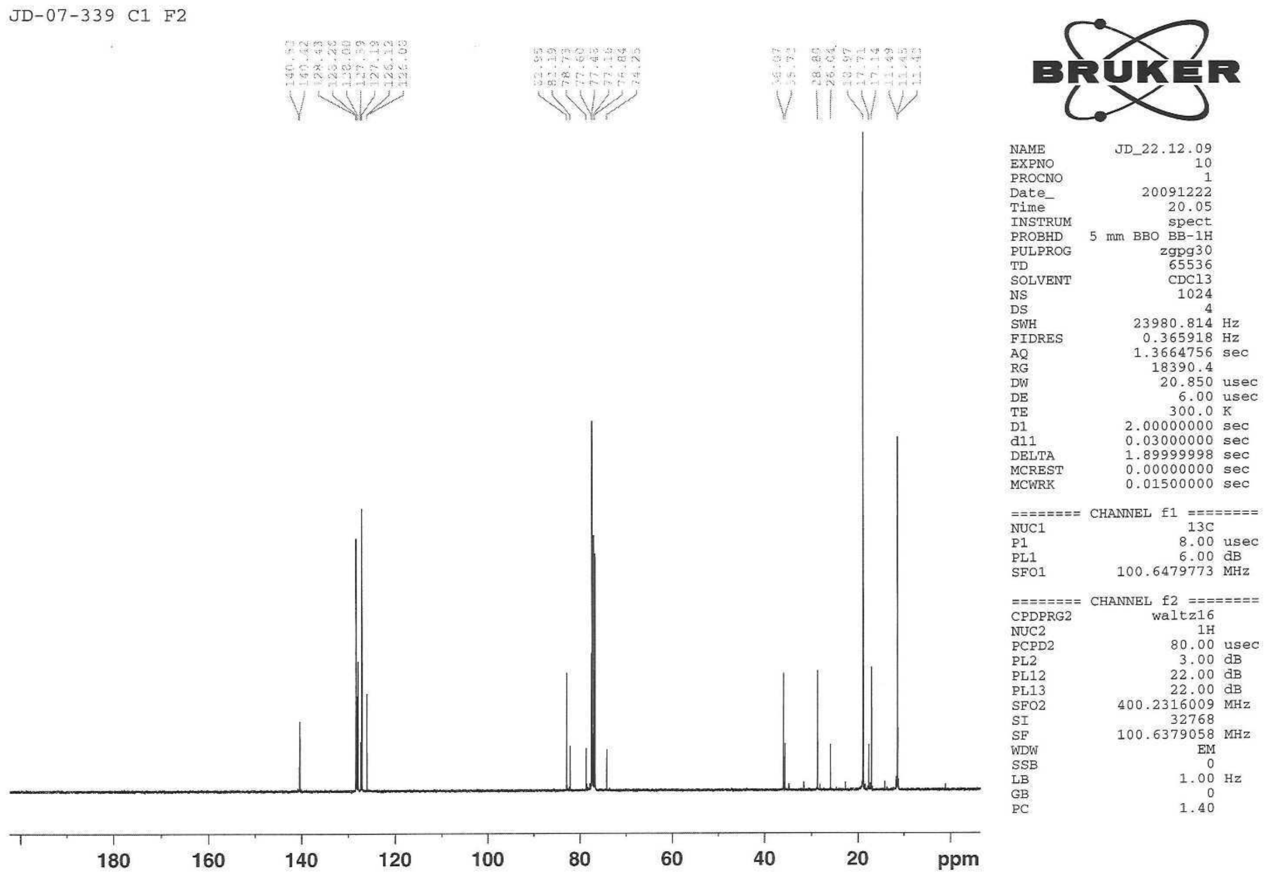

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SOLVENT             CDCl3
NS                   1024
DS                      4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                18390.4
DW               20.850 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

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P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379058 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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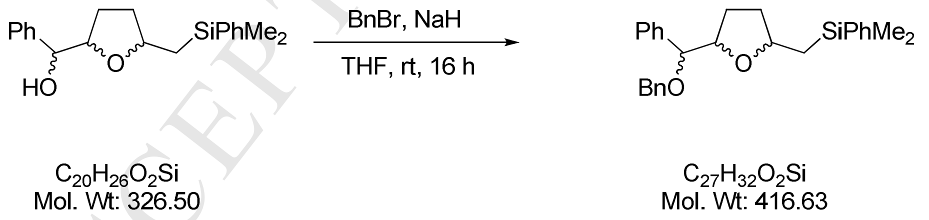
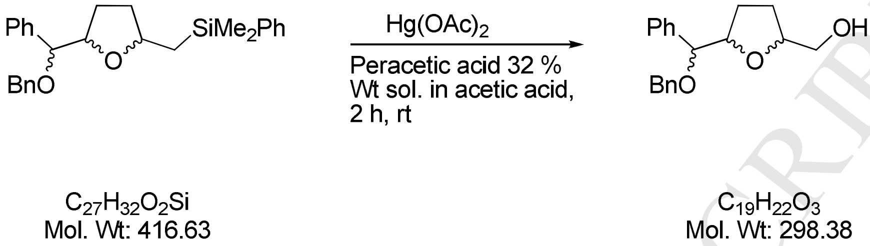
((2-(benzyloxy(phenyl)methyl)tetrahydrofuran-5-yl)methyl)dimethyl(phenyl)silane (22)



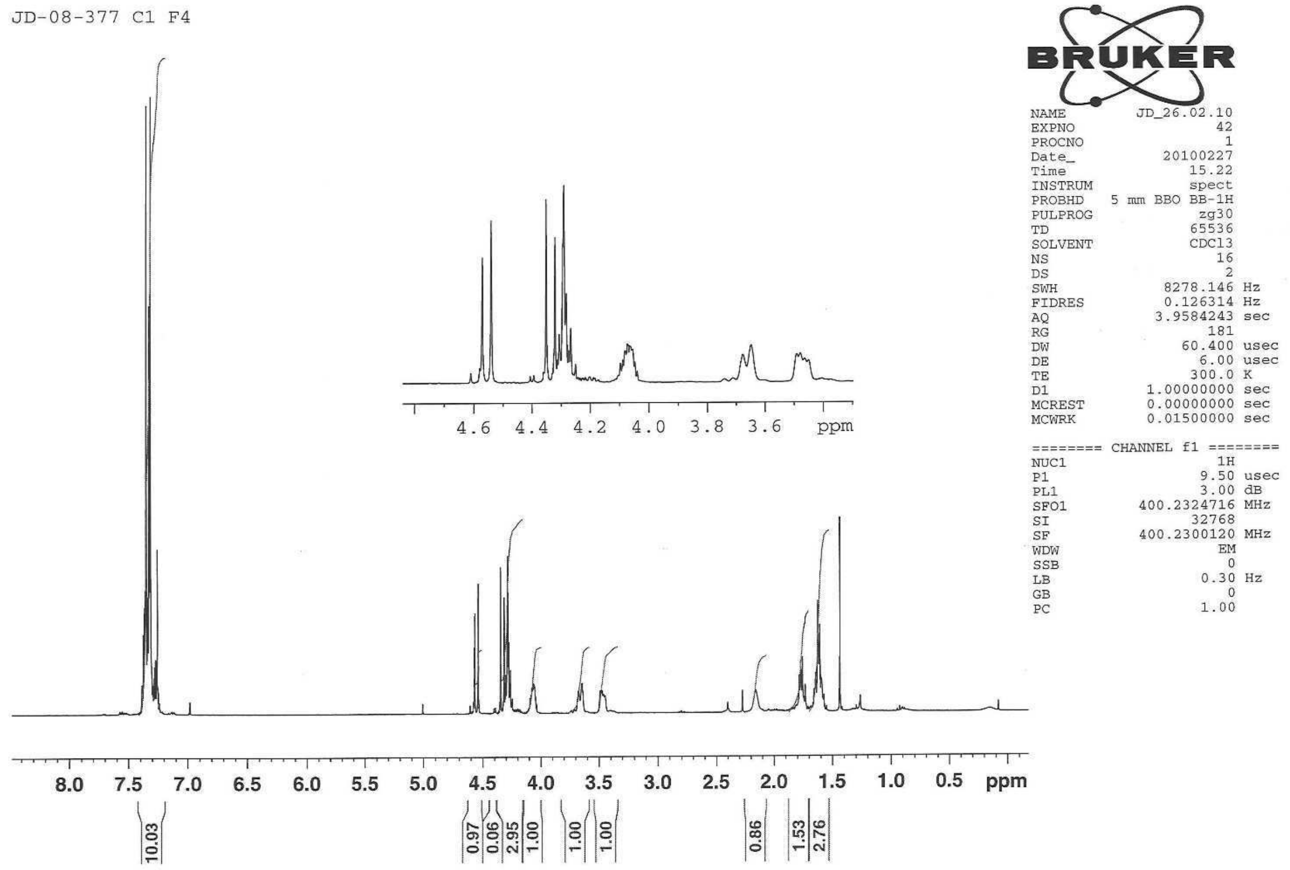
A 60% dispersion of sodium hydride in mineral oil (12.0 mg, 0.50 mmol) was washed with *n*-hexane (2 × 1 mL), dried under reduced pressure and placed under an atmosphere of argon. To the resulting suspension dissolved in THF (1.5 mL) was added, dropwise, benzyl bromide (0.06 g, 0.04 mL, 0.35 mmol) and a solution of (2-((dimethyl(phenyl)silyl)methyl)-tetrahydrofuran-5-yl)(phenyl)methanol (0.13 g, 0.38 mmol) in THF (1 mL) at room temperature. The resulting solution was stirred for 15 h at 30 °C and monitored by TLC. After this time, the reaction was partitioned between water (10 mL) and DCM (10 mL) and the organic layer separated. The aqueous layer was extracted with DCM (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a colourless oil (0.26 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] afforded the title compound as an inseparable mixture of 4 diastereoisomers (combined yield 0.13 g, 0.31 mmol, 89%) as a colourless oil; R_f 0.76 [20% diethyl ether : hexane]; LRMS (EI^+, *m/z*): 416

([M]$^+$, 1%), 241 (9), 219 (10), 197 (12), 135 (100), 91 (72). Full characterisation of the product was not possible because of the number of diastereoisomers present. The material was used in the next step without further purification.

(±)-(5-(Benzyloxy(phenyl)methyl)tetrahydrofuran-2-yl)methanol (28)



(5-(Benzyloxy(phenyl)methyl)tetrahydrofuran-2-yl)methanol was prepared according to the procedure reported by Fleming *et al.*[113] To a stirred solution of ((5-(benzyloxy(phenyl)methyl)tetrahydrofuran-2-yl)methyl)dimethyl(phenyl)silane (0.12 g, 0.31 mmol) in peracetic acid (30% *wt* sol. in acetic acid, 3 mL) was added in one portion mercury (II) acetate (0.11 g, 0.35 mmol). The reaction was stirred for 2 h then washed with water (10 mL), sat. NaS_2O_3 (10 mL), sat. $NaHCO_3$ (10 mL) The aqueous layer was extracted with DCM (3 × 10 mL) and the organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a white solid (0.19 g). Purification by flash column chromatography [silica gel, gradient elution 50% hexane : diethyl ether – 100% diethylether] isolated a single diastereoisomer of the title compound (0.03 g, 0.10 mmol, 32%) as a colourless viscous oil; R_f 0.14 [80% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 3439 (O-H), 3062, 3030, 2870, 1495, 1454, 1062 (C-O); δ_H (400 MHz; $CDCl_3$) 1.55-1.67 (3H, m, overlapping signals CH_2 C-4 and C$\underline{H}_a$H$_b$ C-3 THF), 1.73-1.82 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.16 (1H, br s, OH), 3.43 (1H, app dd, *J* 11.1 and 5.1, C$\underline{H}_a$H$_b$OH), 3.66 (1H, app br d, *J* 11.7, CH$_a\underline{H}_b$OH), 4.04-4.10 (1H, m, CH C-2 THF), 4.24-4.31 (2H, m, overlapping signals CH C-5 THF and $\underline{H}$COBn), 4.34 (1H, d, *J* 12.1 PhC$\underline{H}_a$H$_b$O), 4.56 (1H, d, *J* 12.1, PhCH$_a\underline{H}_b$O), 7.24-7.39 (10H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 27.3 (CH_2, C-3 THF), 28.9 (CH_2, C-4 THF), 65.0 (CH_2OH), 70.6 (Ph$\underline{C}$H$_2$O), 80.1 (CH, C-2 THF), 82.5 (CH, C-5 THF), 84.0 ($\underline{H}$COBn), 127.6 (p-CH, Ar), 127.9 (2 × o-CH, Ar), 128.0 (2 × *o*-CH, Ar), 128.2 (*p*-CH, Ar), 128.4 (2 × *m*-CH, Ar), 128.5 (2 × *m*-CH, Ar), 138.5 (C, Ar), 139.0 (C, Ar); LRMS (EI$^+$, *m/z*): 298 ([M]$^+$, 1%), 197 (26), 101 (23), 91 (100), 57 (28); HRMS (ESP, *m/z*) 316.1902 [M+NH$_4$]$^+$, $C_{19}H_{26}O_3N$ requires 316.1907.



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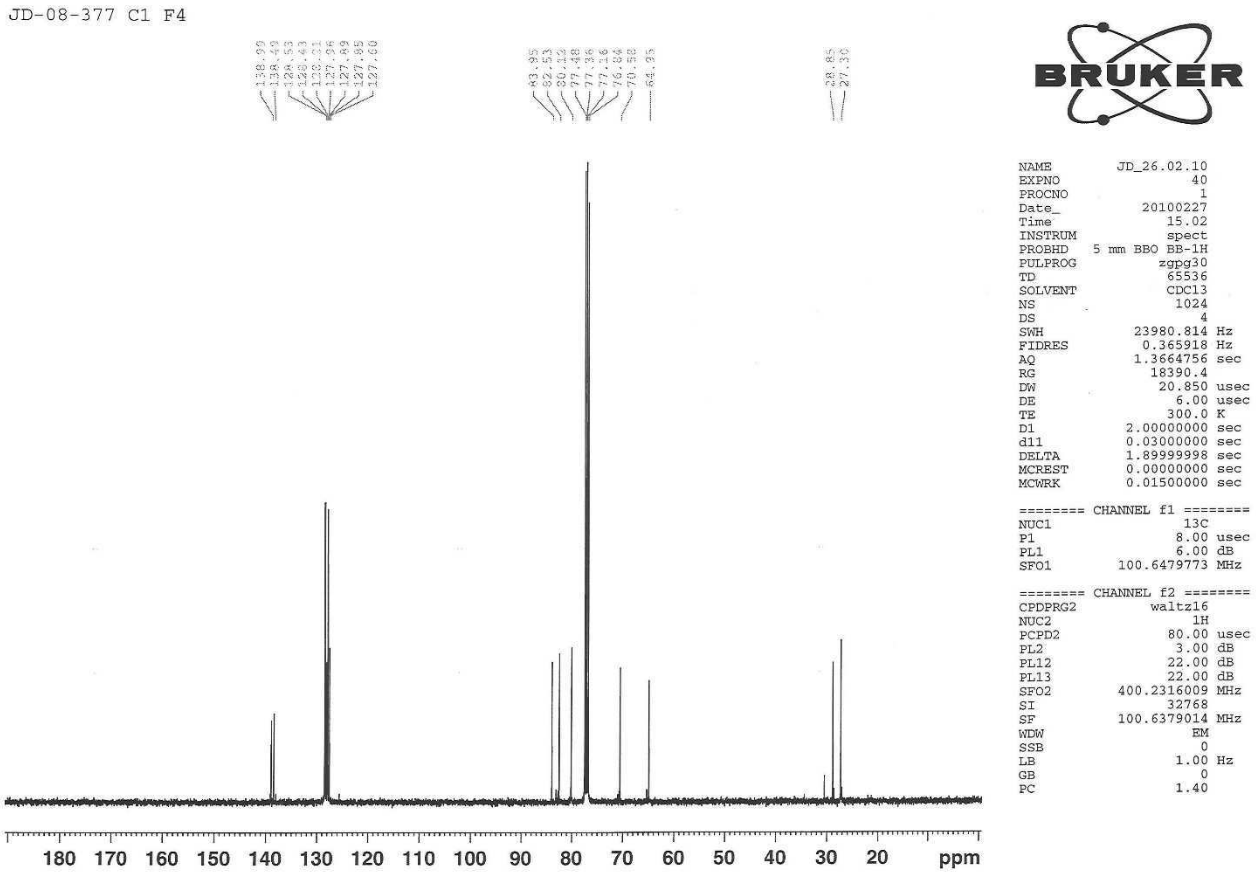

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DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

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PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
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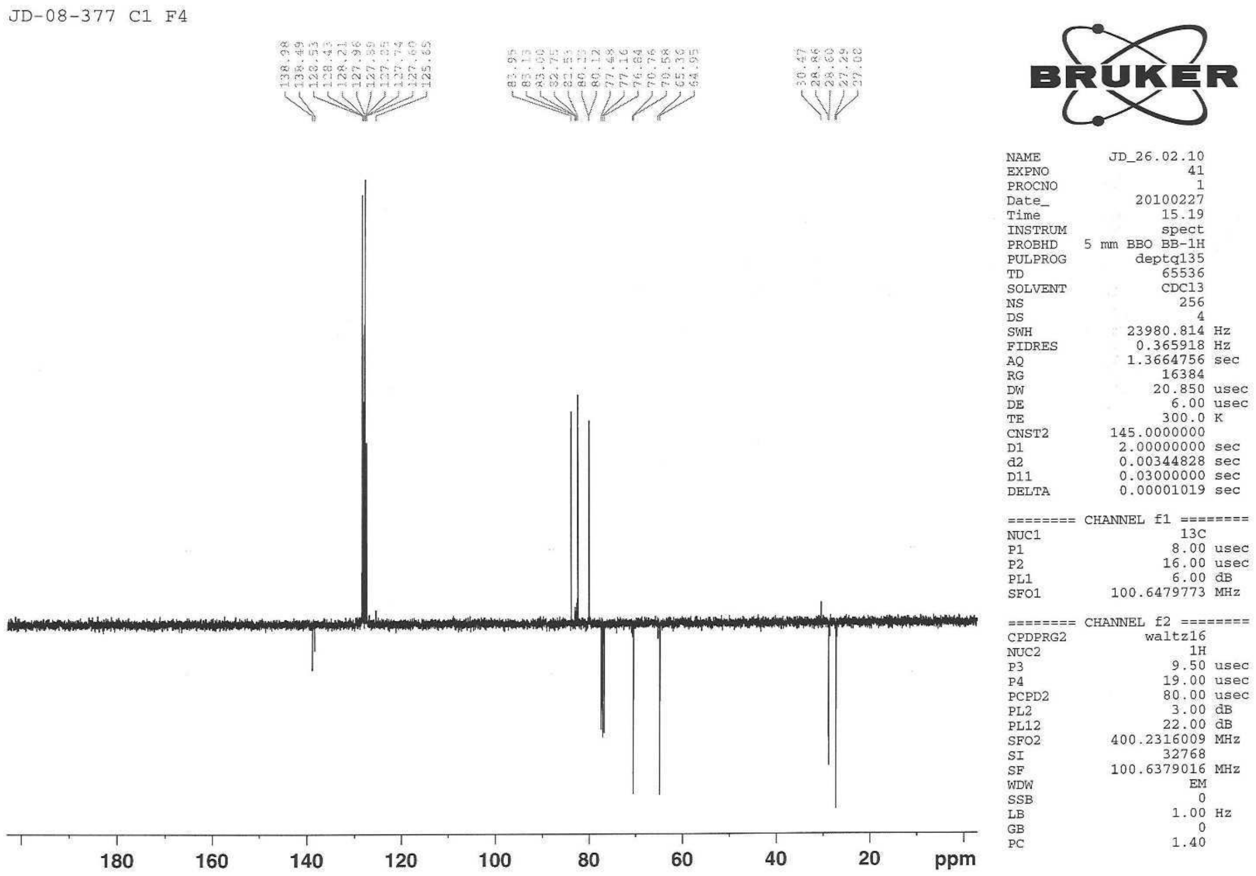

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======== CHANNEL f1 ========
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======== CHANNEL f2 ========
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PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379016 MHz
WDW                    EM
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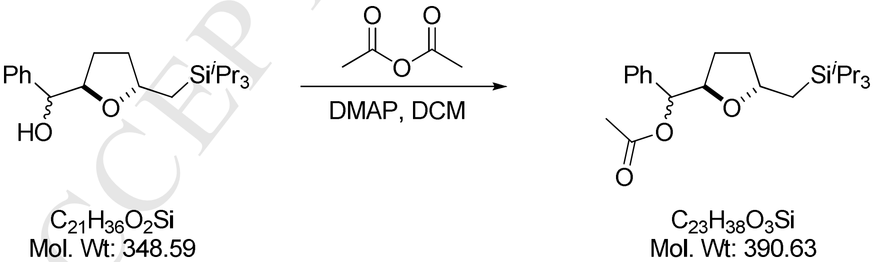
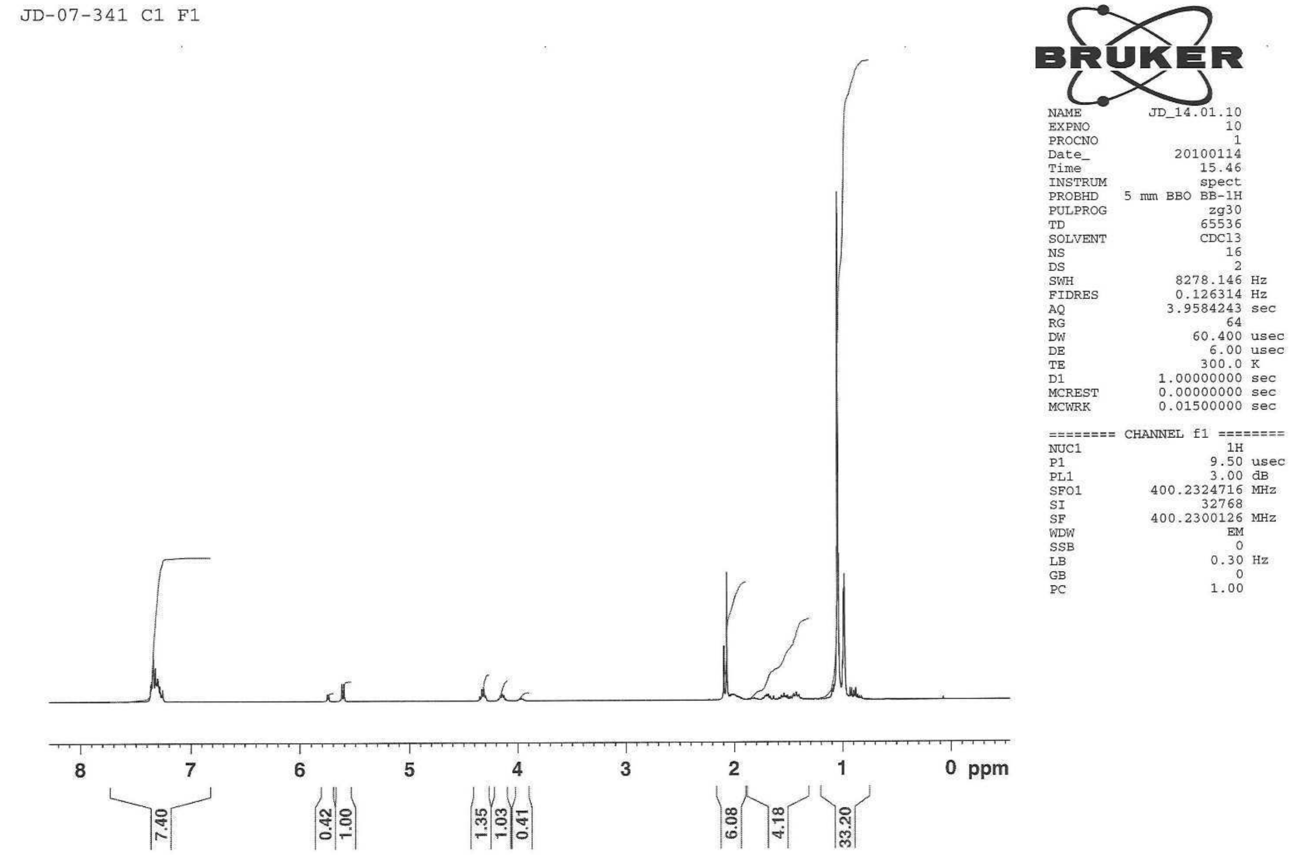
(±)-Phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methyl acetate (23)



To a stirred solution of phenyl(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methanol (0.05 g, 0.14 mmol) in DCM (5 mL) was added acetic anhydride (20.0 μL, 0.21 mmol) and in one portion DMAP (4.00 mg, 0.03 mmol, 20 mol%). The reaction mixture was stirred at room temperature and monitored by TLC. After 15 h the reaction was quenched with a saturated solution of $NaHCO_3$ (3 mL). The organic phase was separated and the aqueous phase extracted with dichloromenthane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude product (0.03 g) as a colourless oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] afforded title compound as an inseparable mixture of the two diastereoisomers (combined yield 31.0 mg, 0.08 mmol, 57%, *dr* 2.4 : 1) as colourless oils; R_f 0.58 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2940, 2864, 1742 (C=O), 1462, 1368, 1232, 1022, 882; Major Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.91 (1H, dd, *J* 14.5 and 6.7, SiC$\underline{H}_a$H$_b$), 0.99-1.10 (22H, m, overlapping signals

$^{i}Pr_3SiCH_a\underline{H}_b$), 1.38-1.48 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.50-1.59 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.67-1.74 (1H, m, $CH_a\underline{H}_b$ C-4 THF), 1.93-2.05 (1H, m, $CH_a\underline{H}_b$ C-3 THF), 2.07 (3H, s, CO_2CH_3), 4.11-4.18 (1H, m, CH C-2 THF), 4.29-4.35 (1H, m, CH C-5 THF), 5.61 (1H, d, *J* 7.9, HCO), 7.27-7.36 (5H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH $Si^{i}Pr_3$), 17.0 ($SiCH_2$), 19.0 (6 × CH_3 $Si^{i}Pr_3$), 21.4 (CH_3, CO_2CH_3), 29.3 (CH_2, C-4 THF), 35.8 (CH_2, C-3 THF), 77.5 (CH, C-2 THF), 78.4 (HCO), 79.8 (CH, C-5 THF), 127.7 (CH, Ar), 128.2 (CH, Ar), 128.5 (CH, Ar), 137.9 (C, Ar), 170.4 (C, CO_2CH_3); Minor Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.85 (1H, dd, *J* 14.4 and 7.4, $SiC\underline{H}_aH_b$), 0.99-1.10 (22H, m, overlapping signals $^{i}Pr_3SiCH_a\underline{H}_b$), 1.38-1.48 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.79-1.88 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.93-2.05 (2H, m, $CH_a\underline{H}_b$ C-3 and $CH_a\underline{H}_b$ C-4 THF), 2.10 (3H, s, CO_2CH_3), 3.97 (1H, dtd, *J* 9.0 7.1 and 5.1, CH C-2 THF), 4.29-4.35 (1H, m, CH C-5 THF), 5.76 (1H, d, *J* 6.6, HCO), 7.27-7.36 (5H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH $Si^{i}Pr_3$), 17.0 ($SiCH_2$), 19.0 (6 × CH_3 $Si^{i}Pr_3$), 21.4 ($CO_2\underline{C}H_3$), 28.4 (CH_2, C-4 THF), 35.6 (CH_2, C-3 THF), 77.6 (HCO), 78.1 (CH, C-2 THF), 80.0 (CH, C-5 THF), 127.5 (CH, Ar), 128.0 (CH, Ar), 128.2 (CH, Ar), 137.8 (C, Ar), 170.4 (C, CO_2CH_3); LRMS (EI^+, *m/z*): M^+ not visible, 331 ($[M-CO_2Me]^+$, 2%), 241 (18), 173 (100), 157 (71), 115 (25), 75 (19); HRMS (ESP, *m/z*) 391.2665 $[M+H]^+$, $C_{20}H_{39}O_3Si$ requires 391.2663. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the $\underline{H}CO$ proton at 5.61(major diastereoisomer) and 5.76 ppm (minor diastereoisomer).



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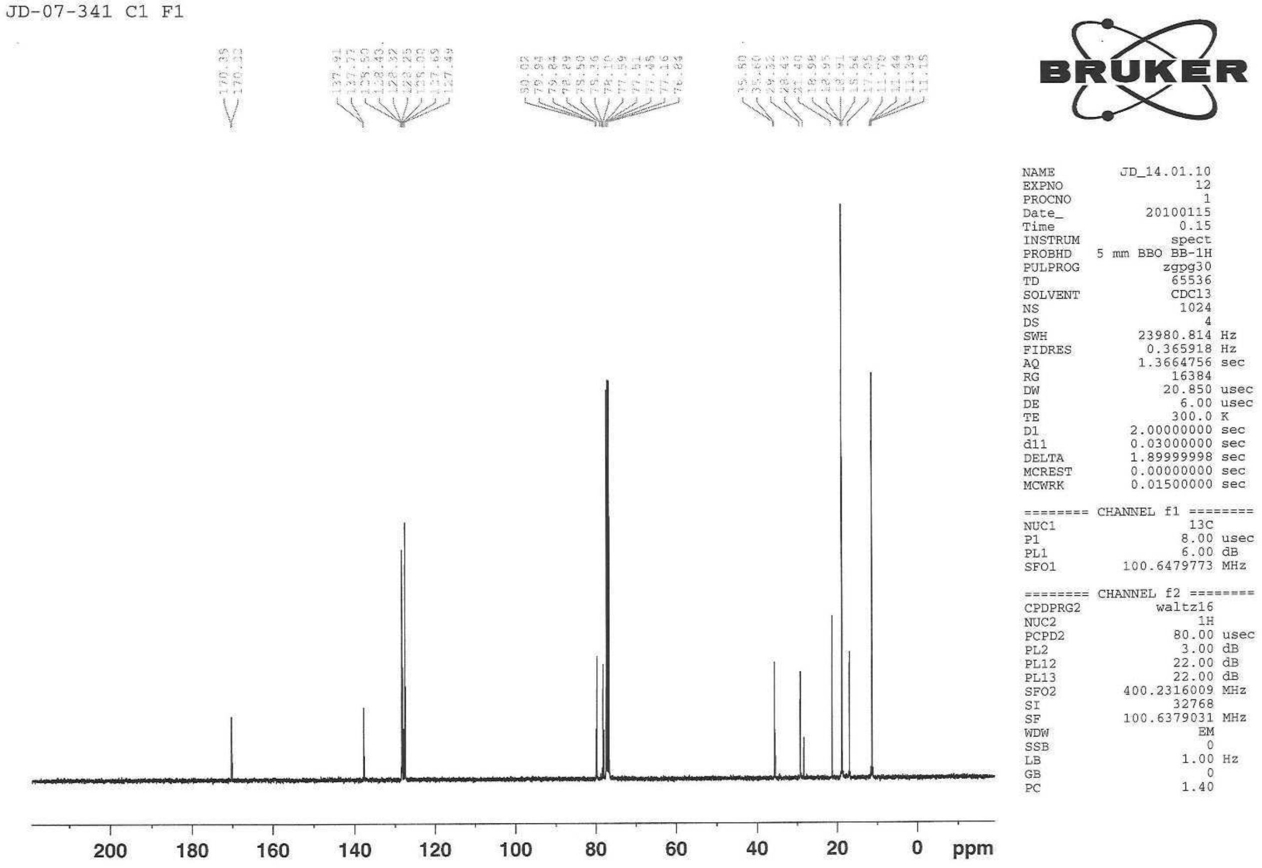

JD-07-341 C1 F1

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SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
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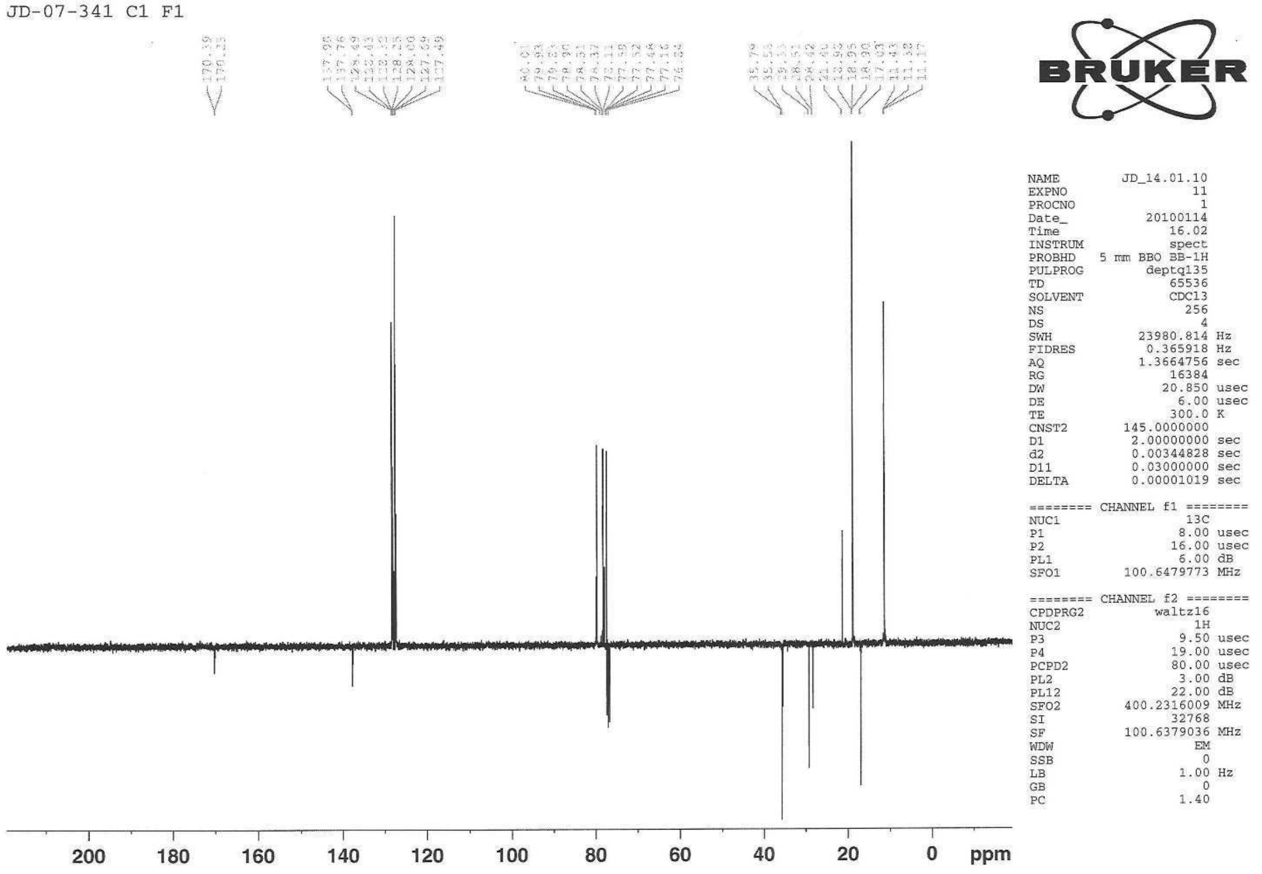

JD-07-341 C1 F1

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======== CHANNEL f1 ========
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======== CHANNEL f2 ========
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WDW                    EM
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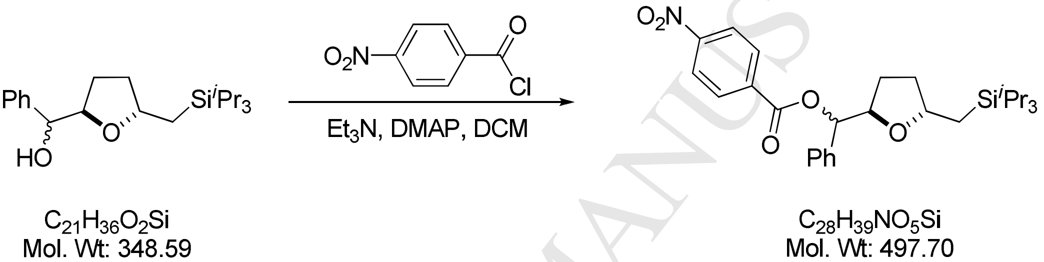
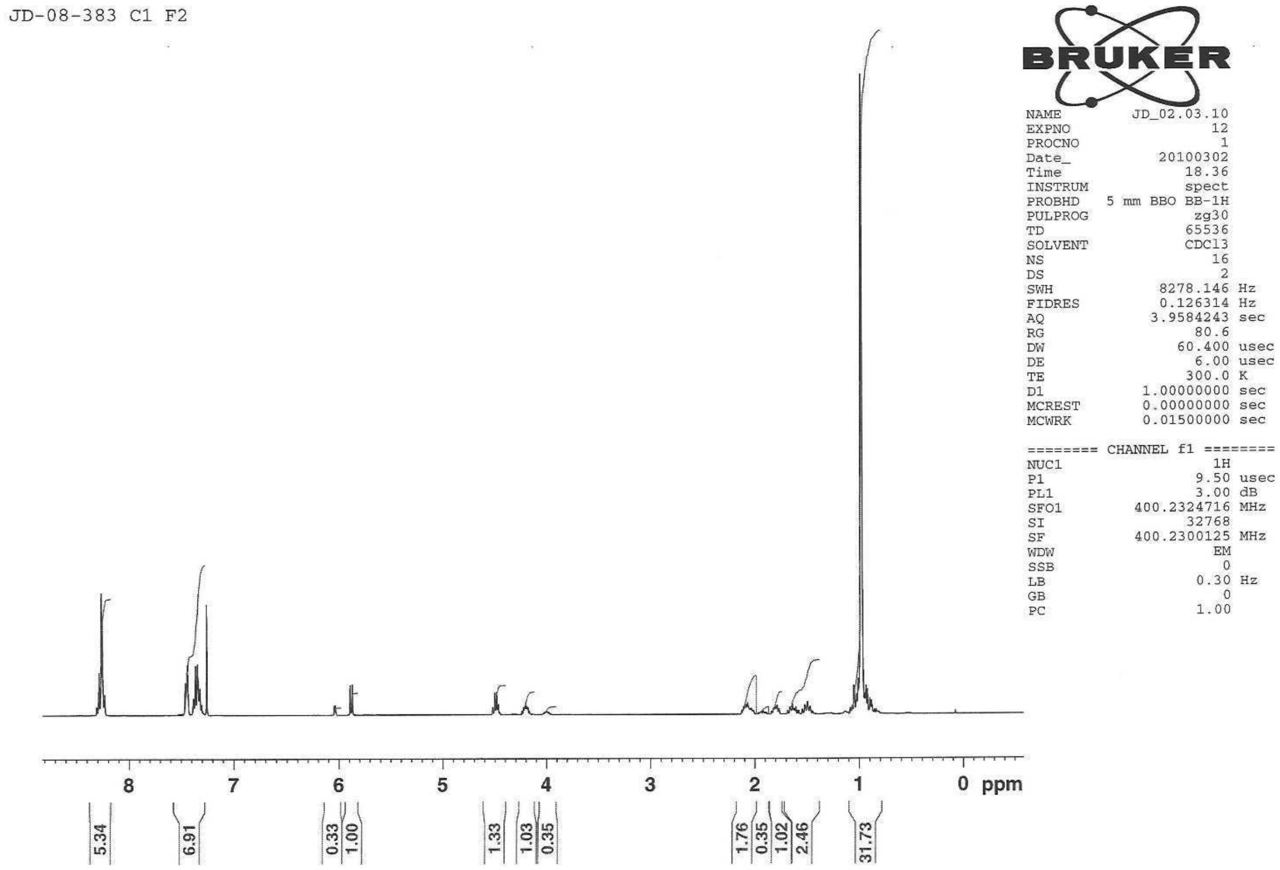
4-Nitrobenzoyl chloride

To a stirred solution of 4-nitrobenzoic acid (1.00 g, 6.00 mmol) in DCM (10 mL) at room temperature was added oxalyl chloride (1.50 g, 1.05 mL, 12.0 mmol) and DMF (5 drops). The reaction was stirred for 3 h at room temperature and the volatiles removed under reduced pressure to give a crystalline solid. The residue was taken up in DCM (10 mL) to give a 0.6 M solution of 4-nitrobenzoyl chloride in DCM which was used immediately in the next reaction.

(±)-Phenyl-(2-((triisopropylsilyl)methyl)tetrahydrofuran-5-yl)methyl 4-nitrobenzoate (24)



To a stirred solution of phenyl(5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)methanol (0.31 g, 0.89 mmol) in DCM (2 mL) was added a solution of freshly prepared 4-nitrobenzoyl chloride in DCM (0.6 M, 1.70 mL, 1.00 mmol). To the resulting yellow/orange solution was added dropwise triethylamine (0.20 g, 0.30 mL, 2.00 mmol) and DMAP (1 crystal). After 24 h the reaction had become a red/brown colour and was partitioned between water (10 mL) and DCM (10 mL). The organic phase was separated, washed with a 10% *w*/*v* aqueous sodium hydrogen carbonate solution (10 mL) and the aqueous phase extracted with dichloromenthane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a brown gum. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethylether : hexane] afforded title compound as an inseparable mixture of diastereoisomers (combined yield 0.29 g, 0.64 mmol, 72%, *dr* 3 : 1) as colourless viscous oils; R_f 0.44 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2941, 2864, 1727 (C=O), 1529 (N=O), 1463, 1346 (N=O), 1270, 1101, 882; Major Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.84-1.08 (23H, m, overlapping signals $^{i}\underline{Pr}_3SiC\underline{H}_2$), 1.45-1.55 (1H, m, C$\underline{H}_aH_b$ C-3 THF), 1.60-1.67 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 1.80 (1H, dtd, *J* 12.6 7.5 and 2.3, CH$_a\underline{H}_b$ C-4 THF), 2.02-2.13 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 4.20 (1H, tt, *J* 8.4 and 5.5, CH C-2 THF), 4.46-4.53 (1H, m, CH C-5 THF), 5.89 (1H, d, *J* 8.0, HCO), 7.31-7.46 (5H, m, Ar), 8.23-8.32 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.5 (3 × CH Si^{i}Pr$_3$), 17.0 ($SiCH_2$), 19.0 (6 × CH_3 Si^{i}Pr$_3$), 29.4 (CH_2, C-4 THF), 36.3 (CH_2, C-3 THF), 77.7 (CH, C-2 THF), 80.0 (CH, C-5 THF), 80.1 (HCO), 123.5 (CH, Ar), 127.7 (CH, Ar), 128.5 (CH, Ar), 128.7 (CH, Ar), 131.0 (CH, Ar), 136.2 (C, Ar), 137.2 (C, Ar), 150.6 (C, Ar), 164.0 (C=O); Minor Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.84-1.08 (23H, m, overlapping signals $^{i}\underline{Pr}_3SiC\underline{H}_2$), 1.45-1.55 (1H, m, C$\underline{H}_aH_b$ C-3 THF), 1.87-1.97 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 2.02-2.13 (1H, m, CH$_a\underline{H}_b$ C-3 and CH$_a\underline{H}_b$ C-4 THF), 3.97-4.20 (1H, m, CH C-2 THF), 4.46-4.53 (1H, m, CH C-5 THF), 6.04 (1H, d, *J* 4.4, HCO), 7.31-7.46 (5H, m, Ar), 8.23-8.32 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH Si^{i}Pr$_3$), 17.1 ($SiCH_2$), 19.0 (6 × CH_3 Si^{i}Pr$_3$), 28.5 (CH_2, C-4 THF), 35.9 (CH_2, C-3 THF), 78.4 (CH, C-2 THF), 79.2 (HCO), 80.0 (CH, C-5 THF), 123.7 (CH, Ar), 127.5 (CH, Ar), 128.4 (CH, Ar), 128.8 (CH, Ar), 130.9 (CH, Ar), 136.0 (C, Ar), 137.0 (C, Ar), 150.7 (C, Ar), 163.9 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 280 (100), 241 (5), 157 (46), 150 (30), 115 (14), 91 (11); HRMS (ESP, *m/z*) 498.2664 [M+H]$^+$, $C_{28}H_{40}O_5NSi$ requires 498.2670. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the HCO proton at 5.89 (major diastereoisomer) and 6.04 ppm (minor diastereoisomer).



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FIDRES           0.126314 Hz
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TE                  300.0 K
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MCREST         0.00000000 sec
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PL1                  3.00 dB
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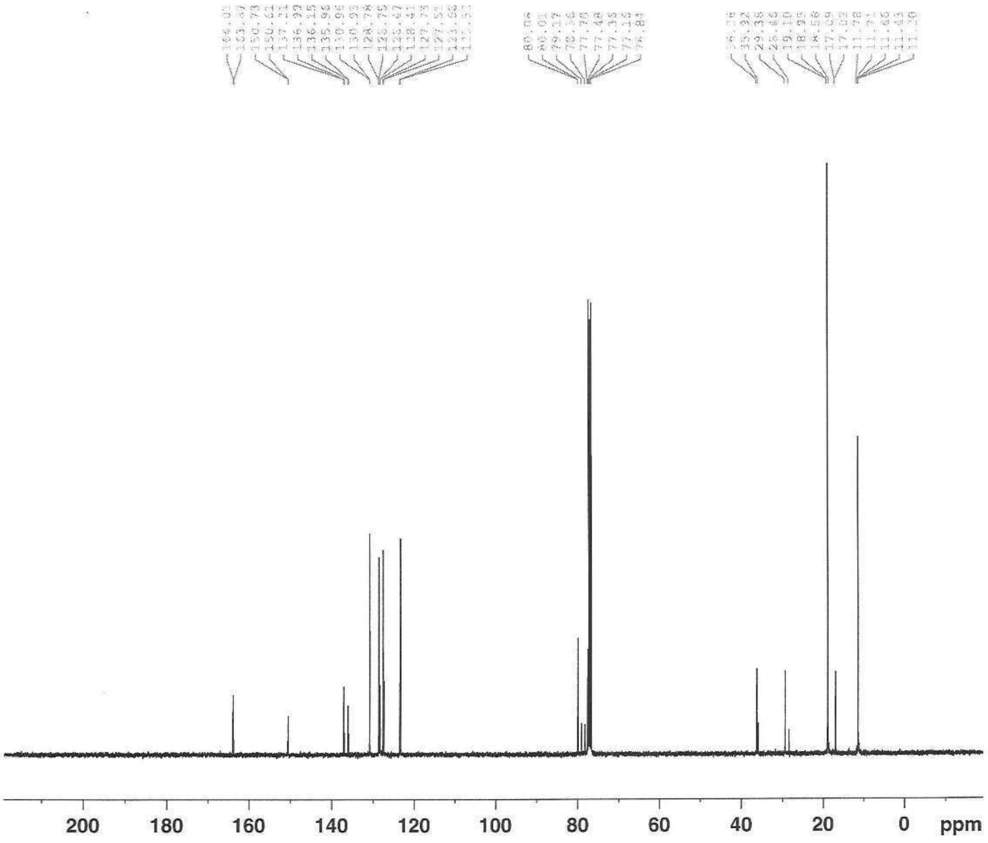
JD-08-383 C1 F2



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MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
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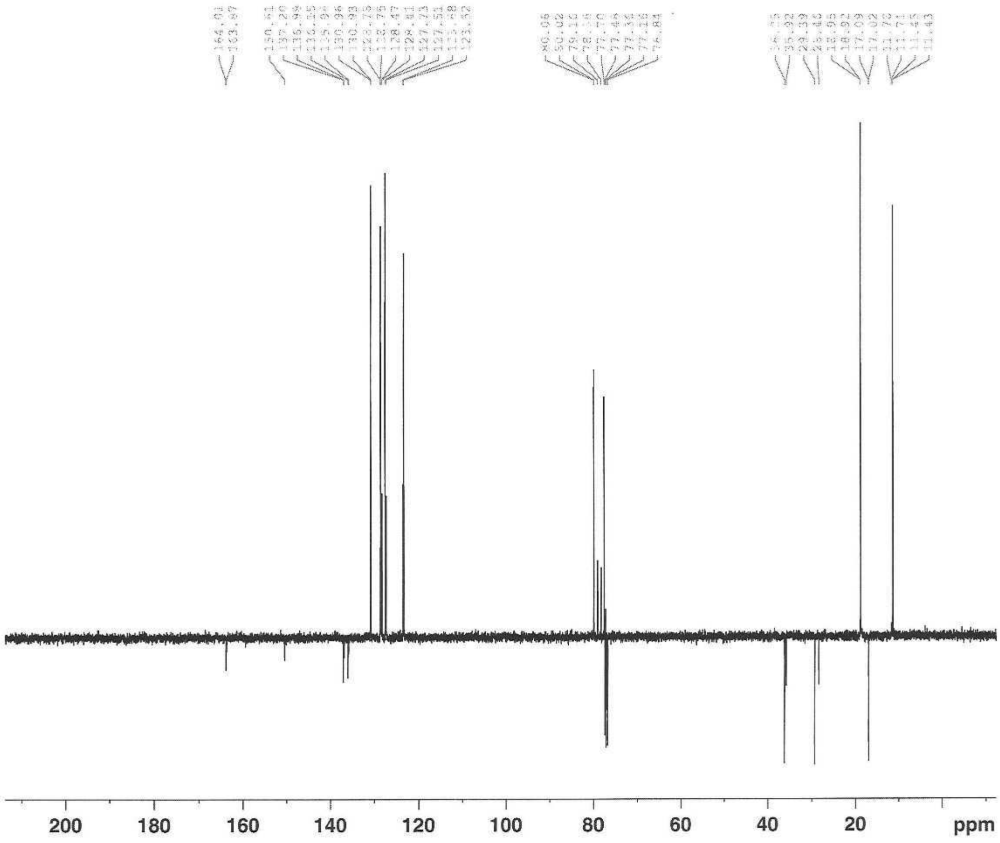
JD-08-383 C1 F2



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SOLVENT              CDCl3
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DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
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PL12                22.00 dB
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SI                  32768
SF            100.6379011 MHz
WDW                    EM
SSB                     0
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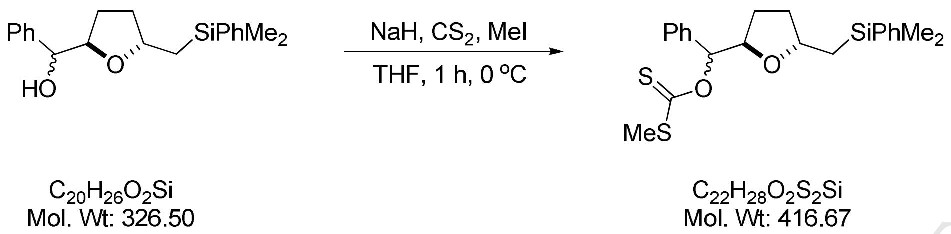
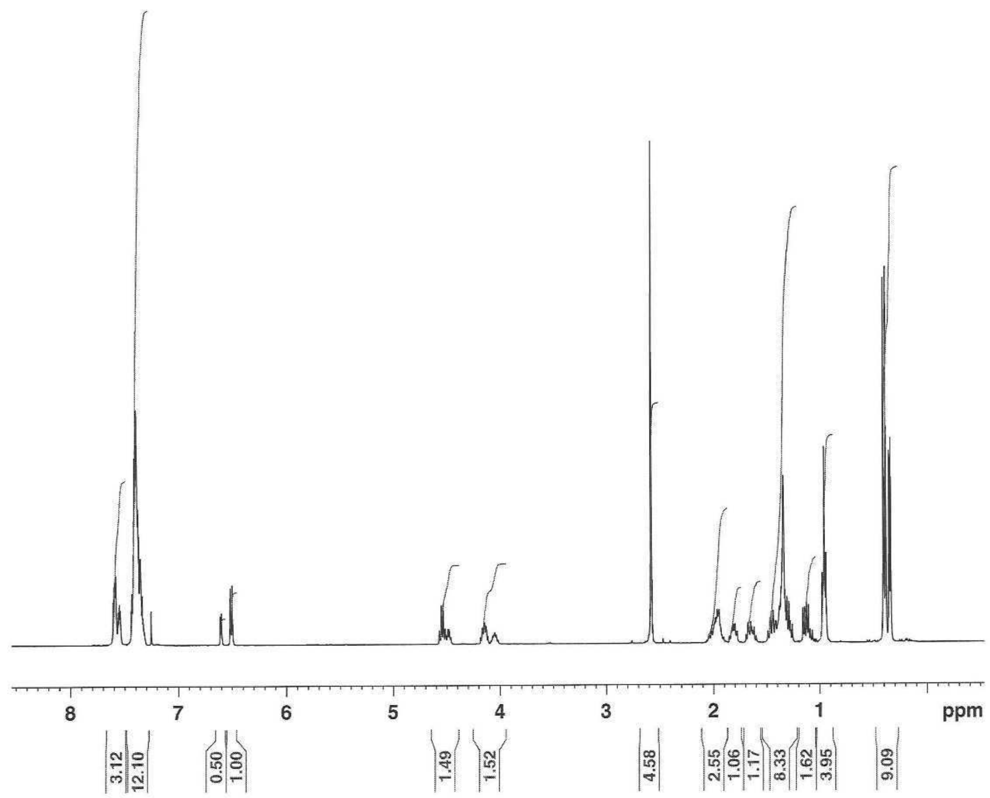
***O*-(2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methyl-*S*-methyl carbonodithioate**



O-(2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methyl-*S*-methyl carbonodithioate was prepared according to the procedure reported by Calter *et al.*[xiii] To a stirred solution of (2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(phenyl)methanol (0.41 g, 1.30 mmol) in THF (25 mL) at 0 °C was added carbon disulphide (5.41 mL, 90.0 mmol) and diiodomethane (5.30 mL, 85.0 mmol). The mixture was stirred at 0 °C for 30 min followed by the addition of sodium hydride (60% suspension in mineral oil, 0.10 g, 2.50 mmol). The reaction was stirred for 1 h at 0 °C and then quenched by the addition of crushed ice (30 g) and allowed to warm to room temperature. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a yellow oil (0.59 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethylether : hexane] afforded the title compound as inseparable mixture of diastereoisomers (combined yield 0.37 g, 0.85 mmol, 69%, *dr* 2.5 : 1) as a colourless oil; R_f 0.75 and 0.70 [20% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2954, 2864, 1427, 1209, 1112, 1049, 819; Major Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.39 (3H, s, $SiCH_3$), 0.41 (3H, s, $SiCH_3$), 1.14 (1H, dd, *J* 14.4 and 6.9, SiC$\underline{H}_a$H$_b$), 1.33 (1H, dd, *J* 14.4 and 7.4, SiCH$_a\underline{H}_b$), 1.39-1.49 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.60-1.70 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 1.78-1.86 (1H, m, CH$_a\underline{H}_b$ C-4 THF), 1.89-2.07 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.59 (3H, s, SCH_3), 4.15 (1H, dtd, *J* 8.9 7.1, 5.2, CH C-2 THF), 4.55 (1H, q, *J* 7.2, C-5 THF), 6.51 (1H, d, *J* 7.1, HCOC), 7.32-7.44 (8H, m, Ar), 7.59-7.61 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 19.0 (SMe), 23.5 ($SiCH_2$), 29.0 (CH_2, C-4 THF), 35.2 (CH_2, C-3 THF), 77.7 (CH, C-2 THF), 79.7 (CH, C-5 THF), 86.7 (H$\underline{C}$OC), 127.9 (CH, Ar), 128.1 (CH, Ar), 128.5 (2 overlapping CH, Ar), 129.0 (CH, Ar), 133.8 (CH, Ar), 136.7 (CH, Ar), 139.2 (C, Ar), 214.9 (O$\underline{C}$S$_2$Me); Minor Diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.34 (3H, s, $SiCH_3$), 0.35 (3H, s, $SiCH_3$), 1.09 (1H, dd, *J* 14.5 and 6.8, SiC$\underline{H}_a$H$_b$), 1.29 (1H, dd, *J* 14.5 and 7.0, SiCH$_a\underline{H}_b$), 1.39-1.49 (1H, m, C$\underline{H}_a$H$_b$ C-3 THF), 1.89-2.07 (3H, m, CH$_a\underline{H}_b$ C-3 and CH_2 C-4 THF), 2.59 (1H, s, SCH_3), 4.02-4.09 (1H, m, CH C-2 THF), 4.49 (1H, td, *J* 7.1 and 4.7, CH C-5 THF), 6.61 (1H, d, *J* 4.7, $\underline{H}$COC), 7.32-7.44 (8H, m, Ar), 7.54-7.57 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.4 ($SiCH_3$), −2.3 ($SiCH_3$), 19.1 (SMe), 23.7 ($SiCH_2$), 28.1 (CH_2, C-4 THF), 35.0 (CH_2, C-3 THF), 78.1 (CH, C-2 THF), 80.0 (CH, C-5 THF), 86.1 (COH), 127.6 (CH, Ar), 127.8 (CH, Ar), 128.2 (CH, Ar), 128.4 (CH, Ar), 129.0 (CH, Ar), 133.7 (CH, Ar), 139.2 (C, Ar), 214.9 (O$\underline{C}$S$_2$Me), one aromatic carbon not visable; HRMS (ESP, *m/z*) 434.1635 $[M+NH_4]^+$, $C_{22}H_{32}O_2NSSi$ requires 434.1638. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the $\underline{H}$COH proton at 6.51 (major diastereoisomer) and 6,61 ppm (minor diastereoisomer).

JD-08-446 C3 F17-23



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======== CHANNEL f1 ========
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SI                  32768
SF            400.2300127 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
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PC                   1.00
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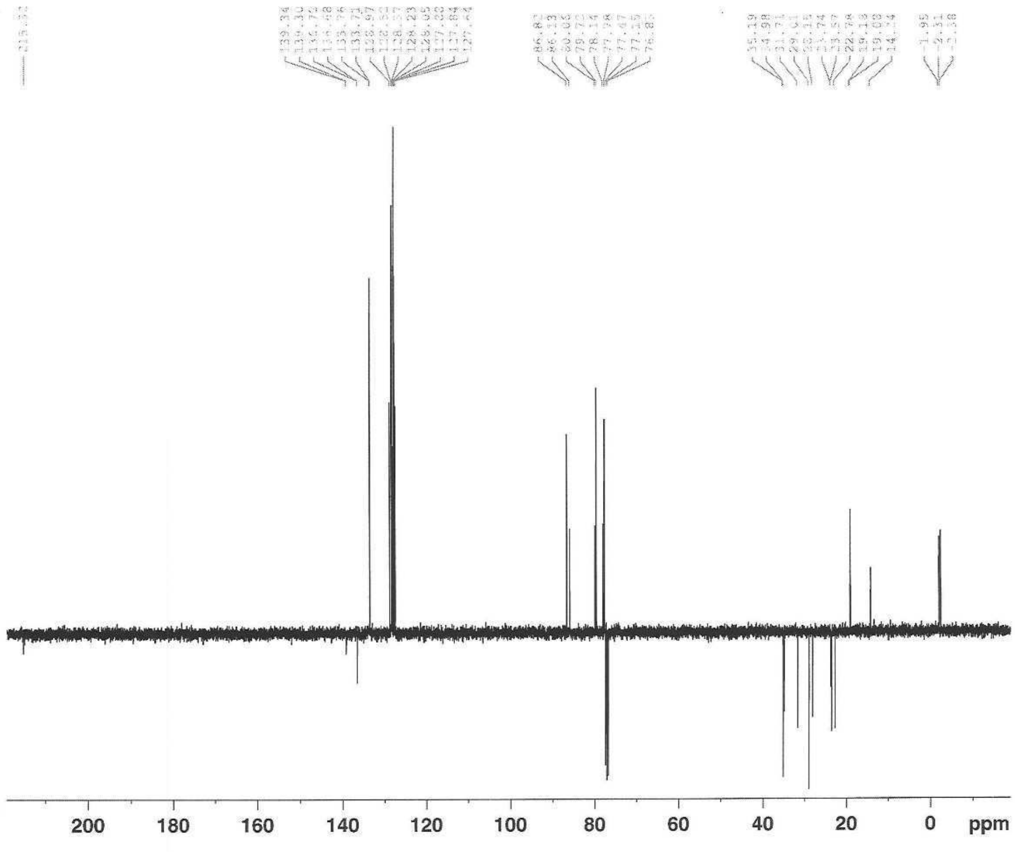
JD-08-446 C3 F17-23



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PROCNO                  1
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NS                    256
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SWH             23980.814 Hz
FIDRES           0.365918 Hz
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RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

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NUC1                  13C
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P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

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NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379031 MHz
WDW                    EM
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GB                      0
PC                   1.40
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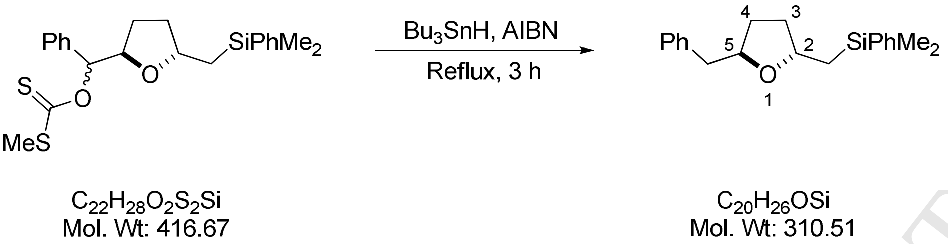
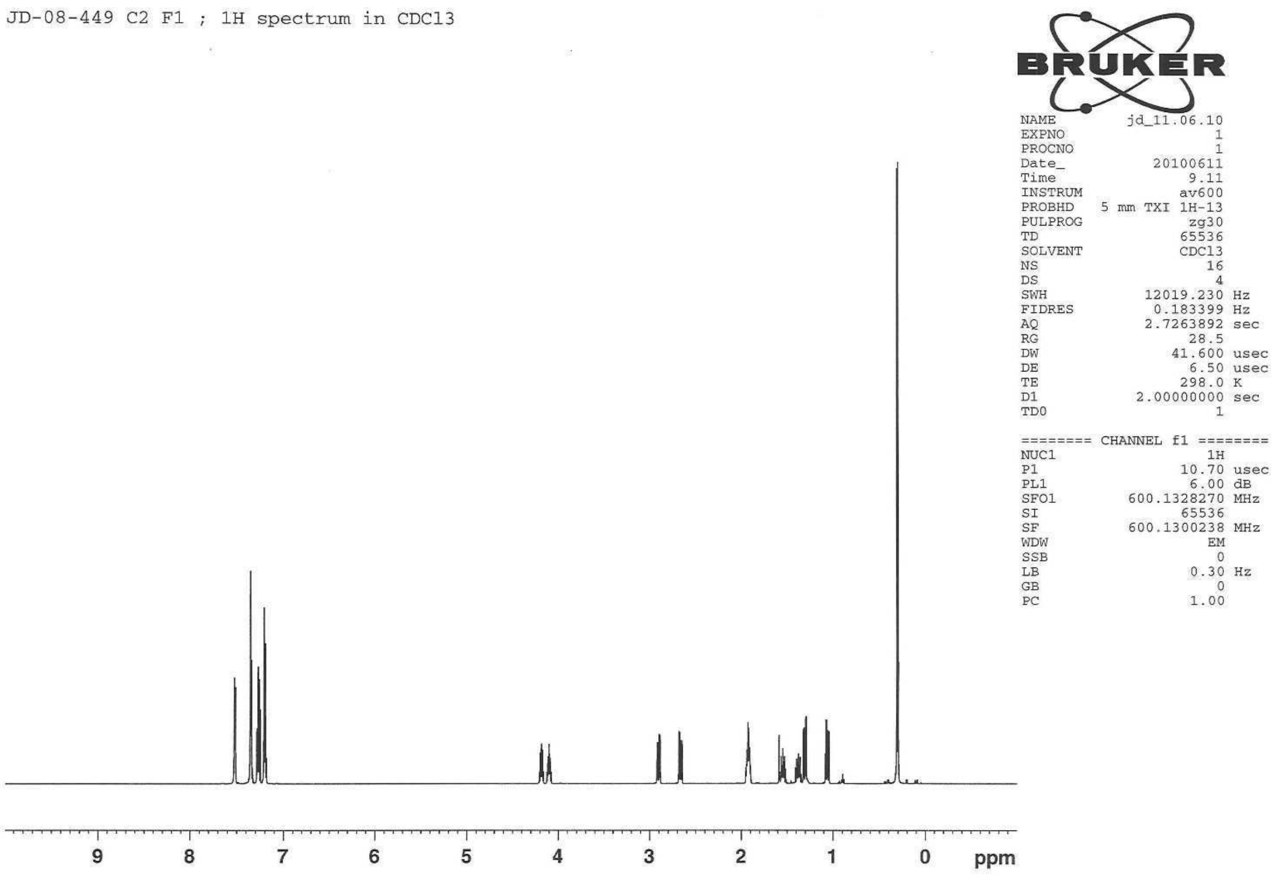
(±)-((5-Benzyltetrahydrofuran-2-yl)methyl)dimethyl(phenyl)silane (25)



A stirred solution of *O*-(5-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-2-yl)(phenyl)methyl-*S*-methyl carbonodithioate (0.20 g, 0.48 mmol) and tri-*n*-butyltin hydride (0.67 mL, 2.50 mmol) in toluene (5.5 mL) was degassed with nitrogen. To the reaction mixture at reflux temperature was added portionwise AIBN (3 × 0.005 g, 0.05 mmol, 10 mol%), after 3 h the reaction was cooled and concentrated *in vacuo* to yield the impure product as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethylether : hexane] afforded the title compound as a single diastereoisomer (0.13 g, 0.40 mmol, 84%) as a colourless oil (Found: C, 77.1; H, 8.4. $C_{20}H_{26}OSi$ requires C, 77.4; H, 8.4%); R_f 0.4 [10% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2957, 1247, 1112, 1074, 835, 819; δ_H (600 MHz; $CDCl_3$) 0.31 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.09 (1H, dd, *J* 14.2 and 8.1, $SiC\underline{H}_aH_b$), 1.32 (1H, dd, *J* 14.2 and 6.3, $SiCH_a\underline{H}_b$), 1.35-1.41 (1H, m, $C\underline{H}_aH_b$ C-3 THF), 1.52-1.58 (1H, m, $C\underline{H}_aH_b$ C-4 THF), 1.90-1.96 (2H, m, overlapping signals $CH_a\underline{H}_b$ C-4 and $CH_a\underline{H}_b$ C-3 THF), 2.67 (1H, dd, *J* 13.5 and 6.8, $PhC\underline{H}_aH_b$), 2.91 (1H, dd, *J* 13.5 and 6.2, $PhCH_a\underline{H}_b$), 4.11 (1H, app tt, *J* 8.2 and 5.8, CH C-2 THF), 4.55 (1H, app dq, *J* 7.9 and 6.4, CH C-5 THF), 7.19-7.21 (3H, m, Ar), 7.26-7.31 (2H, m, Ar), 7.33-7.37 (3H, m, Ar), 7.52-54 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.2 ($SiCH_3$), −1.9 ($SiCH_3$), 24.2 ($SiCH_2$), 32.2 (CH_2, C-4 THF), 35.0 (CH_2, C-3 THF), 42.5 ($PhCH_2$), 76.7 (CH, C-2 THF), 78.9 (CH, C-5 THF), 126.2 (CH, Ar), 127.9 (CH, Ar), 128.3 (CH, Ar), 129.0 (CH, Ar), 129.4 (CH, Ar), 133.8 (CH, Ar), 139.2 (C, Ar), 139.4 (C, Ar); LRMS (EI^+, *m/z*): M^+ not visible, 295 ($[M-Me]^+$, 2%), 233 (4), 219 (19), 135 (100), 105 (6), 91 (20), 75 (20); HRMS (ESP, *m/z*) 328.2093 $[M+NH_4]^+$, $C_{20}H_{30}ONSi$ requires 328.2091.



JD-08-449 C2 F1 ; 1H spectrum in CDCl3

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PROCNO                    1
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TD                    65536
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FIDRES             0.183399 Hz
AQ                2.7263892 sec
RG                     28.5
DW                   41.600 usec
DE                     6.50 usec
TE                    298.0 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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SSB                       0
LB                     0.30 Hz
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PC                     1.00
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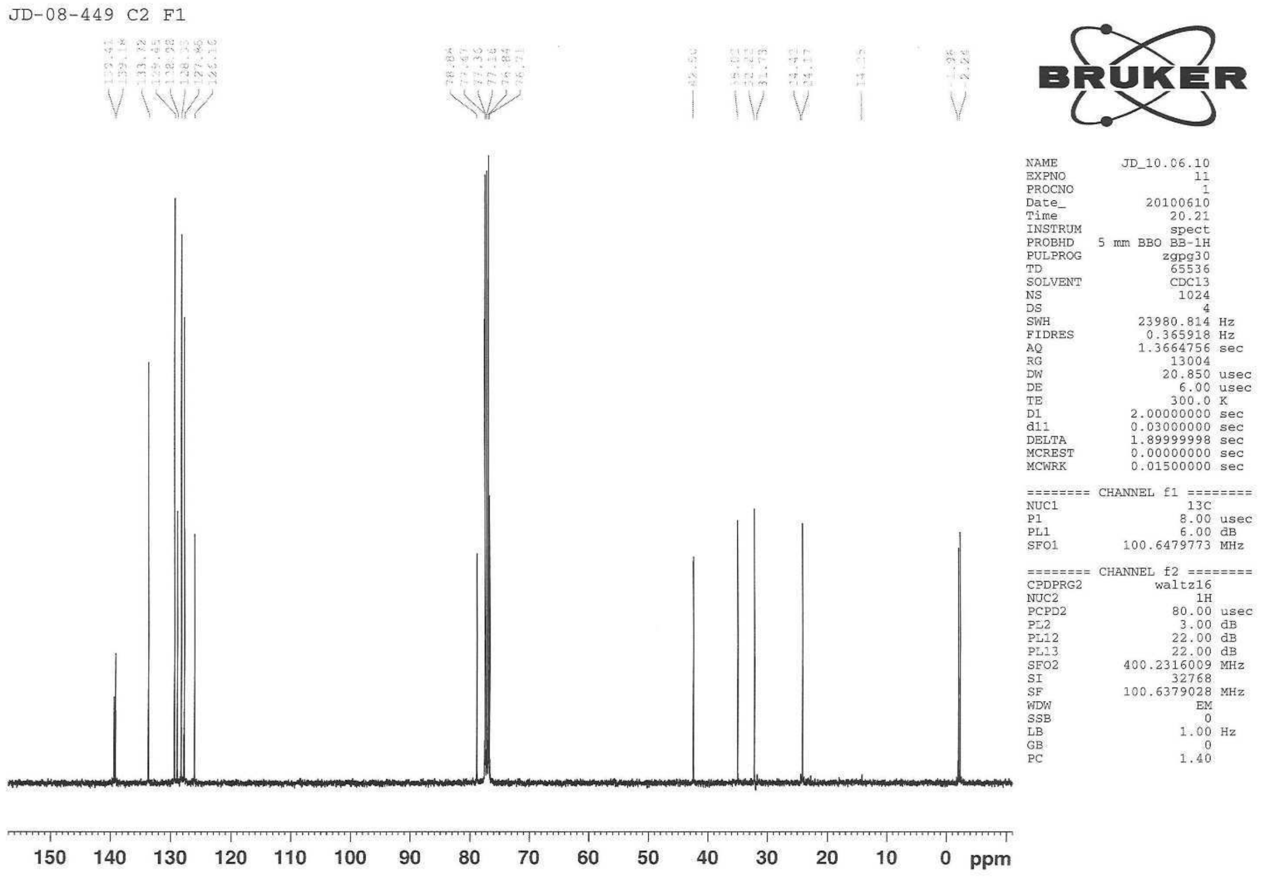

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PROCNO                  1
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FIDRES           0.365918 Hz
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RG                  13004
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
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d11            0.03000000 sec
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MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379028 MHz
WDW                    EM
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LB                   1.00 Hz
GB                      0
PC                   1.40
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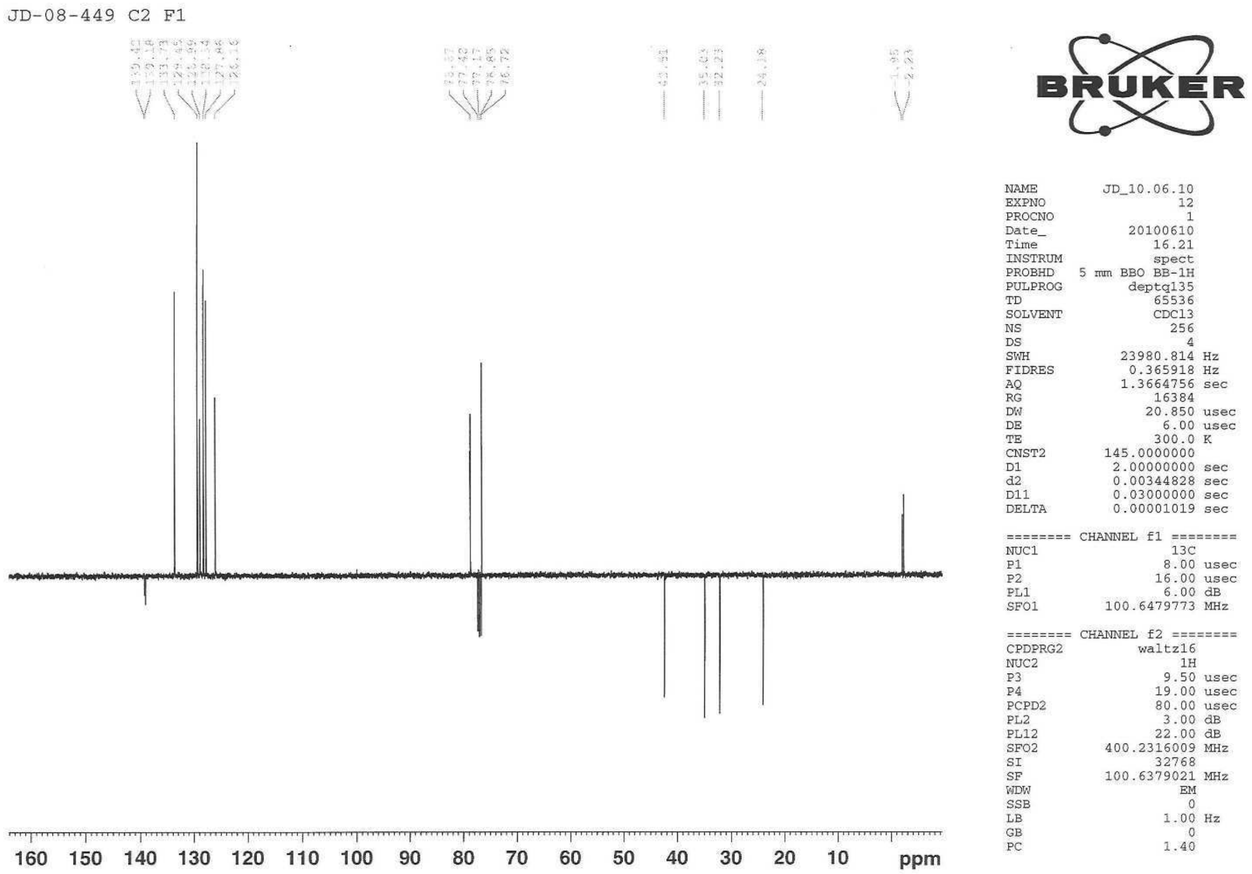

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SOLVENT             CDCl3
NS                    256
DS                      4
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FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379021 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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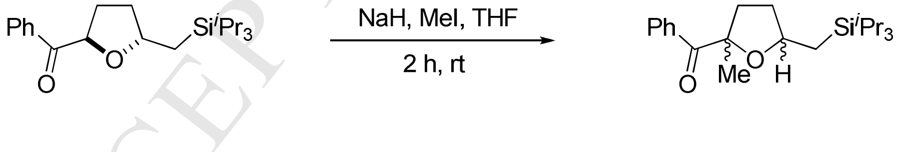
(±)-(2-Methyl-5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (26)

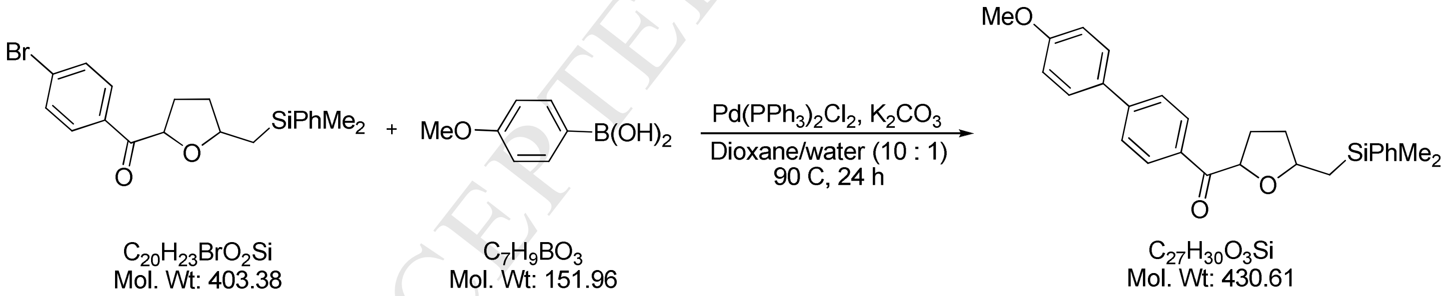


$C_{21}H_{34}O_2Si$
Mol. Wt: 346.58

$C_{22}H_{36}O_2Si$
Mol. Wt: 360.61

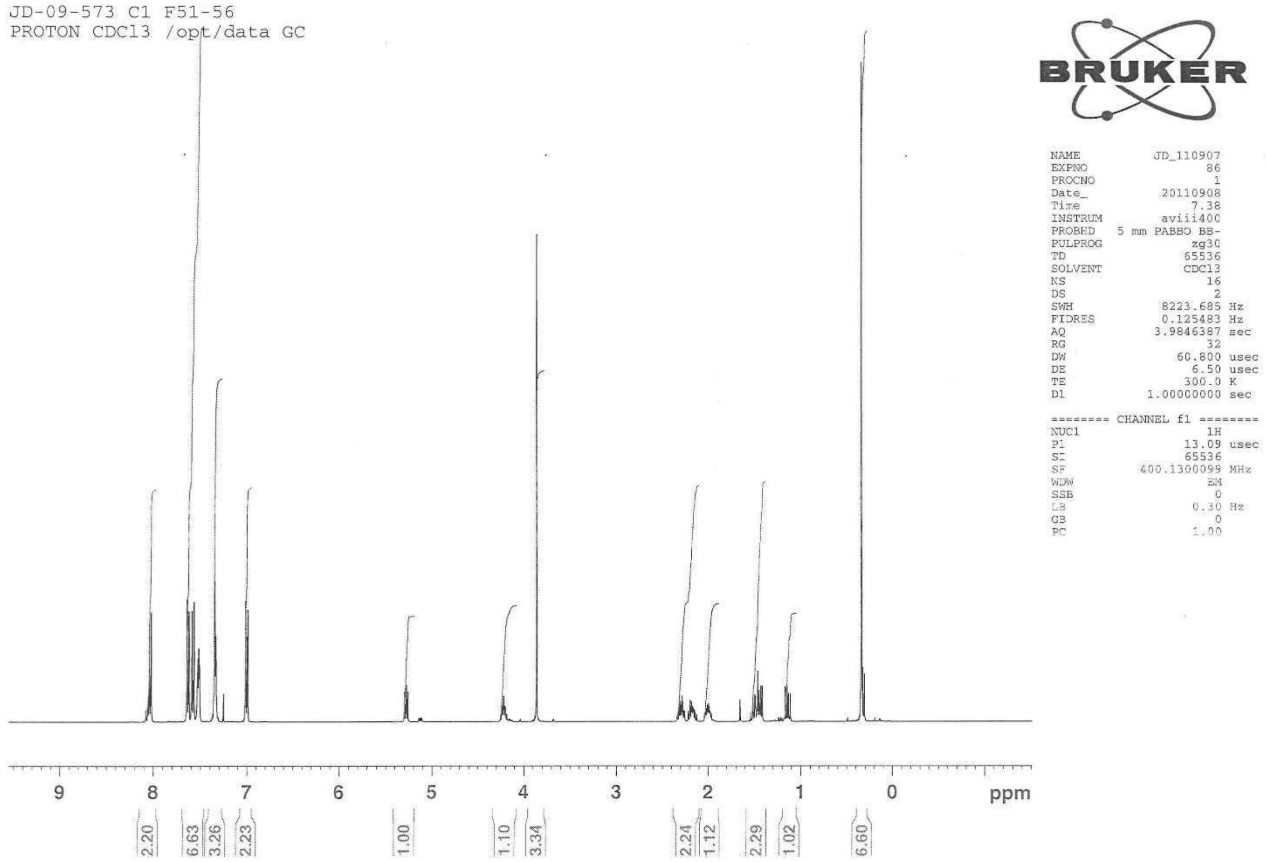
A 60% dispersion of sodium hydride in mineral oil (0.03 g, 0.83 mmol) was washed with *n*-hexane (2 × 2 mL), dried under reduced pressure and placed under an atmosphere of argon. The residue was suspended in THF (1.5 mL) followed by the dropwise addition of a solution of phenyl(5-((triisopropylsilyl)methyl)tetrahydrofuran-2-yl)methanone (0.19 g, 0.55 mmol) in THF (1 mL). After effervescence had ceased and the reaction had become yellow, diiodomethane (0.12 g, 0.05 mL, 0.83 mmol) was added and the reaction stirred for 2 h at room temperature and monitored by TLC. The reaction was quenched with 0.1 M HCl (10 mL), neutralised with saturated aqueous sodium hydrogen carbonate solution (10 mL) and the organic layer separated. The aqueous layer was extracted with DCM (3 × 10 mL). The organic fractions were combined, washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a pale yellow oil (0.16 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded a inseparable diastereoisomeric mixture of compound (combined yield 0.15 g, 0.42 mmol, 76%, *dr* 1.5 : 1) as a colourless oil; R_f 0.53 [10% diethyl ether : hexane]; ν_{max}(film)/cm^{-1} 2941, 2864, 1681, 1462, 1091, 882; Major Diastereoisomer: δ_H (600 MHz; $CDCl_3$) 0.97 (1H, dd, *J* 14.6 and 7.2, $\mathrm{SiC\underline{H}_aH_b}$), 1.92-1.12 (22H, m, overlapping signals $^{i}\underline{\mathrm{Pr}_3}\mathrm{SiCH_a\underline{H_b}}$), 1.43 (1H, ddt, *J* 12.1 10.2 and 8.3, $\mathrm{C\underline{H}_aH_b}$ C-4 THF), 1.55 (3H, s, Me) 1.79 (1H, ddd, *J* 12.8 10.2 and 7.5, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 2.06 (1H, dddd, *J* 12.1 7.6 5.4 and 3.1, $\mathrm{CH_a\underline{H}_b}$ C-4 THF), 2.82 (1H, ddd, *J* 12.8 8.1 and 3.1, $\mathrm{CH_a\underline{H}_b}$ C-3 THF), 4.36 (1H, dddd, *J* 8.9 7.2 6.8 and 5.4, CH C-5 THF), 7.37-7.40 (2H, m, *m*-CH Ph), 7.47-7.51 (1H, m, *p*-CH Ph), 8.19 (2H, dd, *J* 8.4 and 1.3, *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.3 (3 × CH $\mathrm{Si^{\mathit{i}}Pr_3}$), 17.4 ($SiCH_2$), 18.9 (6 × CH_3 $\mathrm{Si^{\mathit{i}}Pr_3}$), 26.4 ($CH_3$), 35.2 ($CH_2$, C-4 THF), 37.1 ($CH_2$, C-3 THF), 78.8 (CH, C-5 THF), 88.9 (CH, C-2 THF), 127.9 (2 × *m*-CH, Ph), 130.6 (2 × *o*-CH, Ph), 132.4 (*p*-CH, Ph), 135.4 (C, Ph), 203.0 (C=O); Minor Diastereoisomer: δ_H (600 MHz; $CDCl_3$) 1.92-1.12 (22H, m, overlapping signals $^{i}\underline{\mathrm{Pr}_3}\mathrm{SiCH_a\underline{H_b}}$), 1.14 (1H, dd, *J* 14.5 and 7.0, $\mathrm{SiCH_a\underline{H}_b}$) 1.59-1.60 (1H, m, C-4 THF), 1.61 (3H, s, Me) 1.83 (1H, ddd, *J* 12.7 9.1 and 5.0, $\mathrm{C\underline{H}_aH_b}$ C-3 THF), 1.98-2.03 (1H, m, $\mathrm{C\underline{H}_aH_b}$ C-4 THF), 2.67 (1H, dt, *J* 12.7 and 8.1, $\mathrm{CH_a\underline{H}_b}$ C-3 THF), 3.94 (1H, m, C-5 THF), 7.37-7.40 (2H, m, *m*-CH, Ph), 7.47-7.51 (1H, m, *p*-CH, Ph), 8.17 (2H, dd, *J* 8.4 and 1.2, *o*-CH Ph); δ_C (100.6 MHz; $CDCl_3$) 11.4 (3 × CH $\mathrm{Si^{\mathit{i}}Pr_3}$), 17.8 ($SiCH_2$), 18.9 (6 × CH_3 $\mathrm{Si^{\mathit{i}}Pr_3}$), 27.0 ($CH_3$), 34.7 ($CH_2$, C-4 THF), 36.2 ($CH_2$, C-3 THF), 78.4 (CH, C-5 THF), 88.9 (CH, C-2 THF), 128.0 (2 × *m*-CH, Ph), 130.1 (2 × *o*-CH, Ph), 132.5 (*p*-CH, Ph), 135.2 (C, Ph), 204.9 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 317 ($[M-{}^{i}Pr]^+$, 70%), 255 (100), 157 (59), 115 (65), 105 (67), 91 (27), 77 (32); HRMS (ESP, *m/z*) 361.2554 $[M+NH_4]^+$, $C_{22}H_{37}O_2Si$ requires 361.2557. Diastereoselectivity calculated by analysis of the ^1H NMR integrals for the C-5 protons of the THF ring, 4.36 (major diastereoisomer) and 3.94 ppm (minor diastereoisomer).

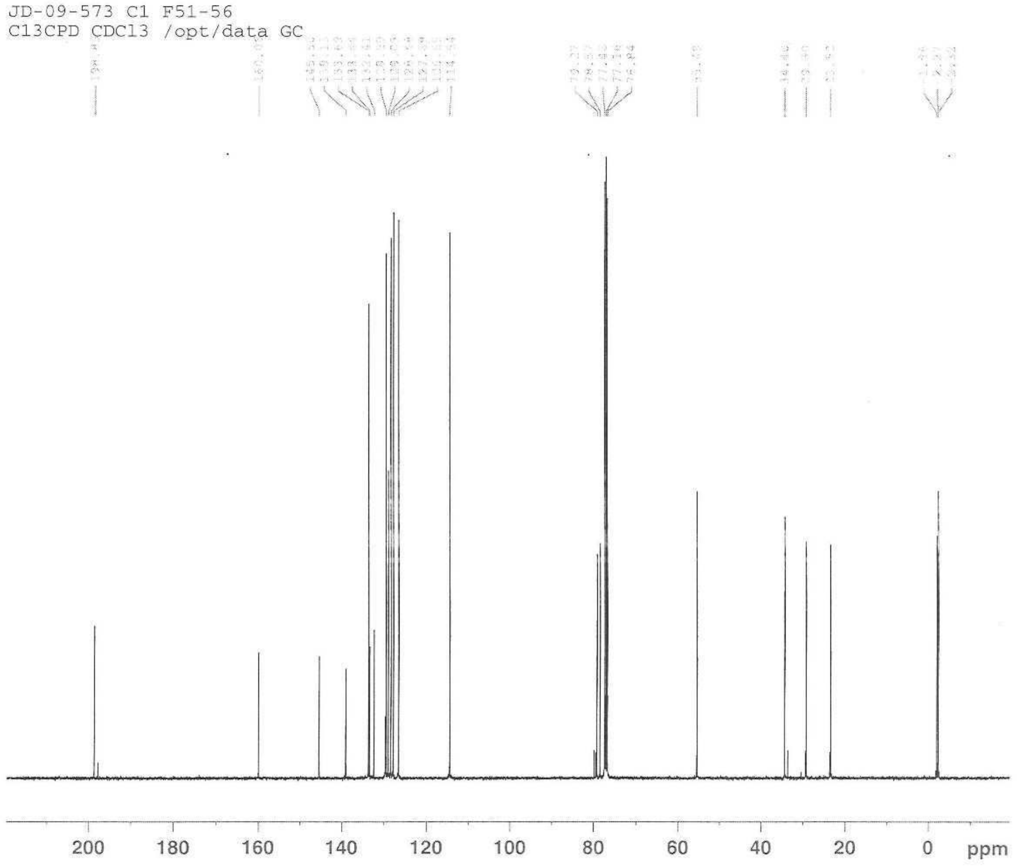
(±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4'-methoxybiphenyl-4-yl)methanone (27)



To a stirred mixture of 4-methyloxyphenyl borinic acid (0.034 g, 0.22 mmol), potassium carbonate (0.041 g, 0.30 mmol), (±)-2-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-5-yl)(4-bromophenyl)methanone (0.060 g, 0.15 mmol, *trans* diastereoisomer) in dioxane/water (10 : 1, 1.5 mL) was added and bis(triphenylphosphine)palladium dichloride (0.021 g, 0.03 mmol). The resulting mixture was degassed with nitrogen, heated at 90 °C and monitored by TLC. After 24 h the reaction was diluted with diethyl ether and filtered through a pad of silica washing with diethyl ether (2 × 10 mL). The filtrate was concentrated *in vacuo* to give the impure product as a brown oil (0.14 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as a white solid (0.053 g, 0.12 mmol, 82%, *dr* (*trans* : *cis*) 1 : 0.08); R_f 0.17 [20% diethyl ether : hexane]; mp 179-183 °C (hexane); ν_{max}(film)/cm^{-1} 2953, 1687 (C=O), 1599, 1248, 1180, 1112, 820 (Si-C), 726; *trans* diastereoisomer: δ_H (400 MHz; $CDCl_3$) 0.35 (6H, s, $Si(CH_3)_2$), 1.14 (1H, dd, *J* 14.2 and 8.1, $\mathrm{SiC\underline{H}_aH_b}$), 1.44 (1H, dd, *J* 14.2 and 6.2, $\mathrm{SiCH_a\underline{H}_b}$), 1.49 (1H, app dq, *J* 11.8 and 8.7, C$\underline{H}_a$H$_b$ C-3 THF), 1.97-2.04 (1H, m, CH$_a\underline{H}_b$ C-3 THF), 2.13-2.23 (1H, m, C$\underline{H}_a$H$_b$ C-4 THF), 2.26-2.34 (1H, m, CH$_a\underline{H}_b$ C-4 THF), 3.87 (3H, s, OMe), 4.18-4.26 (1H, m, CH C-2 THF), 5.28 (1H, dd, *J* 8.0 and 6.8, CH C-5 THF), 7.00 (2H, app d, *J* 8.6, Ar), 7.33-7.36 (3H, m, Ar), 7.51-7.65 (2H, m, Ar), 7.58 (2H, app d, *J* 8.6, Ar), 7.63 (2H, app d, *J* 8.3, Ar), 8.03 (2H, app d, *J* 8.3, Ar); δ_C (100.6 MHz; CDCl$_3$) −2.3 (SiCH$_3$), −2.0 (SiCH$_3$), 23.5 (SiCH$_2$), 29.3 (CH$_2$, C-4 THF), 34.4 (CH$_2$, C-3 THF), 55.5 (OCH$_3$), 78.6 (CH, C-2 THF), 79.3 (CH, C-5 THF), 114.5 (2 × CH, Ar), 126.7 (2 × CH, Ar), 127.9 (2 × CH, Ar), 128.5 (2 × CH, Ar), 129.1 (CH, Ar), 129.6 (2 × CH, Ar), 132.4 (C, Ar), 133.4 (C, Ar), 133.7 (2 × CH, Ar), 139.0 (C, Ar), 145.5 (C, Ar), 160.1 (C, Ar), 198.3 (CO); LRMS (EI$^+$, *m/z*): 430 ([M]$^+$ 7%), 345 (14), 219 (13), 211 (21), 135 (100), 75 (15); HRMS (CI$^+$, *m/z*) 453.1845 [M+Na]$^+$, $C_{27}H_{30}O_3NaSi$ requires 453.1856.

Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the C-5 protons of the THF ring, 5.28 (ppm) and 5.13 (ppm) *trans* and *cis* respectively.





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JD-09-573 C1 F51-56
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FIDRES          0.366798 Hz
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TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec

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SF           100.6127593 MHz
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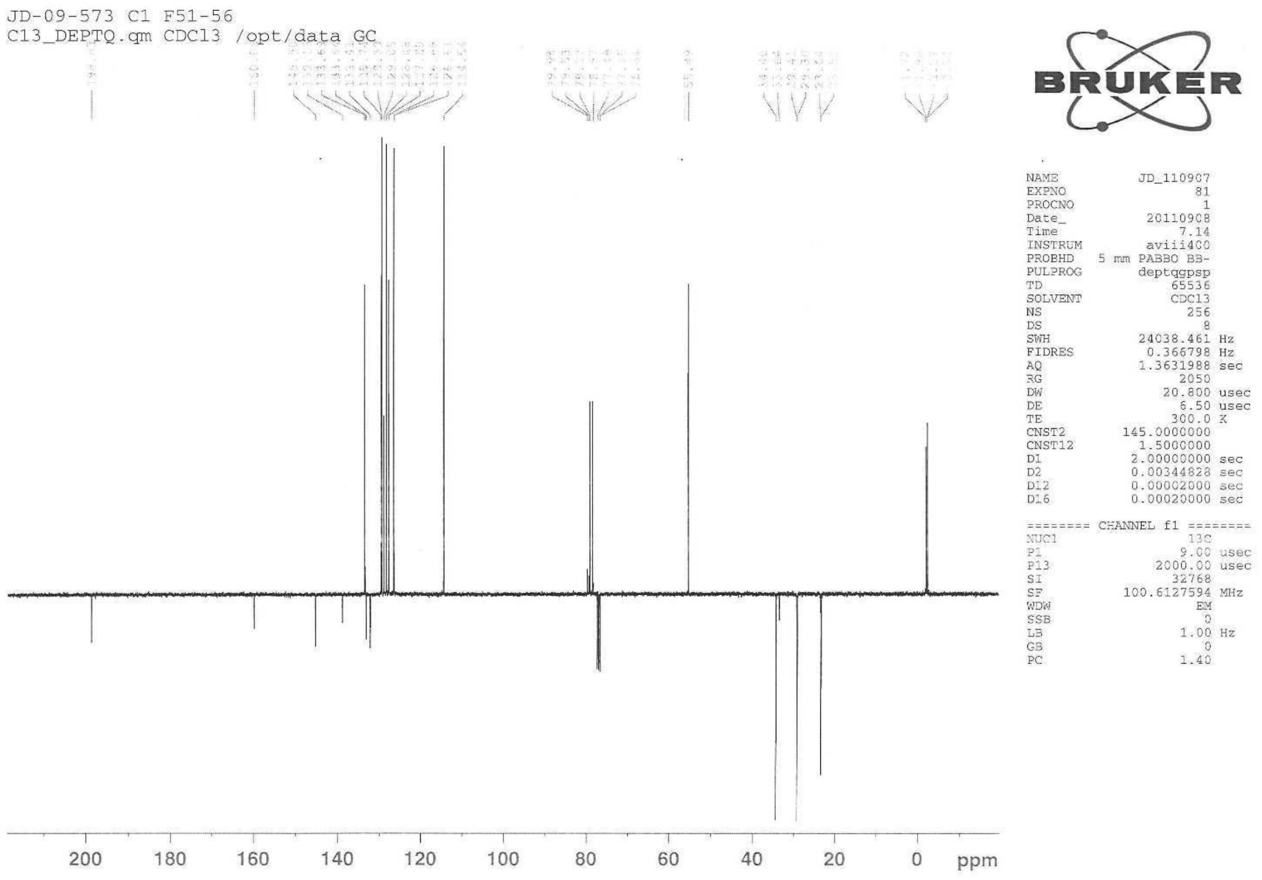

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CNST12          1.5000000
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D12            0.00002000 sec
D16            0.00020000 sec

======== CHANNEL f1 ========
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SI                  32768
SF            100.6127594 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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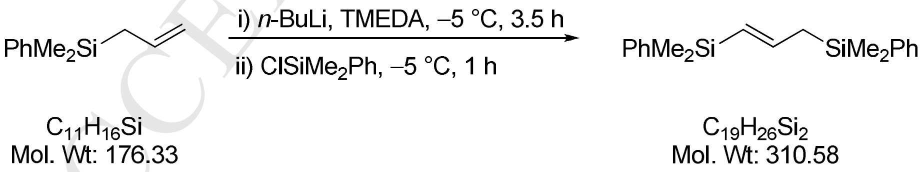
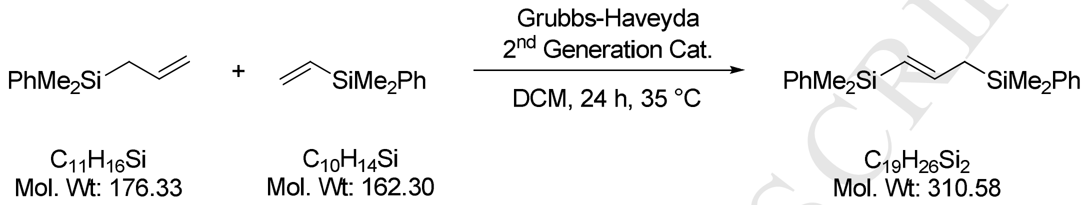
1-Dimethyl(phenyl)silyl-3-dimethy(phenyl)silylpropene (32)

a) by metallation:

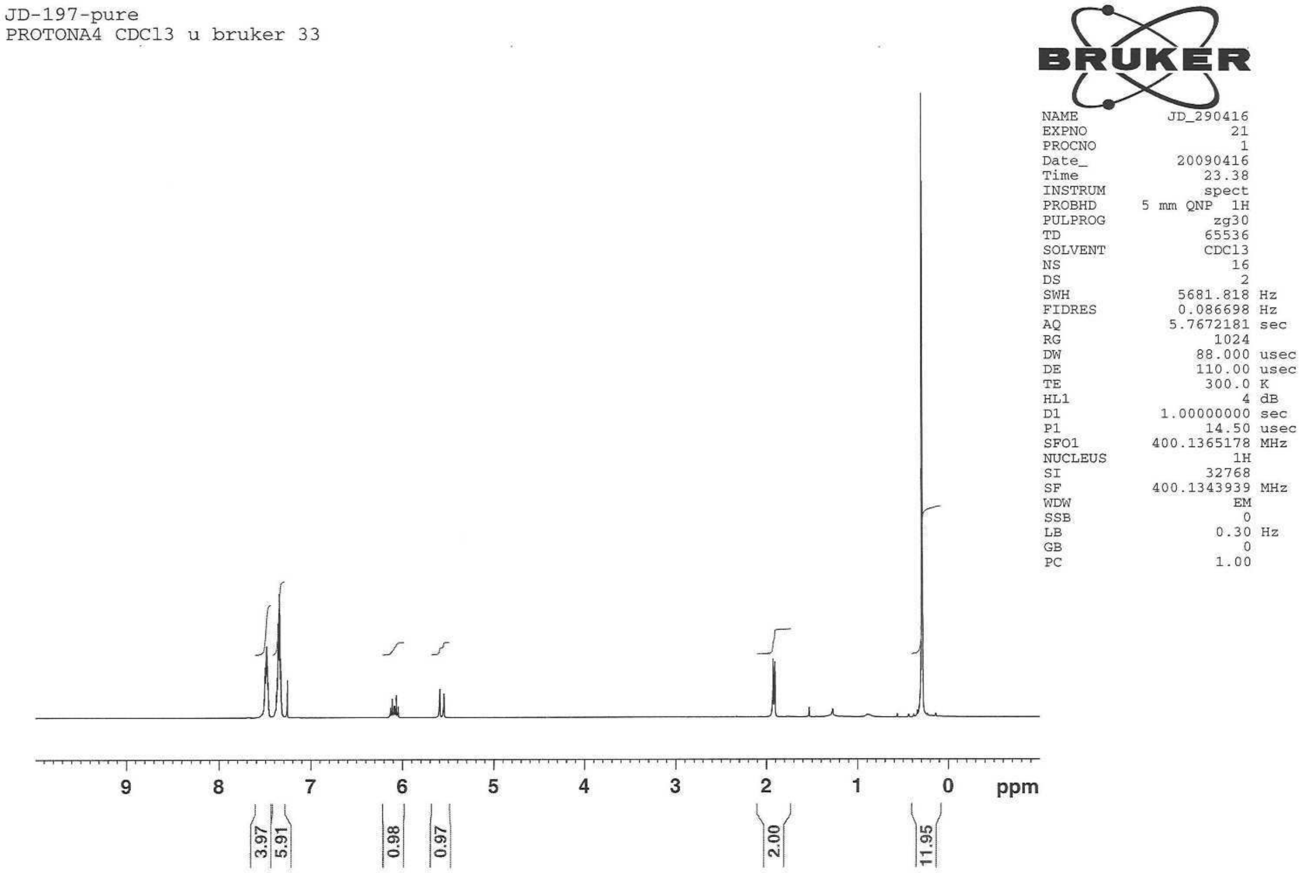


1-Dimethyl(phenyl)silyl-3-dimethy(phenyl)silylpropene was prepared according to the procedure reported by Fleming *et al.* Dimethylphenylsilylpropene (3.52 g, 20.0 mmol) was added dropwise to a stirred mixture of freshly distilled *N*,*N*,*N*,*N*-tetramethylethylenediamine (3.50 mL, 23.0 mmol) and *n*-butyllithium (9.0 mL of a 2.5 M solution in hexane, 22.5 mmol) at −5 °C and the mixture kept at −5 ºC for 3.5 h. Chlorodimethylphenylsilane (3.39 mL, 21.0 mmol) was added dropwise and the mixture was kept at −5 ºC for 1 h (colour changed from orange to yellow), then poured into 1 M HCl (20 mL) and extracted with petroleum spirit (40-60 ºC). The extract was washed with 1 M HCl (20 mL), water (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a pale yellow/brown oil (6.02 g). Purification by flash column chromatography [silica gel, hexane] afforded the desired product (5.35 g, 17.0 mmol, 86%) as a colourless oil; R_f 0.36 [petroleum spirit 40-60 ºC]; ν_{max}(film)/cm^{-1} 3069, 2956, 1603 (C=C), 1486, 1247, 1139, 809; δ_H (400 MHz; $CDCl_3$) 0.29 (6H, s, 2 × CH_3), 0.29 (6H, s, 2 × CH_3), 1.92 (2H, d, *J* 7.8, $C\underline{H}_2CH=CH$), 5.57 (1H, d, *J* 18.4, $CH_2CH=C\underline{H}$), 6.09 (1H, dt, *J* 18.4 and 7.8, $CH_2C\underline{H}=CH$), 7.33-7.40 (6H, m, Ar), 7.47-7.51 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.2 (2 × CH_3), −2.1 (2 × CH_3), 27.9 ($\underline{C}H_2CH=CH$), 126.6 ($CH_2CH=\underline{C}H$), 127.8 (2 × *m*-CH, Ar), 127.9 (2 × *m*-CH, Ar), 128.9 (*p*-CH, Ar), 129.2 (*p*-CH, Ar), 133.8 (2 × *o*-CH, Ar), 134.0 (2 × *o*-CH, Ar), 138.6 (C, Ar), 139.7 (C, Ar), 145.4 ($CH_2\underline{C}H=CH$); LRMS (EI$^+$, *m/z*): 310 (M$^+$, 1%), 295 (2), 197 (17), 160 (32), 135 (100), 105 (10); HRMS (ESP, *m/z*) 311.1651 [M+H]$^+$, $C_{19}H_{27}Si_2$ requires 311.1646.

b) by metathesis:

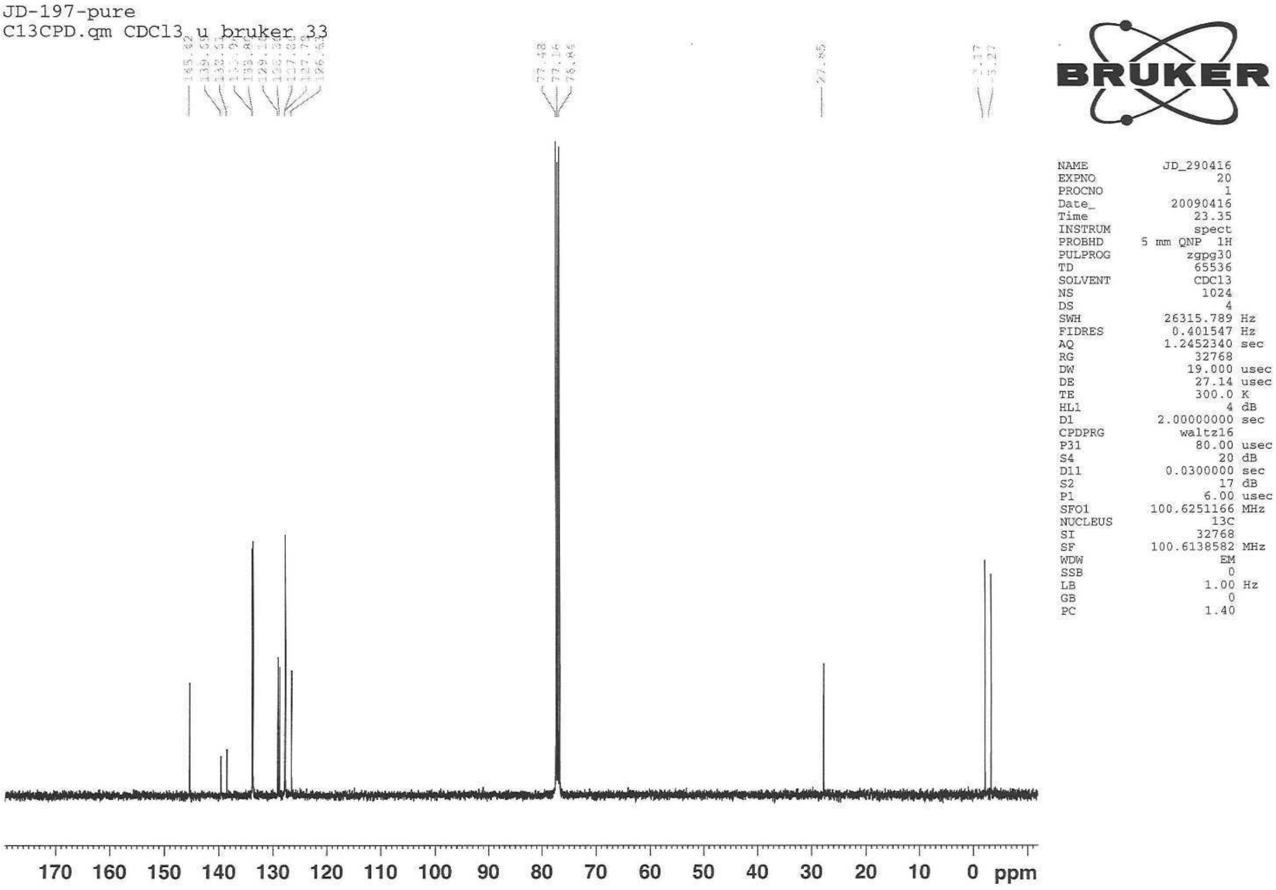


To a stirred mixture of allyldimthylphenylsilane (0.56 g, 3.20 mmol) and vinyldimethylphenylsilane (2.60 g, 16.0 mmol) in argon degassed DCM (10 mL) was added rapidly a solution of (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium (0.10 g, 0.16 mmol, 10 mol%) in DCM (1 mL). The reaction immediately changed colour from green to brown and was heated at 35 °C and monitored by TLC. After 24 h the reaction was concentrated to approximately one quarter of the volume under reduced pressure and filtered through a pad of silica gel eluting with DCM (2 × 100 mL). The filtrate was concentrated *in vacuo* to yield the impure product as a pale green/brown residue (2.24 g). Purification by flash column chromatography [silica gel, hexane] afforded the desired product (0.27 g, 0.87 mmol, 27%, *dr* 17:1 *trans*:*cis*) as a colourless oil; R_f 0.34 [petroleum spirit 40-60 ºC]; *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.29 (6H, s, 2 × CH_3), 0.29 (6H, s, 2 × CH_3), 1.92 (2H, d, *J* 7.8, $C\underline{H}_2CH=CH$), 5.57 (1H, d, *J* 18.4, $CH_2CH=C\underline{H}$), 6.09 (1H, dt, *J* 18.4 and 7.8, $CH_2C\underline{H}=CH$), 7.33-7.40 (6H, m, Ar), 7.47-7.51 (4H, m, Ar); *cis* isomer: 0.31 (6H, s, 2 × CH_3), 0.30 (6H, s, 2 × CH_3), 1.85 (2H, dd, *J* 8.5 and 1.3, $C\underline{H}_2CH=CH$), 5.53 (1H, dt, *J* 13.9, $CH_2CH=C\underline{H}$), 6.46 (1H, dt, *J* 13.9 and 8.5, $CH_2C\underline{H}=CH$), 7.34-7.39 (6H, m, Ar), 7.47-7.58 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.2 (2 × CH_3), −2.1 (2 × CH_3), 27.9 ($\underline{C}H_2CH=CH$), 126.6 ($CH_2CH=\underline{C}H$), 127.8 (2 × *m*-CH, Ar), 127.9 (2 × *m*-CH, Ar), 128.9 (*p*-CH, Ar), 129.2 (*p*-CH, Ar), 133.8 (2 × *o*-CH, Ar), 134.0 (2 × *o*-CH, Ar), 138.6 (C, Ar), 139.7 (C, Ar), 145.4 ($CH_2\underline{C}H=CH$). All other characterisation data the same as above, the ratio of diastereoisomers calculated by analysis of the ^{1}H NMR integrals for the $SiCHC\underline{H}CH$ proton at 6.09 ppm (*trans* diastereoisomer) and 6.46 ppm (*cis* diastereoisomer).



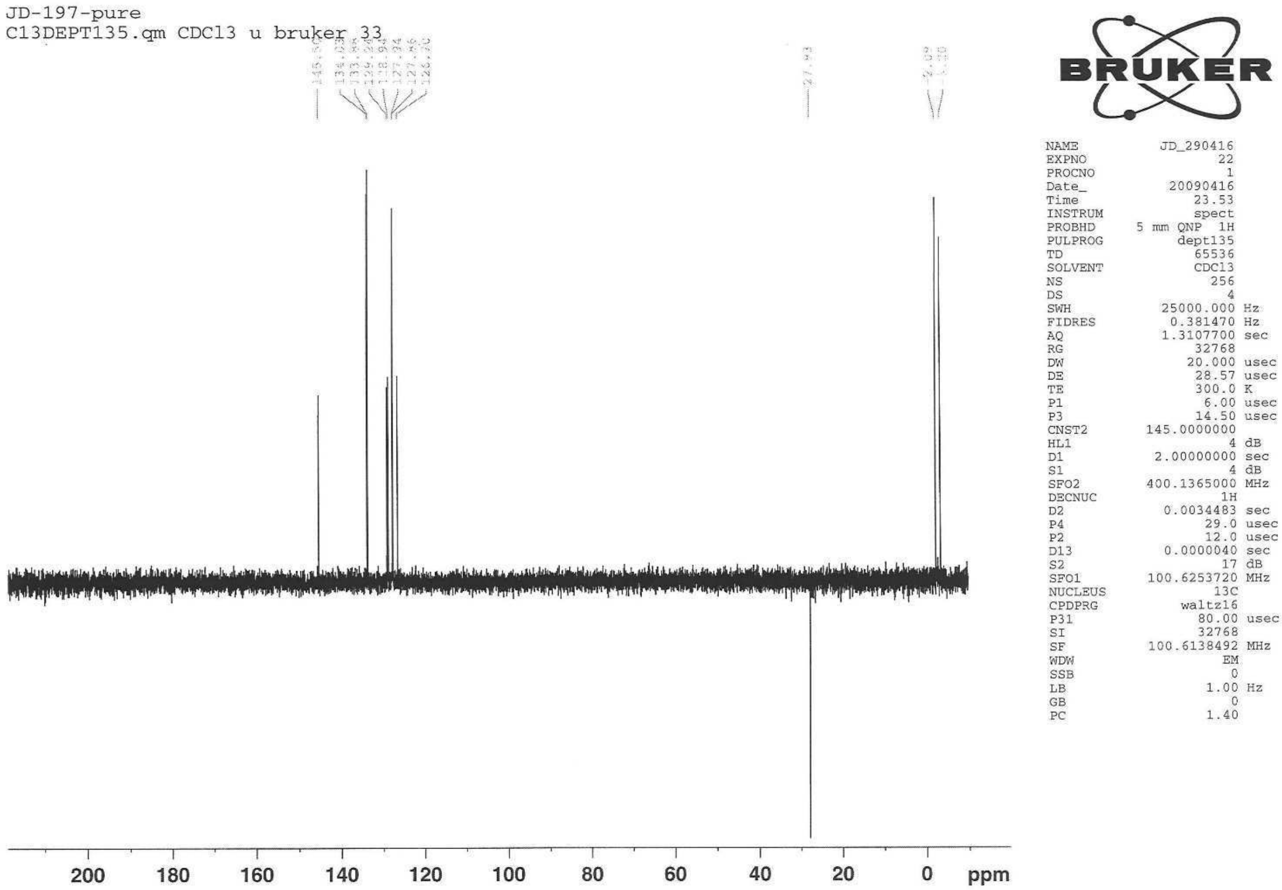
```
JD-197-pure
PROTONA4 CDCl3 u bruker 33
```

```
NAME            JD_290416
EXPNO                  21
PROCNO                  1
Date_            20090416
Time                23.38
INSTRUM             spect
PROBHD       5 mm QNP  1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              5681.818 Hz
FIDRES           0.086698 Hz
AQ              5.7672181 sec
RG                   1024
DW                 88.000 usec
DE                 110.00 usec
TE                  300.0 K
HL1                     4 dB
D1             1.00000000 sec
P1                  14.50 usec
SFO1          400.1365178 MHz
NUCLEUS                1H
SI                  32768
SF            400.1343939 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



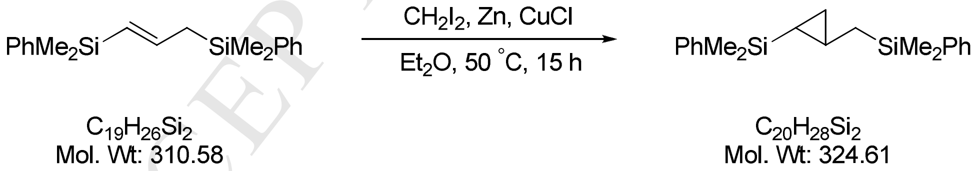
JD-197-pure
C13CPD.qm CDCl3 u bruker 33

```
NAME           JD_290416
EXPNO                 20
PROCNO                 1
Date_           20090416
Time               23.35
INSTRUM            spect
PROBHD    5 mm QNP  1H
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            26315.789 Hz
FIDRES          0.401547 Hz
AQ             1.2452340 sec
RG                 32768
DW                19.000 usec
DE                 27.14 usec
TE                 300.0 K
HL1                    4 dB
D1            2.00000000 sec
CPDPRG           waltz16
P31                80.00 usec
S4                    20 dB
D11           0.0300000 sec
S2                    17 dB
P1                  6.00 usec
SFO1         100.6251166 MHz
NUCLEUS              13C
SI                 32768
SF           100.6138582 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

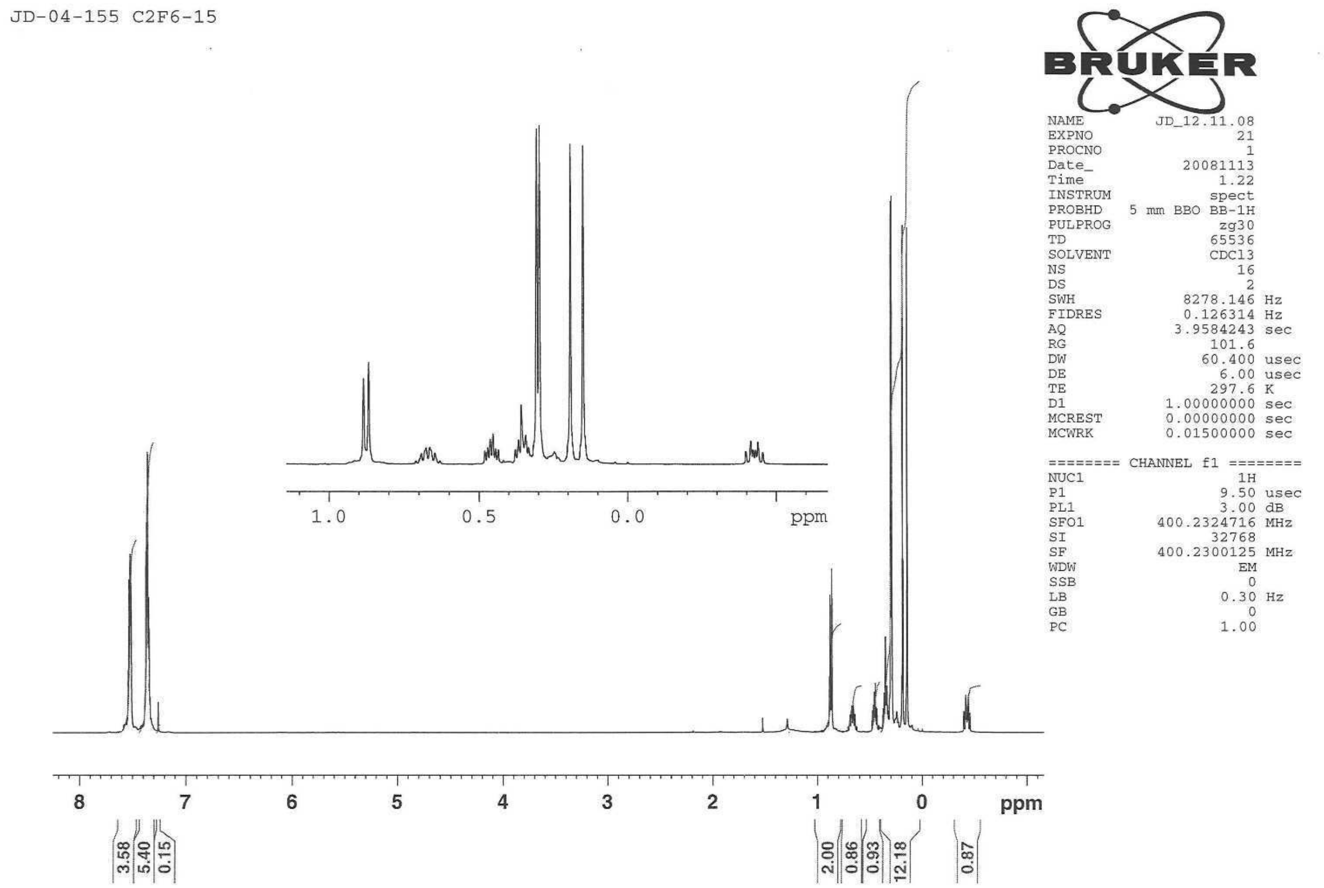


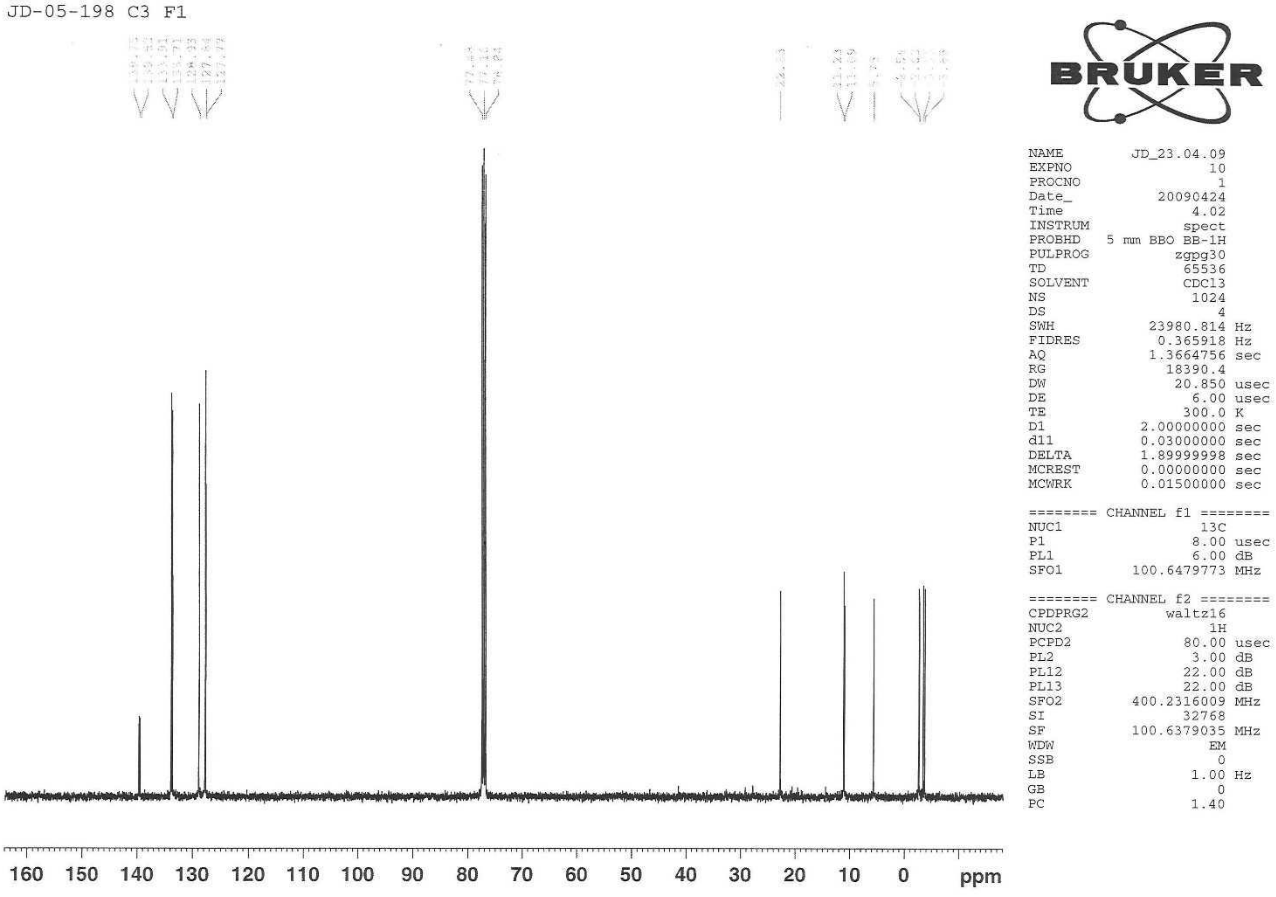
```
NAME            JD_290416
EXPNO                  22
PROCNO                  1
Date_            20090416
Time                23.53
INSTRUM             spect
PROBHD   5 mm QNP  1H
PULPROG          dept135
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             25000.000 Hz
FIDRES           0.381470 Hz
AQ              1.3107700 sec
RG                  32768
DW                 20.000 usec
DE                  28.57 usec
TE                  300.0 K
P1                   6.00 usec
P3                  14.50 usec
CNST2         145.0000000
HL1                     4 dB
D1             2.00000000 sec
S1                      4 dB
SFO2          400.1365000 MHz
DECNUC                 1H
D2              0.0034483 sec
P4                   29.0 usec
P2                   12.0 usec
D13             0.0000040 sec
S2                     17 dB
SFO1          100.6253720 MHz
NUCLEUS               13C
CPDPRG            waltz16
P31                 80.00 usec
SI                  32768
SF            100.6138492 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

(±)-((2-(Dimethyl(phenyl)silyl)cyclopropyl)methyl)dimethyl(phenyl)silane (29)



To a stirred suspension of zinc powder (4.29 g , 65.0 mmol) and copper chloride (6.43 g, 65.0 mmol) in anhydrous diethyl ether (100 mL) which had been heated at reflux temperature for 30 min and allowed to cool to room temperature was added 1-dimethyl(phenyl)silyl-3-dimethy(phenyl)silylpropene (4.03 g, 13.0 mmol) and diiodomethane (6.96 g, 2.09 mL, 26.0 mmol). The reaction was heated at reflux temperature for 24 h, cooled to room temperature and filtered through celite washing with diethyl ether (50 mL). The filtrate was washed with 1M HCl (2 x 30 mL) followed by 10% *w*/*v* aqueous sodium bicarbonate solution until pH 7. The combined aqueous layers were extracted with diethyl ether (3 × 30 mL) and the combine organic layers were washed with brine (20 mL), 10% *w*/*v* aqueous sodium thiosulphate solution (2 × 20 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a colourless oil (4.05 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica (1 : 3) eluting with petroleum ether (40-60 °C) gave the desired product (2.35 g, 7.20 mmol, 56%) as a colourless oil; R_f 0.32 [petroleum ether (40-60 °C]; ν_{max}(film)/cm^{-1} 3068, 3049, 2955, 2896, 1487, 1247, 1113, 828, 806; δ_H (400 MHz; $CDCl_3$) −0.43 (1H, dt, *J* 9.8 and 6.5, SiCH), 0.15 (3H, s, $SiCH_3$), 0.19 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 0.31 (3H, s, $SiCH_3$), 0.33-0.38 (1H, m, $C\underline{H}_aH_b$ cyclopropyl), 0.46 (1H, td, *J* 7.1 and 3.6, $CH_a\underline{H}_b$ cyclopropyl), 0.63-0.71 (1H, m, $SiCH_2C\underline{H}$), 0.88 (2H, d, *J* 6.8, $SiC\underline{H}_2CH$), 7.34-7.37 (6H, m, Ar), 7.51-7.54 (4H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.6 ($SiCH_3$), −3.3 ($SiCH_3$), −2.6 ($SiCH_3$), −2.5 ($SiCH_3$), 5.7 ($PhMe_2Si\underline{C}H$), 11.1 (CH_2 cyclopropyl), 11.2 ($SiCH_2\underline{C}H$), 22.8 ($Si\underline{C}H_2CH$), 127.8 (2 × *m*-CH, Ar), 127.8 (2 × *m*-CH, Ar), 128.9 (2 × *p*-CH, Ar), 133.7 (2 × *o*-CH, Ar), 133.9 (2 × *o*-CH, Ar), 139.5 (C, Ar), 139.7 (C, Ar); LRMS (EI$^+$, *m/z*): 324 (M$^+$, 23%), 271 (24), 197 (16), 174 (20), 135 (100), 112 (9); HRMS (EI, *m/z*) 324.1725 [M]$^+$, $C_{20}H_{28}Si_2$ requires 324.1724.



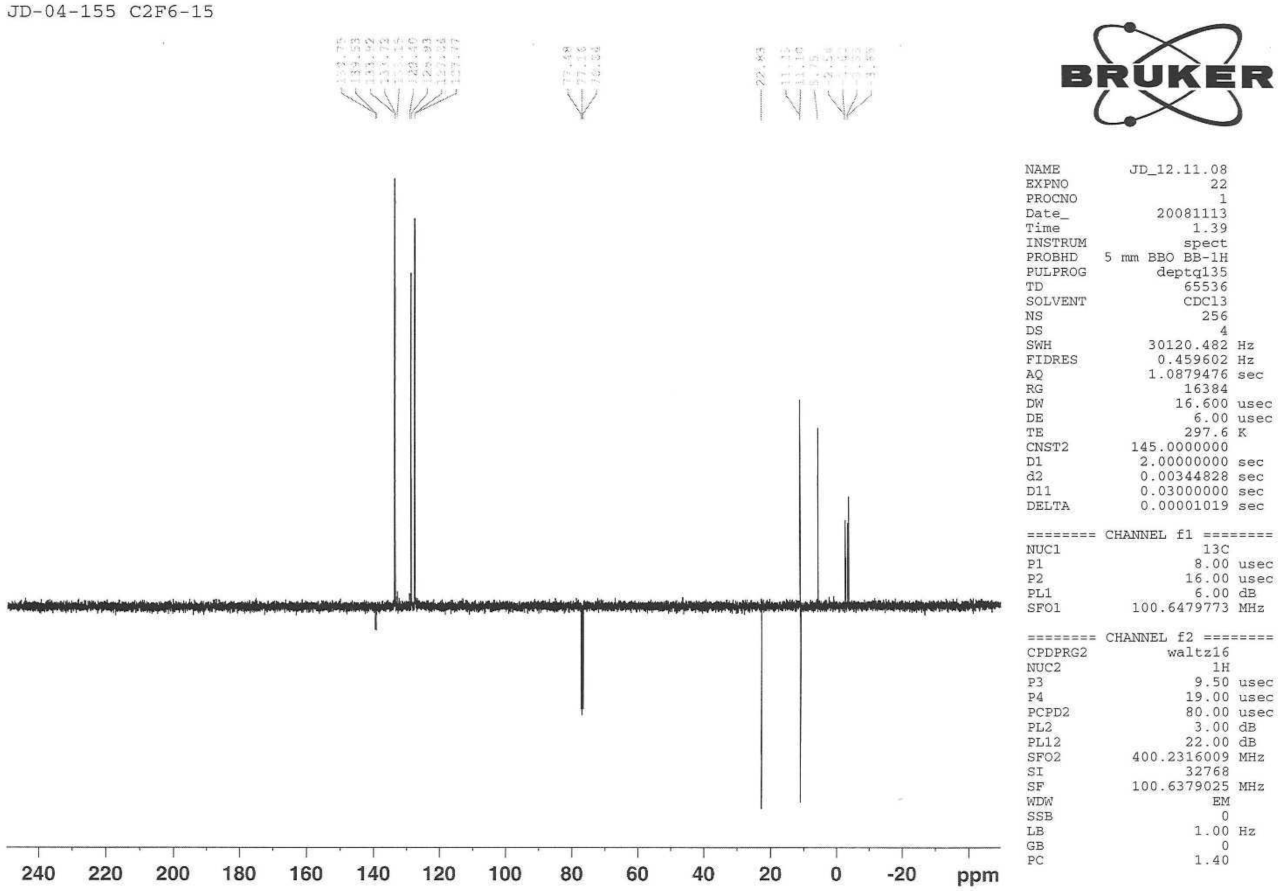


JD-05-198 C3 F1

```
NAME          JD_23.04.09
EXPNO                  10
PROCNO                  1
Date_            20090424
Time                 4.02
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               18390.4
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379035 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

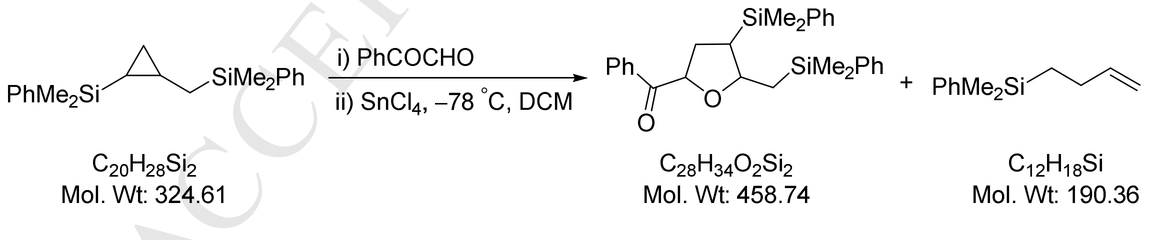


```
NAME          JD_12.11.08
EXPNO                  22
PROCNO                  1
Date_            20081113
Time                 1.39
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG         deptq135
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ             1.0879476 sec
RG                  16384
DW                 16.600 usec
DE                   6.00 usec
TE                  297.6 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

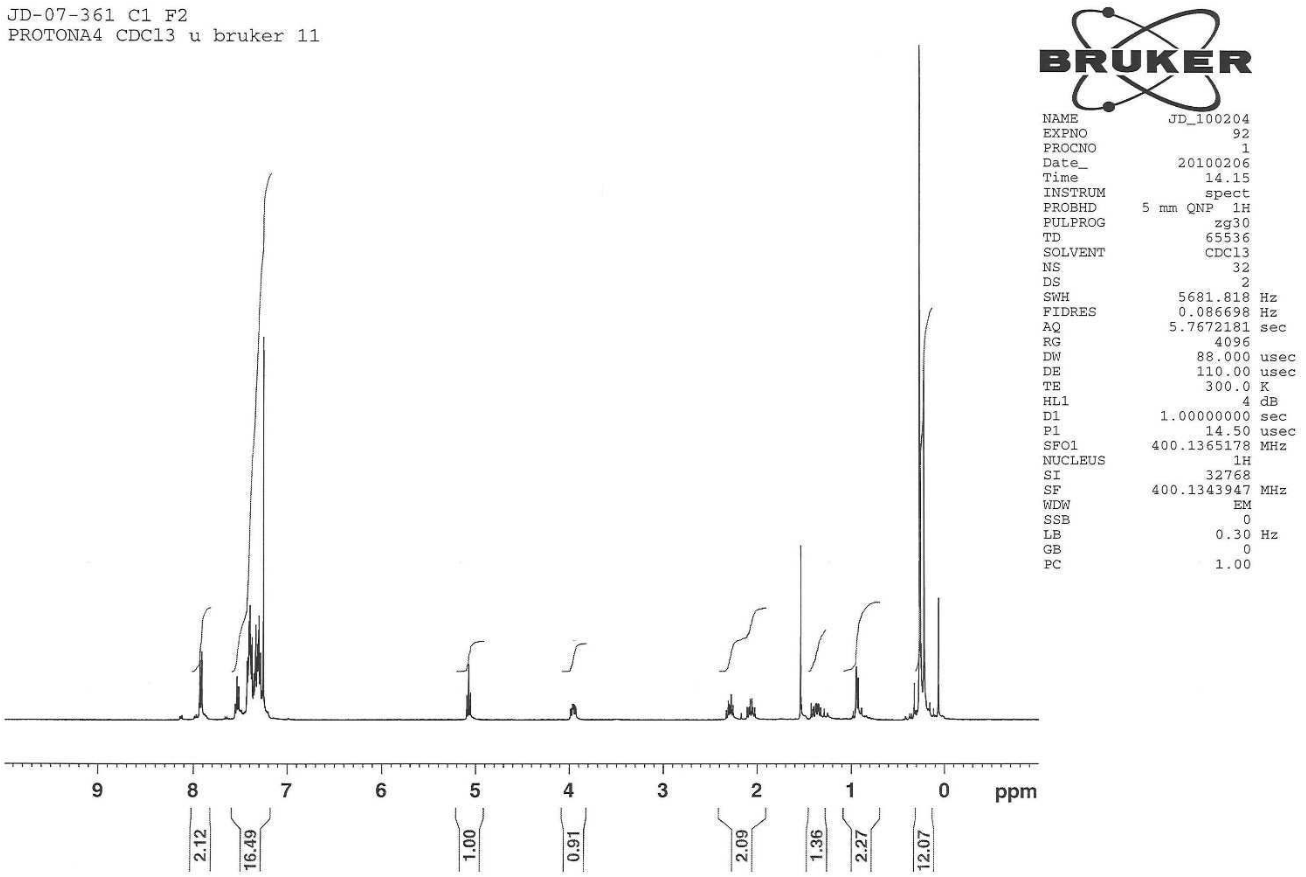
======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379025 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

(±)-(4-(dimethyl(phenyl)silyl)-5-((dimethyl(phenyl)silyl)methyl)tetrahydrofuran-2-yl)(phenyl)methanone (33) and but-3-enyldimethyl(phenyl)silane (35)



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (2 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (2 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of a solution of (±)-((2-(Dimethyl(phenyl)silyl)cyclopropyl)methyl)dimethyl(phenyl)silane (0.19 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 5 h the reaction was quenched by the addition of wet acetone (5 mL) and allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.38 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] afforded the desired product as single diastereoisomer (7 mg, 0.01 mmol, 2%) as a colourless oil; R_f 0.44 [20% diethyl ether : hexane]; δ_H (600 MHz; $CDCl_3$); 0.22 (3H, s, $SiCH_3$), 0.27 (3H, s, $SiCH_3$), 0.27 (6H, s, 2 × CH_3), 0.89-0.98 (2H, m, $SiCH_2$), 1.37 (1H, ddd, *J* 12.1 10.6 and 8.2, CH C-4 THF), 2.07 (1H, app td, *J* 12.5 and 7.7, $C\underline{H}_aH_b$ C-3 THF), 2.30 (1H, app dt, *J* 12.8 and 7.9, $CH_a\underline{H}_b$ C-3 THF), 3.96 (1H, ddd, *J* 10.5 8.7 and 4.1 CH C-5 THF), 5.08 (1H, app t, *J* 7.7, CH C-2 THF), 7.29-7.55 (13H, m, Ar), 7.93 (2H, app dd, *J* 8.4 and 1.3, 2 × *o*-CH -C(O)Ph); δ_C (100.6 MHz; $CDCl_3$) −4.2 ($SiCH_3$), −4.0 ($SiCH_3$), −2.4 ($SiCH_3$), −1.8 ($SiCH_3$), 23.4 ($SiCH_2$), 32.8 (CH_2, C-3 THF), 36.7 (CH, C-4 THF), 79.7 (CH, C-2 THF), 80.8 (CH, C-5 THF), 127.7 (CH, Ar), 128.0 (CH, Ar), 128.5 (CH, Ar), 129.2 (CH, Ar), 129.4 (CH, Ar), 133. 1 (CH, Ar), 133.8 (CH, Ar), 133.9 (CH, Ar), 135.6 (C, Ar), 137. 5 (C, Ar), 139.9 (C, Ar), 199.6 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 353 ($[M{-}PhCO]^+$, 2%), 239 (2), 209 (26), 135 (100), 105 (8), 67 (25); HRMS (ESI, *m/z*) 476.2429 $[M+NH_4]^+$, $C_{28}H_{38}O_2NSi_2$ requires 476.2436.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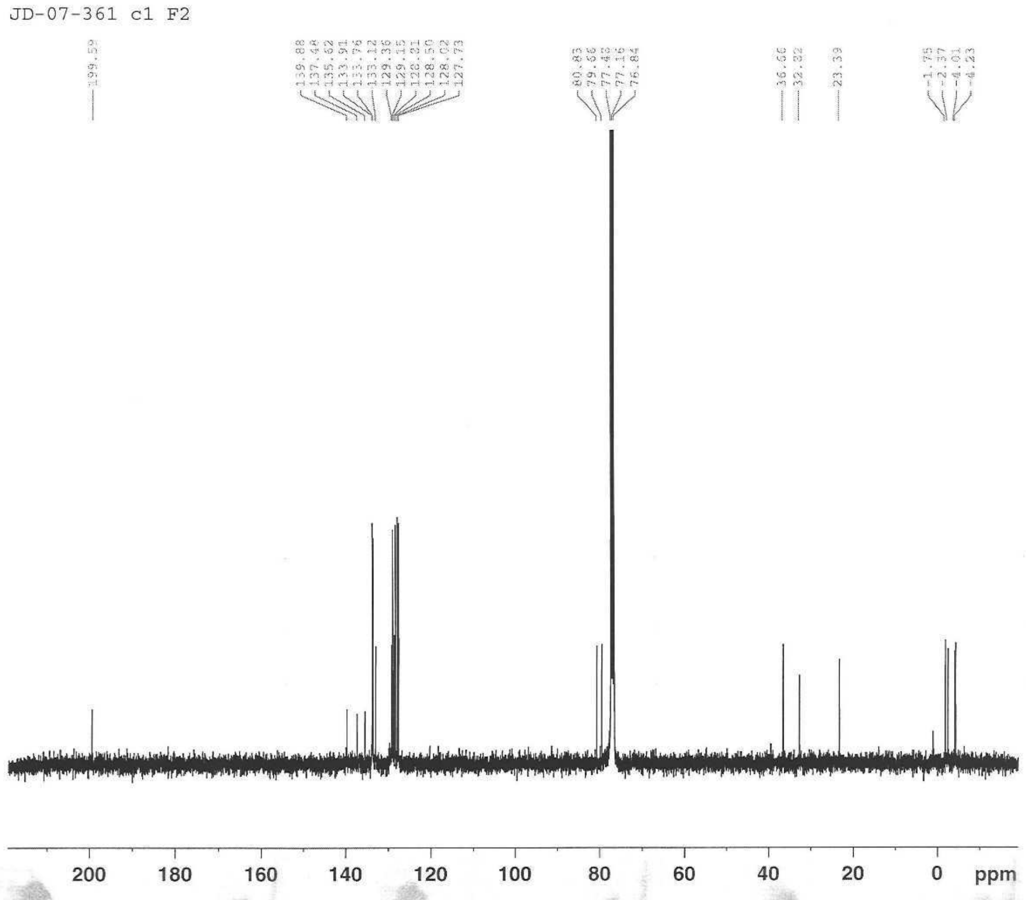
JD-07-361 C1 F2
PROTONA4 CDCl3 u bruker 11
```

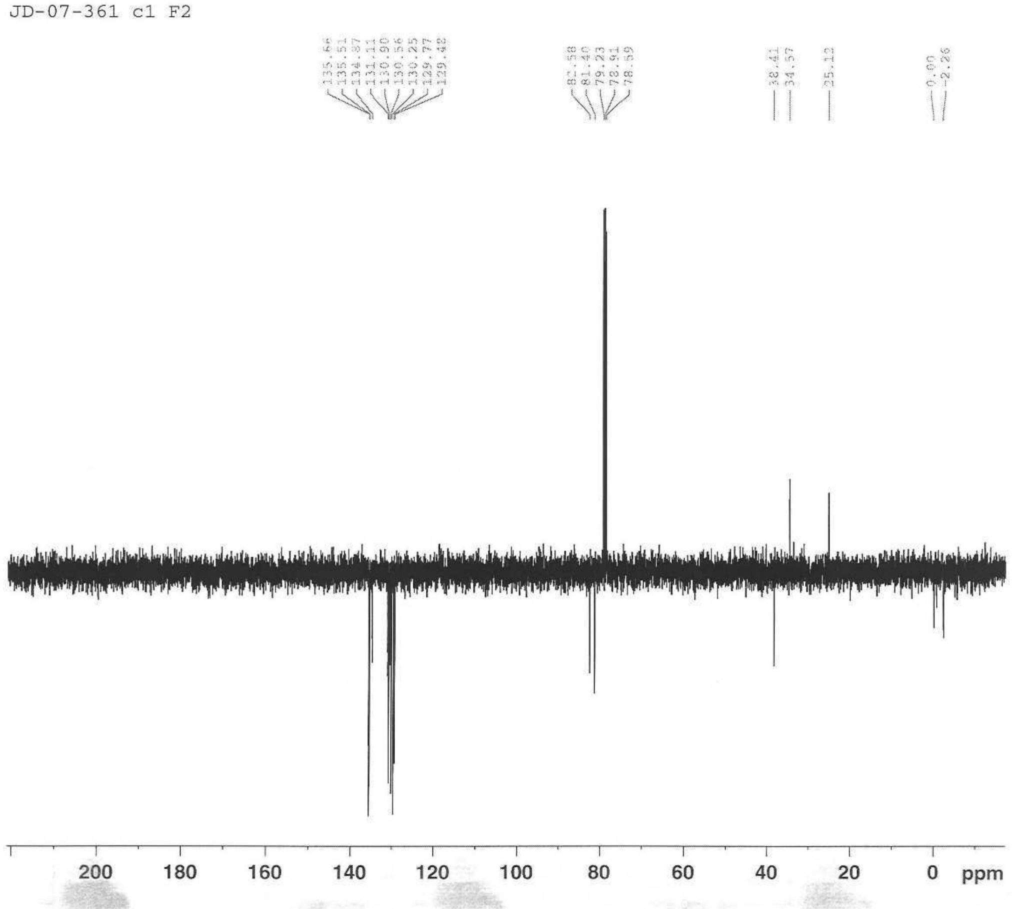
```
NAME           JD_100204
EXPNO                 92
PROCNO                 1
Date_           20100206
Time               14.15
INSTRUM            spect
PROBHD      5 mm QNP  1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             5681.818 Hz
FIDRES          0.086698 Hz
AQ             5.7672181 sec
RG                  4096
DW                88.000 usec
DE                110.00 usec
TE                 300.0 K
HL1                    4 dB
D1            1.00000000 sec
P1                 14.50 usec
SFO1         400.1365178 MHz
NUCLEUS               1H
SI                 32768
SF           400.1343947 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



```
NAME        JD_11.02.10
EXPNO                10
PROCNO                1
Date_          20100212
Time               1.52
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG              18390.4
DW               20.850 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
PL1                6.00 dB
SFO1        100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                3.00 dB
PL12              22.00 dB
PL13              22.00 dB
SFO2        400.2316009 MHz
SI                32768
SF          100.6379011 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

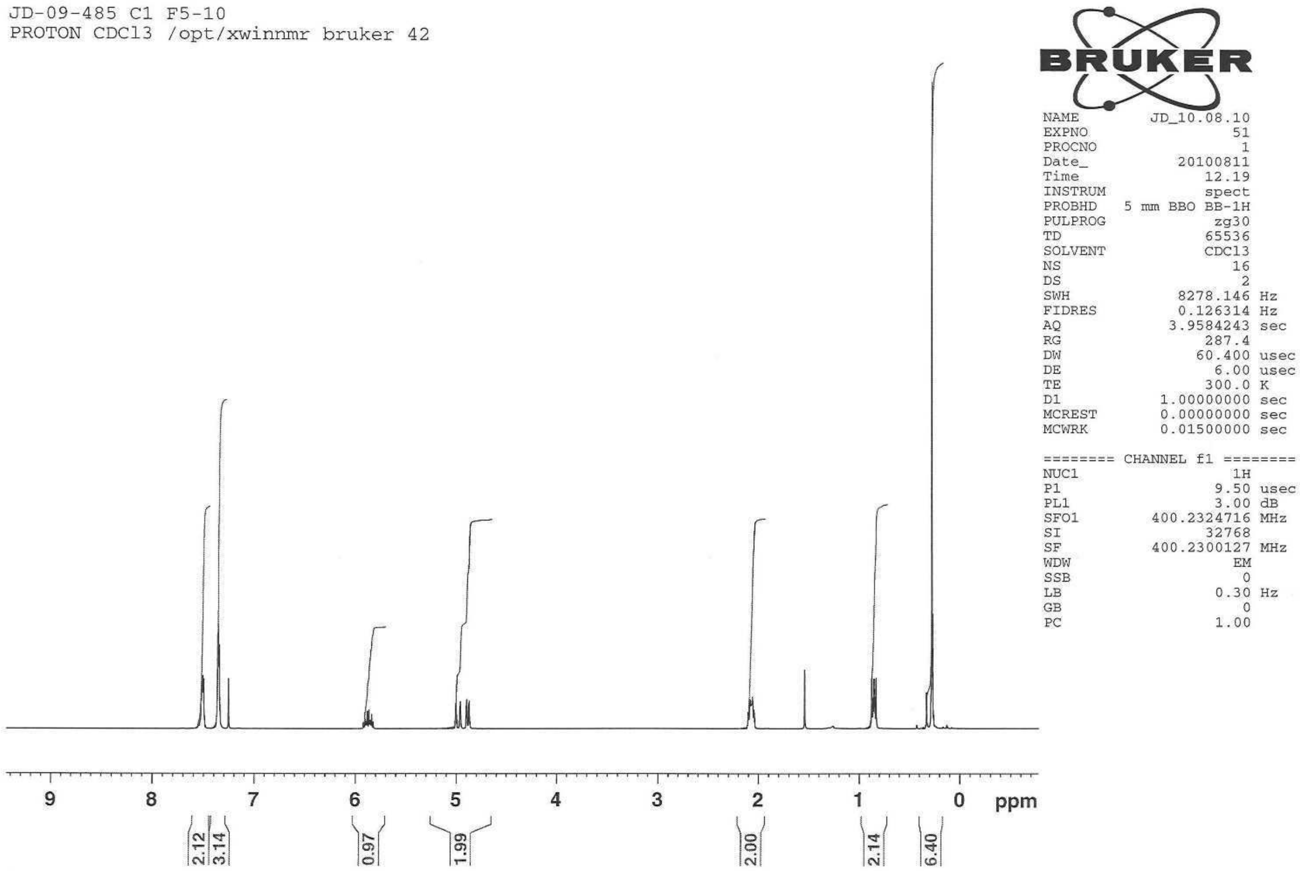


```
NAME          JD_11.02.10
EXPNO                  11
PROCNO                  1
Date_            20100212
Time                 2.09
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG         deptq135
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6377257 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

But-3-enyldimethyl(phenyl)silane (35): (0.02 g, 0.12 mmol, 20%) as a colourless oil; R_f 0.35 [hexane]; δ_H (400 MHz; $CDCl_3$); 0.28 (6H, s, $SiMe_2$), 0.84-0.88 (2H, m, $SiCH_2$), 2.04-2.10 (2H, m, $C\underline{H}_2CH=CH_2$), 4.89 (1H, app d, *J* 10.1, $CH_2CH=C\underline{H}_{cis}H_{trans}$), 4.99 (1H, app dd, $CH_2CH=CH_{cis}\underline{H}_{trans}$), 5.88 (1H, ddt, *J* 17.1 10.1 and 6.2, $CH_2C\underline{H}=CH_2$), 7.35-7.37 (3H, m, SiPh), 7.51-7.56 (2H, m, SiPh); δ_C (100.6 MHz; $CDCl_3$) -2.9 ($SiMe_2$), 14.9 ($SiCH_2$), 28.1 ($\underline{C}H_2CH=CH_2$), 112.9 ($CH_2CH=\underline{C}H_2$), 127.9 (2 × *m*-CH, SiPh), 129.0 (p-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.4 (*ipso*-C, SiPh), 141.7 ($CH_2\underline{C}H=CH_2$); LRMS (EI^+, *m/z*): 190 ($[M]^+$, 4%), 175 (13), 162 (11), 135 (100), 121 (27), 105 (13). The spectral data is in good agreement with previously reported values.



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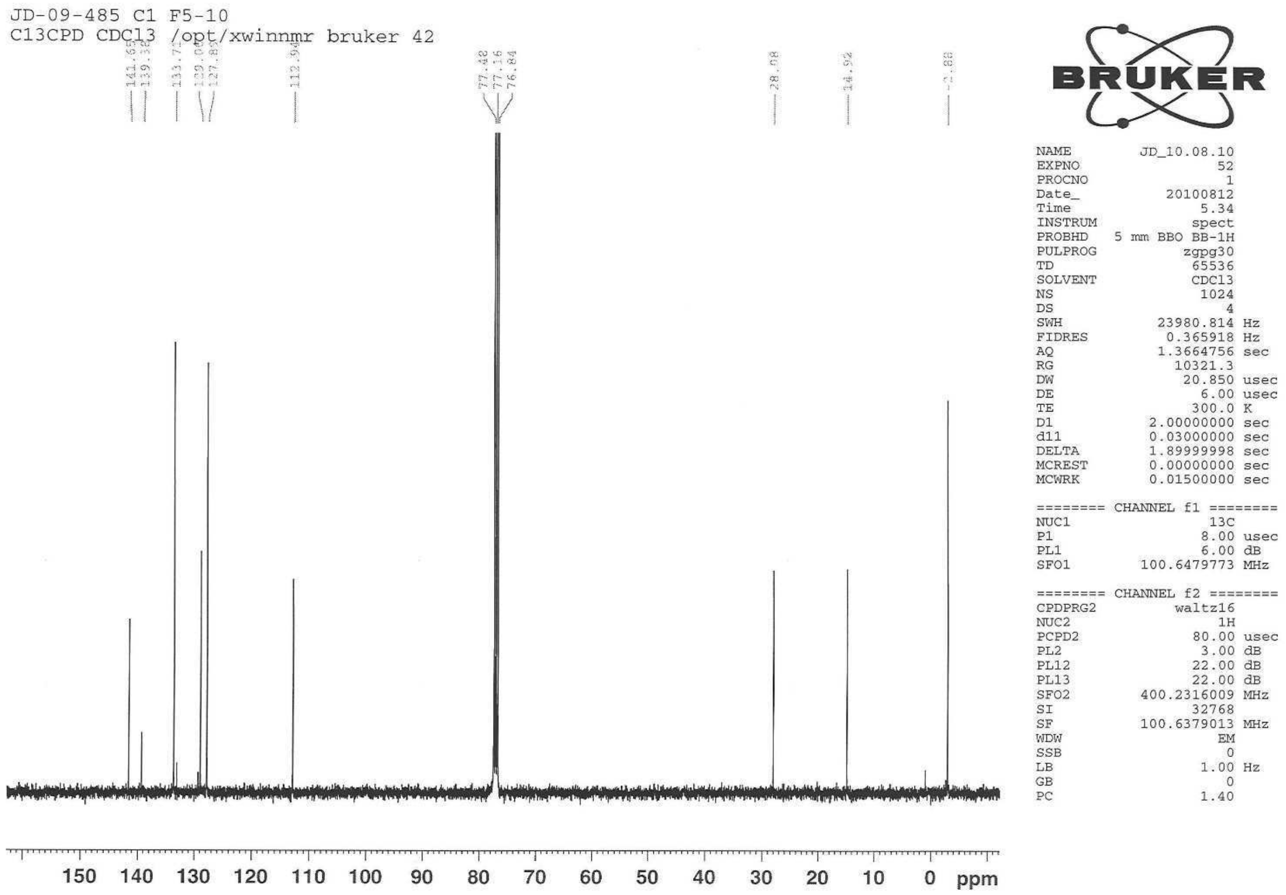
JD-09-485 C1 F5-10
PROTON CDCl3 /opt/xwinnmr bruker 42
```

```
NAME          JD_10.08.10
EXPNO                  51
PROCNO                  1
Date_            20100811
Time                12.19
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  287.4
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300127 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



JD-09-485 C1 F5-10
C13CPD CDCl3 /opt/xwinnmr bruker 42

```
NAME          JD_10.08.10
EXPNO                  52
PROCNO                  1
Date_            20100812
Time                 5.34
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                10321.3
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379013 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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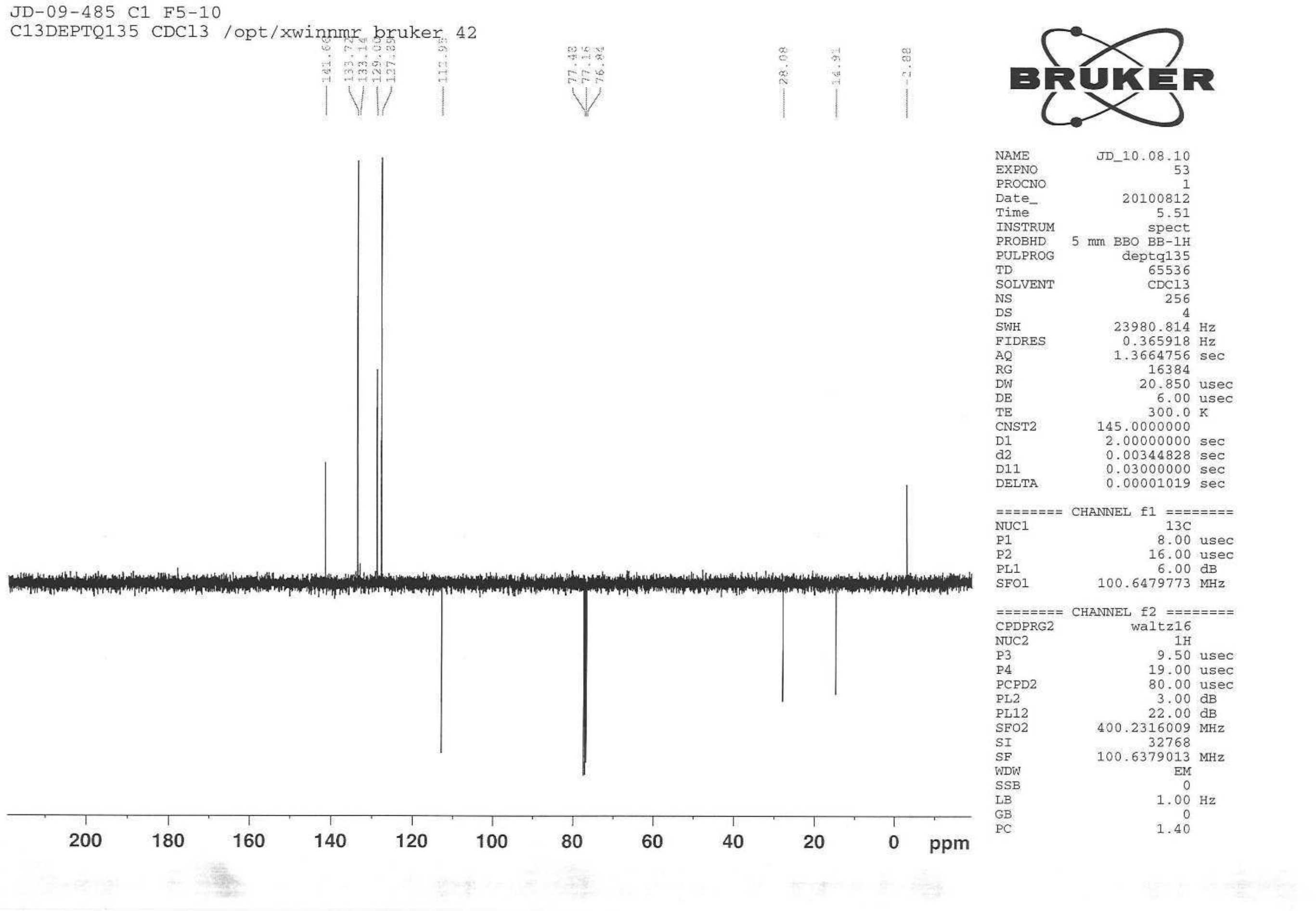

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PROCNO                  1
Date_            20100812
Time                 5.51
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TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
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FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
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NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379013 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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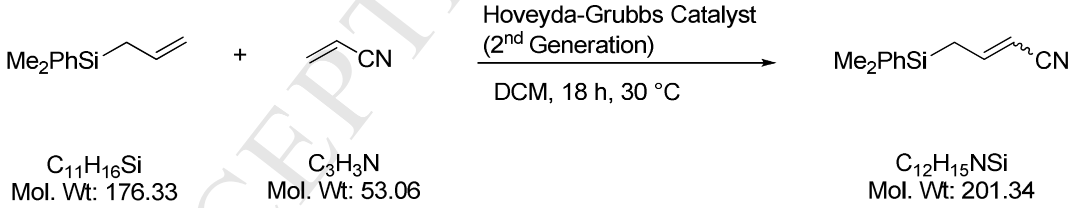
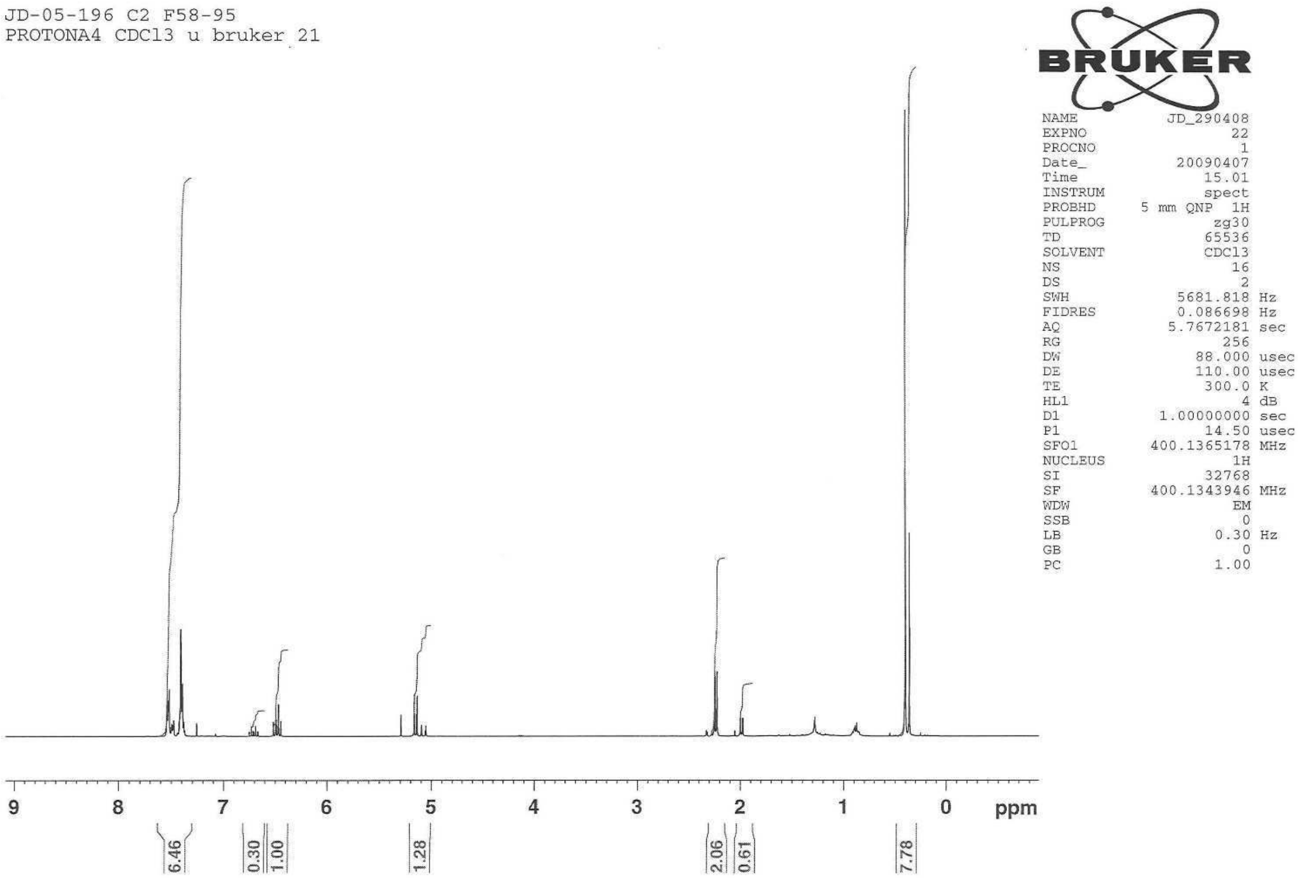
4-(Dimethyl(phenyl)silyl)but-2-enenitrile



To a stirred solution of dimethylphenylallylsilane (0.56 g, 3.2 mmol) and acyrlonitrile (0.51 g, 0.37 mL, 9.6 mmol) in argon degassed DCM (10 mL) was added a solution of (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)-ruthenium (0.1 g, 0.16 mmol, 5 mol %) in DCM (1 mL) The reaction immediately changed colour from green to black and was heated at 35 °C and monitored by TLC. After 24 h the solvent was removed *in vacuo* to give the impure product (0.72 g). Purification by flash column chromatography [silica gel, gradient elution 100 % petroleum ether (40-60 °C) - 20 % diethylether : petroleum ether (40-60 °C)] afforded an inseparable mixture of the two geometric isomers of the product (combined yield 0.14 g, 2.0 mmol, 64 %, dr. *cis* : *trans* 1 : 0.3) as a colourless oil: R_f 0.33 [10 % diethylether : petroleum ether (40-60 °C)]; *cis* isomer: δ_H (400 MHz; $CDCl_3$) 0.41 (6H, s, $SiMe_2$), 2.24 (2H, dd, *J* 9.0 and 1.0, $SiCH_2$), 5.15 (1H, dt, *J* 10.8 and 1.0, CH=C$\underline{H}$CN), 6.48 (1H, dt, *J* 10.8 and 9.0, C$\underline{H}$=CHCN), 7.37-7.42 (3H, m, Ph), 7.52-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) -3.3 ($SiMe_2$), 24.9 ($SiCH_2$), 96.4 (CH=$\underline{C}$HCN), 116.8

(CH=CH$\underline{\text{C}}$N), 128.1 (2 × *m*-CH, Ph), 129.7 (*p*-CH, Ph), 133.6 (2 × *o*-CH, Ph), 136.7 (*ipso*-C, Ph), 152.9 ($\underline{\text{C}}$H=CHCN); *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.37 (6H, s, $SiMe_2$), 1.99 (2H, dd, *J* 8.8 and 1.4, $SiCH_2$), 5.08 (1H, dt, *J* 16.1 and 1.4, CH=C$\underline{\text{H}}$CN), 6.71 (1H, dt, *J* 16.1 and 8.8, C$\underline{\text{H}}$=CHCN), 7.37-7.42 (3H, m, Ph), 7.48-7.50 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) -3.4 ($SiMe_2$), 25.8 ($SiCH_2$), 97.1 (CH=$\underline{\text{C}}$HCN), 118.2 (CH=CH$\underline{\text{C}}$N), 128.2 (2 × *m*-CH, Ph), 129.8 (*p*-CH, Ph), 133.5 (2 × *o*-CH, Ph), 136.4 (*ipso*-C, Ph), 153.9 ($\underline{\text{C}}$H=CHCN). Diastereomeric ratio calculated by analysis of the ^{1}H NMR integrals for the C$\underline{\text{H}}$=CHCN protons, 6.48 (*cis* diastereoisomer) and 6.71 ppm (*trans* diastereoisomer).



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JD-05-196 C2 F58-95
PROTONA4 CDCl3 u bruker 21
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TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
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FIDRES          0.086698 Hz
AQ             5.7672181 sec
RG                   256
DW                88.000 usec
DE                110.00 usec
TE                 300.0 K
HL1                    4 dB
D1            1.00000000 sec
P1                 14.50 usec
SFO1         400.1365178 MHz
NUCLEUS               1H
SI                 32768
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WDW                   EM
SSB                    0
LB                  0.30 Hz
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PC                  1.00
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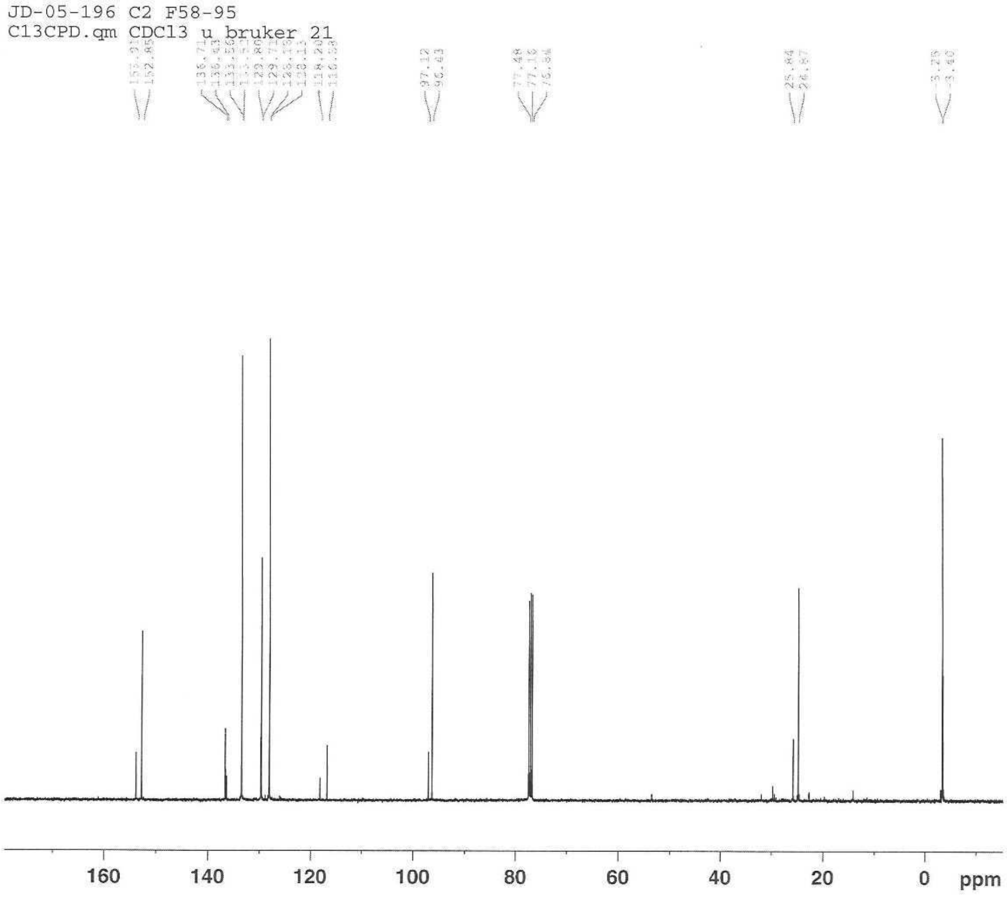

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PROCNO                  1
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PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
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SWH             26315.789 Hz
FIDRES           0.401547 Hz
AQ              1.2452340 sec
RG                  32768
DW                 19.000 usec
DE                  27.14 usec
TE                  300.0 K
HL1                     4 dB
D1             2.00000000 sec
CPDPRG            waltz16
P31                 80.00 usec
S4                     20 dB
D11            0.0300000 sec
S2                     17 dB
P1                   6.00 usec
SFO1         100.6251166 MHz
NUCLEUS               13C
SI                  32768
SF           100.6138666 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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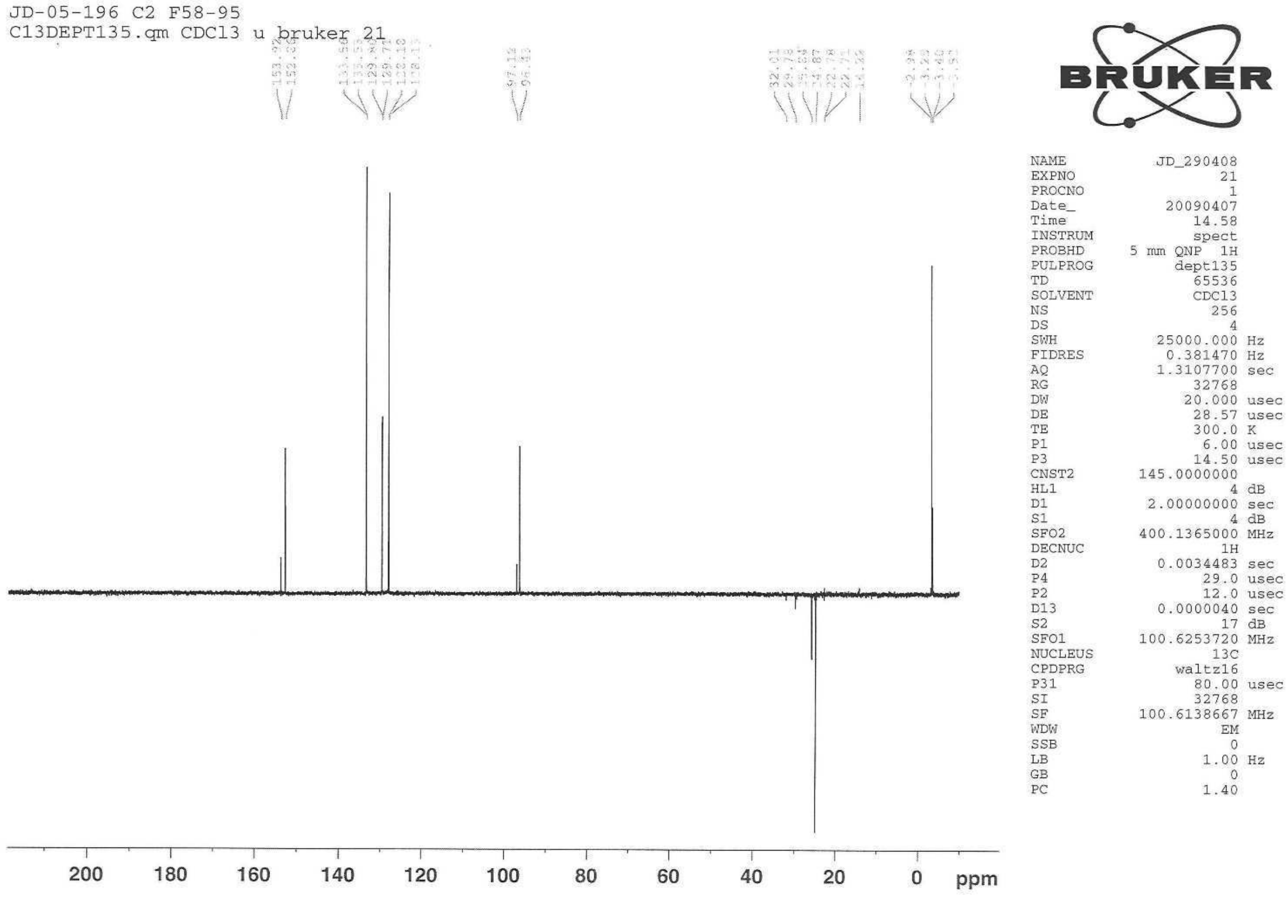

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JD-05-196 C2 F58-95
C13DEPT135.qm CDCl3 u bruker 21
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EXPNO                21
PROCNO                1
Date_          20090407
Time              14.58
INSTRUM           spect
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PULPROG         dept135
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           25000.000 Hz
FIDRES         0.381470 Hz
AQ            1.3107700 sec
RG                32768
DW               20.000 usec
DE                28.57 usec
TE                300.0 K
P1                 6.00 usec
P3                14.50 usec
CNST2       145.0000000
HL1                   4 dB
D1           2.00000000 sec
S1                    4 dB
SFO2        400.1365000 MHz
DECNUC               1H
D2            0.0034483 sec
P4                 29.0 usec
P2                 12.0 usec
D13           0.0000040 sec
S2                   17 dB
SFO1        100.6253720 MHz
NUCLEUS             13C
CPDPRG          waltz16
P31               80.00 usec
SI                32768
SF          100.6138667 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
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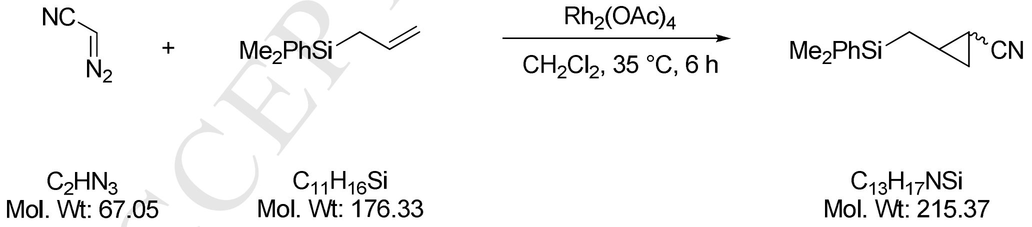
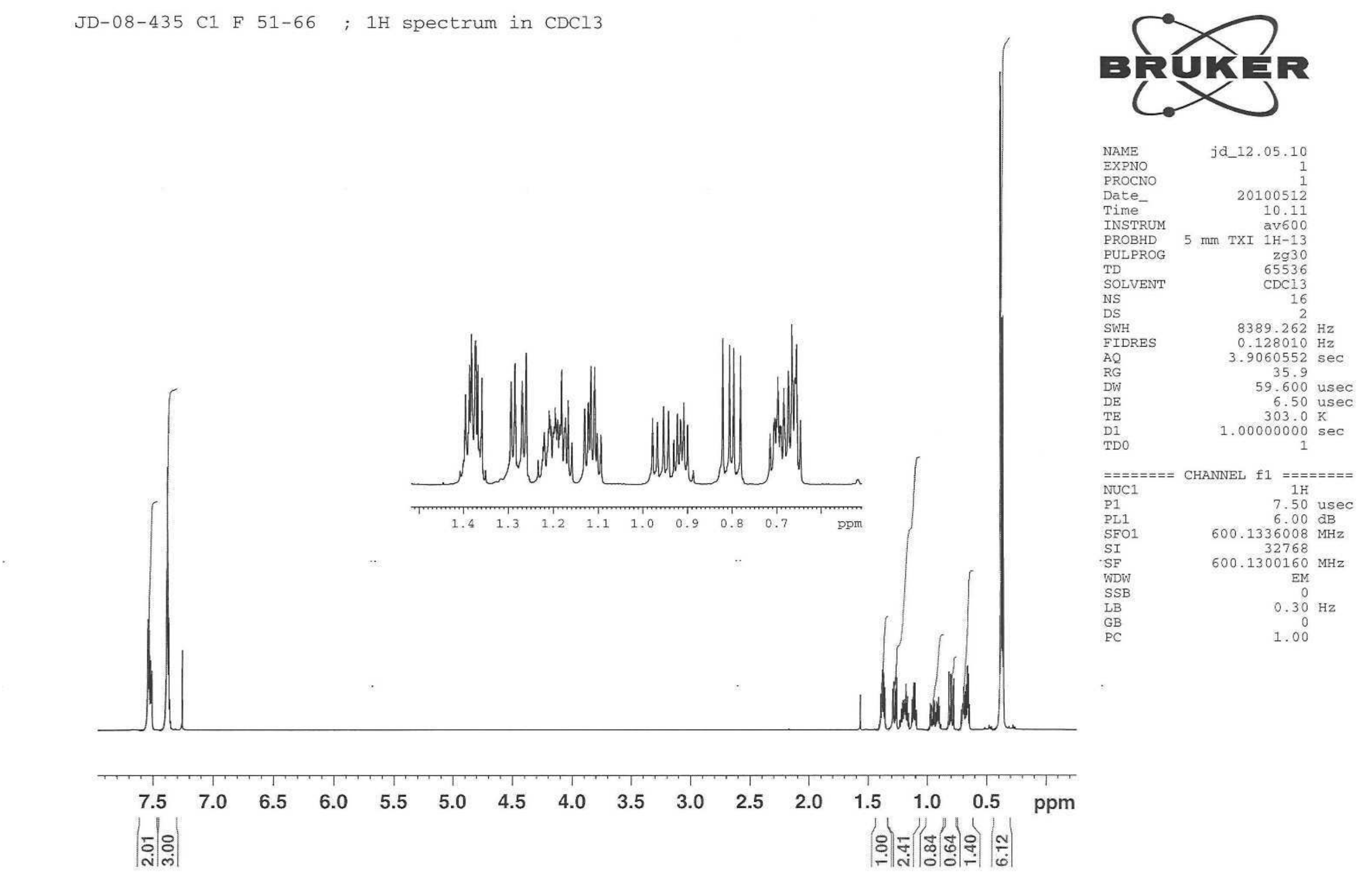
2-((Dimethyl(phenyl)silyl)methyl)cyclopropanecarbonitrile (30)



Diazoacetonitrile was prepared according to the procedure reported by Witiak *et. al*. To a suspension of α-aminoacetonitrile bisulfite (3.68 g, 24.0 mmol) in DCM (28 mL) at 0 °C was cautiously added dropwise an aqueous solution of sodium nitrite (4.96 g, 72.0 mmol) in distilled water (22 mL) at a rate that the temperature of the reaction did not rise above 0 °C. During the addition effervescence was observed to occur. The reaction was allowed to stir for 30 min at 0 °C after which time a green solution and precipitate existed. The organic layer was separated and the aqueous layer further extracted with DCM (20 mL). The combined organic phases were washed with 1% aqueous sodium hydrogen carbonate solution (10 mL), separated, dried ($MgSO_4$), filtered and place under and inert atmosphere. The solution (0.5 M solution of diazoacetinitle in DCM) was used immediately and without purification as diazacetonitrile has been reported to be highly explosive at high concentrations. To a stirred mixture of allyldimethylphenylsilane (2.47 g, 14.0 mmol) and dirhodium tetraacetate dihydrate (0.17 g, 0.38 mmol) in degassed DCM (2.4 mL) heated at 35 °C was added using a syringe pump (4 mL/h) diethyl 2-diazomalonate (24.0 mL, 12.0 mmol, 0.5 M solution in DCM). The reaction was heated at 35 °C (oil bath) for 6 h, filtered and concentrated *in vacuo* to give the impure product as a red oil (2.65 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 10% diethyl ether : hexane] afforded an inseparable mixture of the two geometric isomers the desired (0.73 g, 3.40 mmol, 30%, *dr* 1 : 0.6) as a colourless oil; R_f 0.20 [10% diethyl ether - hexane]; ν_{max}(film)/cm^{-1} 3070 (CH cyclopropyl), 2956, 2897, 2233 (C≡N), 1427, 1427, 1250, 1114, 831; major isomer: δ_H (600 MHz; $CDCl_3$) 0.38 (3H, s, SiMe), 0.39 (3H, s, SiMe), 0.65-0.72 (1H, m $C\underline{H}_aH_b$ cyclopropyl), 0.80 (1H, dd, *J* 14.8 and 9.2, $SiC\underline{H}_aH_b$), 1.11 (1H, td, *J* 8.4 and 5.1, $CH_a\underline{H}_b$ cyclopropyl), 1.16-1.23 (1H, m, CHCN), 1.28 (1H, dd, *J* 14.8 and 5.2, $SiCH_a\underline{H}_b$), 1.35-1.41 (1H, m, CH cyclopropyl), 7.36-7.40 (3H, m, Ph), 7.51-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −2.9 (SiMe), −2.8 (SiMe), 4.1 (CH cylopropyl), 15.0 ($\underline{C}$HCN cyclopropyl), 15.4 (CH_2 cyclopropyl), 17.3 ($SiCH_2$), 120.9 (CN), 128.0 (2 × *m*-CH, Ph), 129.4 (*p*-CH, Ph), 133.7 (2 × *o*-CH, Ph), 138.1 (C, Ph); minor isomer: δ_H (600 MHz; $CDCl_3$) 0.36 (3H, s, SiMe), 0.37 (3H, s, SiMe), 0.65-0.72 (2H, m, overlapping signals $SiC\underline{H}_aH_b$ and $C\underline{H}_aH_b$ cyclopropyl), 0.90-0.93 (1H, m, CH cyclopropyl), 0.96 (1H, dd, *J* 14.8 and 6.4, $SiCH_a\underline{H}_b$), 1.16-1.23 (1H, m, $CH_a\underline{H}_b$ cyclopropyl), 1.35-1.41 (1H, m, CHCN), 7.36-7.40 (3H, m, Ph), 7.51-7.55 (2H, m, Ph); δ_C (100.6 MHz; $CDCl_3$) −3.1 (SiMe), −2.9 (SiMe), 4.4 (CH cylopropyl), 15.8 (CH_2 cyclopropyl), 18.1 ($\underline{C}$HCN cyclopropyl), 20.4 ($SiCH_2$), 122.0 (CN), 128.1 (2 × *m*-CH, Ph), 129.5 (*p*-CH, Ph), 133.6 (2 × *o*-CH, Ph), 137.9 (C, Ph); LRMS (EI$^+$, *m/z*): 215 ([M]$^+$, 3%), 200 (6), 135 (100) 105 (10); HRMS (EI, *m/z*) 215.1127 [M]$^+$, $C_{13}H_{17}NSi$ requires 215.1125.



JD-08-435 C1 F 51-66 ; 1H spectrum in CDCl3

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PROCNO                  1
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8389.262 Hz
FIDRES           0.128010 Hz
AQ              3.9060552 sec
RG                   35.9
DW                 59.600 usec
DE                   6.50 usec
TE                  303.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                   7.50 usec
PL1                  6.00 dB
SFO1          600.1336008 MHz
SI                  32768
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SSB                     0
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PC                   1.00
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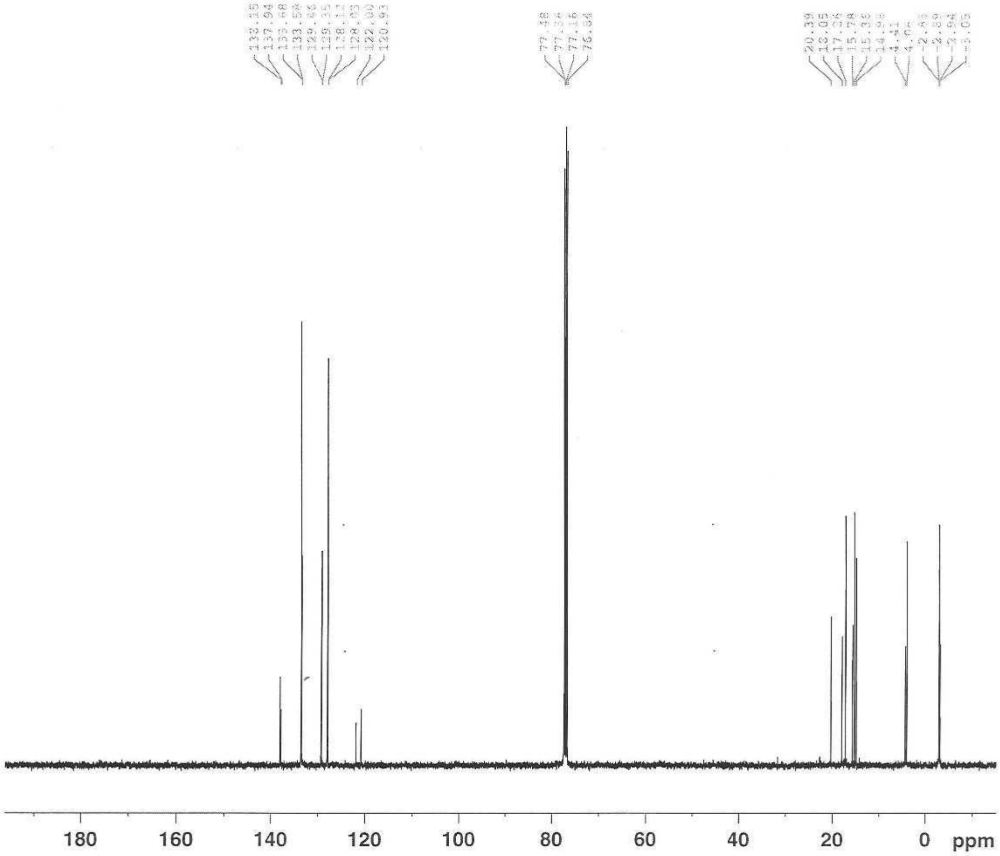
JD-08-435 C1 F50-65



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EXPNO                   41
PROCNO                   1
Date_             20100510
Time                 20.16
INSTRUM              spect
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PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
PL13                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379036 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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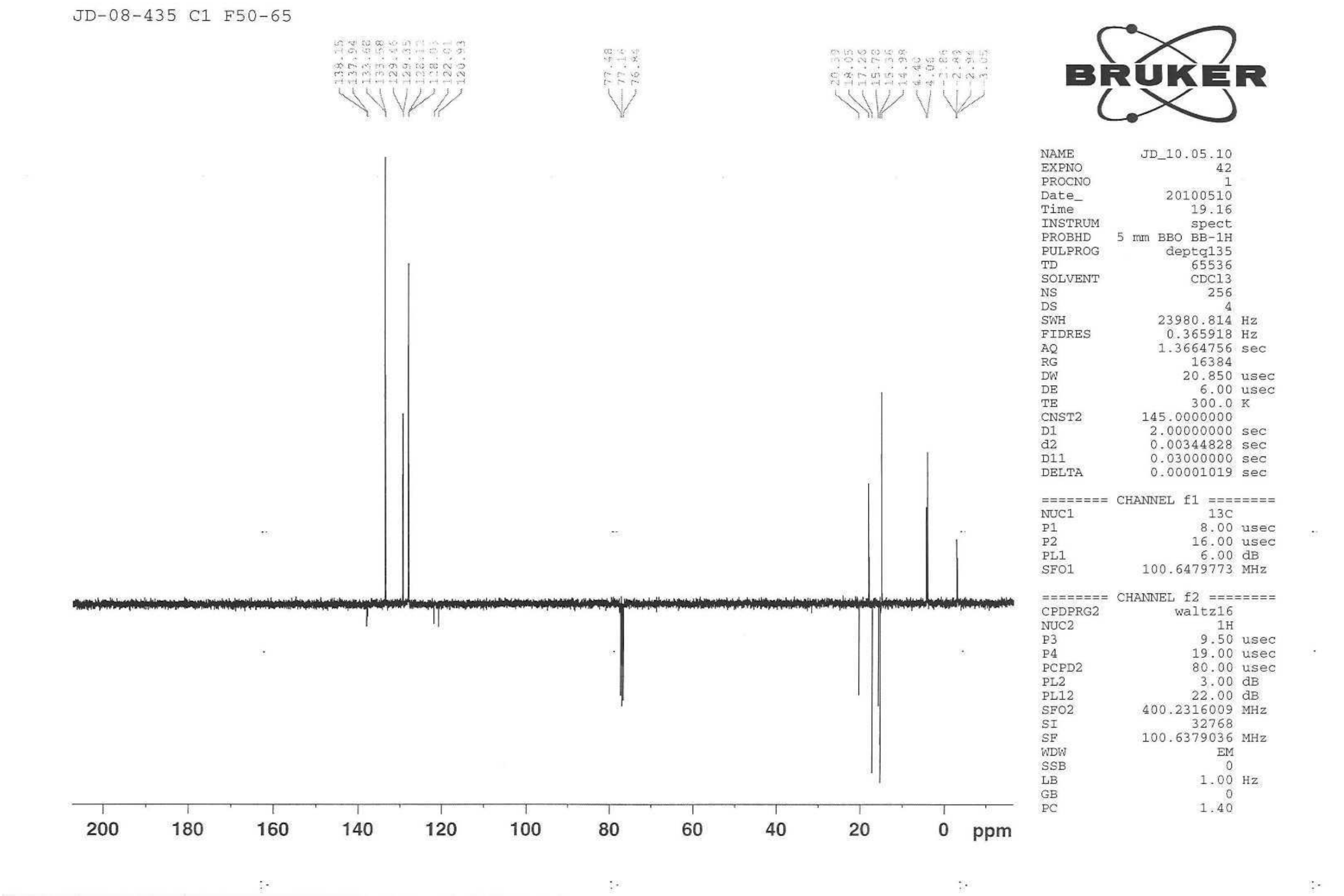
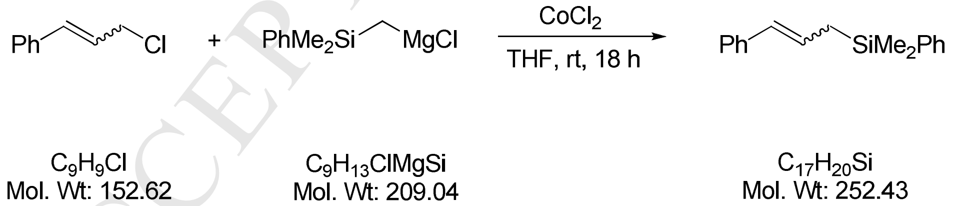


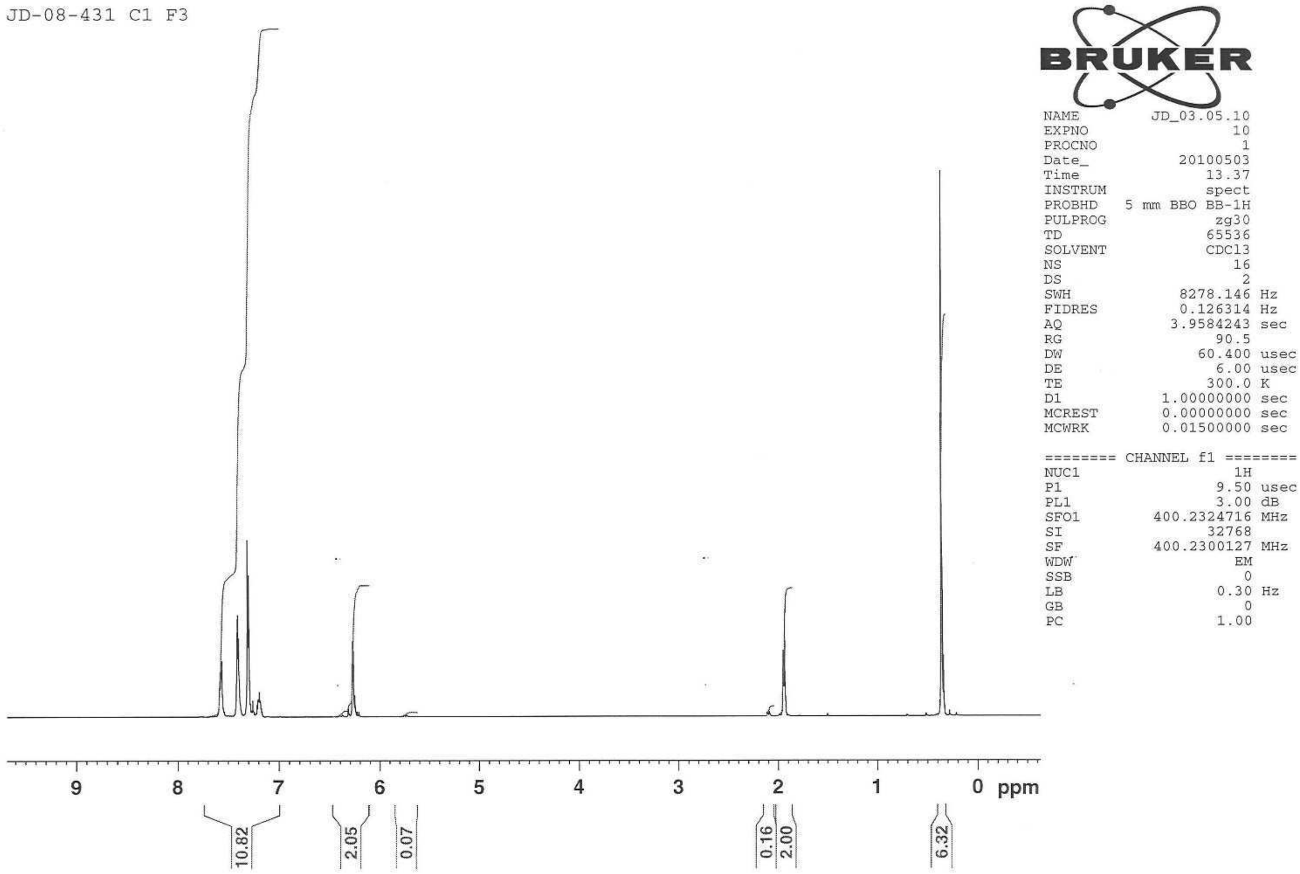
(*E*/*Z*)-3-dimethylphenylsilyl-1-phenyl-1-propene (39)



Preparation of anhydrous cobalt (II) chloride: Cobalt chloride hexahydrate (approx 2 g) was weighed into a 25 mL flask, placed under vacuum (0.05 mmHg) and gently heated with a heat gun. The red solid was observed to “bump” as the water was removed and change to a bright blue solid. The anhydrous cobalt (II) chloride was placed under nitrogen and used immediately.

Preparation of dimethylphenylsilylmethylmagnesium chloride: To a stirred suspension of magnesium turnings (2.26 g, 93.0 mmol) in THF (19 mL) was added dropwise neat 1,2-dibromoethane (0.82 g, 0.40 mL, 4.52 mmol). After effervescence had subsided (chloromethyl)dimethylphenylsilane (3.70 g, 3.60 mL, 20.0 mmol) was added at such a rate to maintain a gentle reflux during the course of the addition. The reaction mixture was allowed to stir for 15 min at room temperature to give a light gray solution of dimethylphenylsilylmethylmagnesium chloride (approx. 1 M in THF).

Preparation of (*E*/*Z*)-3-dimethylphenylsilyl-1-phenyl-1-propene based on the procedure reported by Affo *et. al*. To a blue solution of anhydrous cobalt (II) chloride (0.31 g, 2.40 mmol) and β-bromostyrene (2.20 g, 1.55 mL, 12.0 mmol, *E*/*Z* =1: 0.1) in THF (12 mL) was added dropwise a solution of dimethylphenylsilylmagnesium chloride (18.0 mL, 18.0 mmol, 1 M solution in THF) at 0 °C. During the addition the reaction mixture became a brown colour. The ice bath was removed and the reaction allowed to stir at room temperature over 18 h then partitioned between saturated aqueous ammonium chloride solution (30 mL) and ethyl acetate (20 mL). The organic phase was separated and the aqueous phase extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product as a brown oil (4.25 g). Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 2% diethyl ether : hexane] afforded the desired product (3.08 g, 12.0 mmol, 98%, *trans* : *cis* 1 : 0.1) as a mixture of isomers and as a colourless oil; R_f 0.19 [hexane]; ν_{max}(film)/cm^{-1} 3023, 2955, 1640 (C=C), 1427, 1248, 1113, 813; *trans* isomer: δ_H (400 MHz; $CDCl_3$) 0.37 (6H, s, $SiMe_2$), 1.95 (2H, d, *J* 6.8, $SiCH_2$), 6.22-6.32 (2H, m, C$\underline{H}$=C$\underline{H}$), 7.18-7.21 (1H, m, Ar), 7.28-7.32 (4H, m, Ar), 7.39-7.43 (3H, m, Ar), 7.57-7.59 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.2 ($SiMe_2$), 23.2 ($SiCH_2$), 125.7 (CH, Ar), 126.4 (CH, Ar), 127.3 (CH=CH), 128.0 (CH, Ar), 128.6 (CH, Ar), 129.1 (CH=CH), 129.2 (CH, Ar), 133.8 (CH, Ar), 138.5 (C, Ar), 138.7 (C, Ar); *cis* isomer: δ_H (400 MHz; $CDCl_3$) 0.35 (6H, s, $SiMe_2$), 2.11 (2H, dd, *J* 9.0 and 1.1, $SiCH_2$), 5.75 (1H, dt, *J* 11.7 and 9.0, $CH_2C\underline{H}$=CH), 6.39 (1H, d, *J* 11.7, CH_2CH=C$\underline{H}$), 7.19-7.41 (8H, m, Ar), 7.51-7.56 (8H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −3.0 ($SiMe_2$), 18.8 ($SiCH_2$), 126.3 (CH, Ar), 127.7 (CH=CH), 127.8 (CH, Ar), 128.2 (CH=CH), 128.4 (CH, Ar), 128.7 (CH, Ar), 129.2 (CH, Ar), 133.7 (CH, Ar), 138.2 (C, Ar), 138.7 (C, Ar); LRMS (EI$^+$, *m/z*): 252 ([M]$^+$, 9%), 135 (100), 115 (9) 105 (15), 91 (6); HRMS (EI, *m/z*) 252.1331 [M]$^+$, $C_{17}H_{20}Si$ requires 252.1331. Diastereoselectivity calculated by analysis of the ^{1}H NMR integrals for the SiC$\underline{H}_2$ protons at 1.95 (*E*-diastereoisomer) and 2.11 ppm (*Z*-diastereoisomer).



JD-08-431 C1 F3

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TD                  65536
SOLVENT             CDCl3
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FIDRES           0.126314 Hz
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RG                   90.5
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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PL1                  3.00 dB
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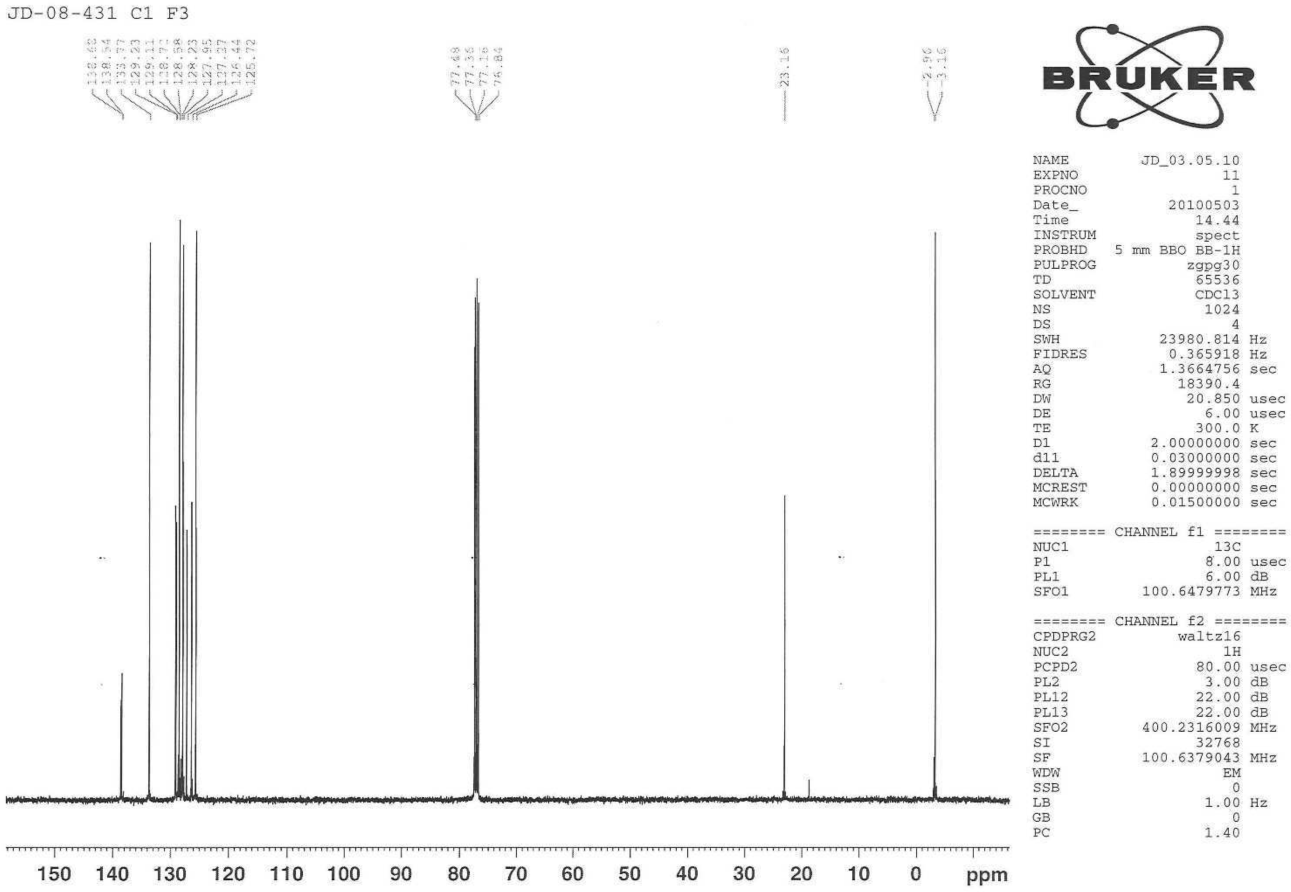

JD-08-431 C1 F3

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EXPNO                  11
PROCNO                  1
Date_            20100503
Time                14.44
INSTRUM             spect
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PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379043 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
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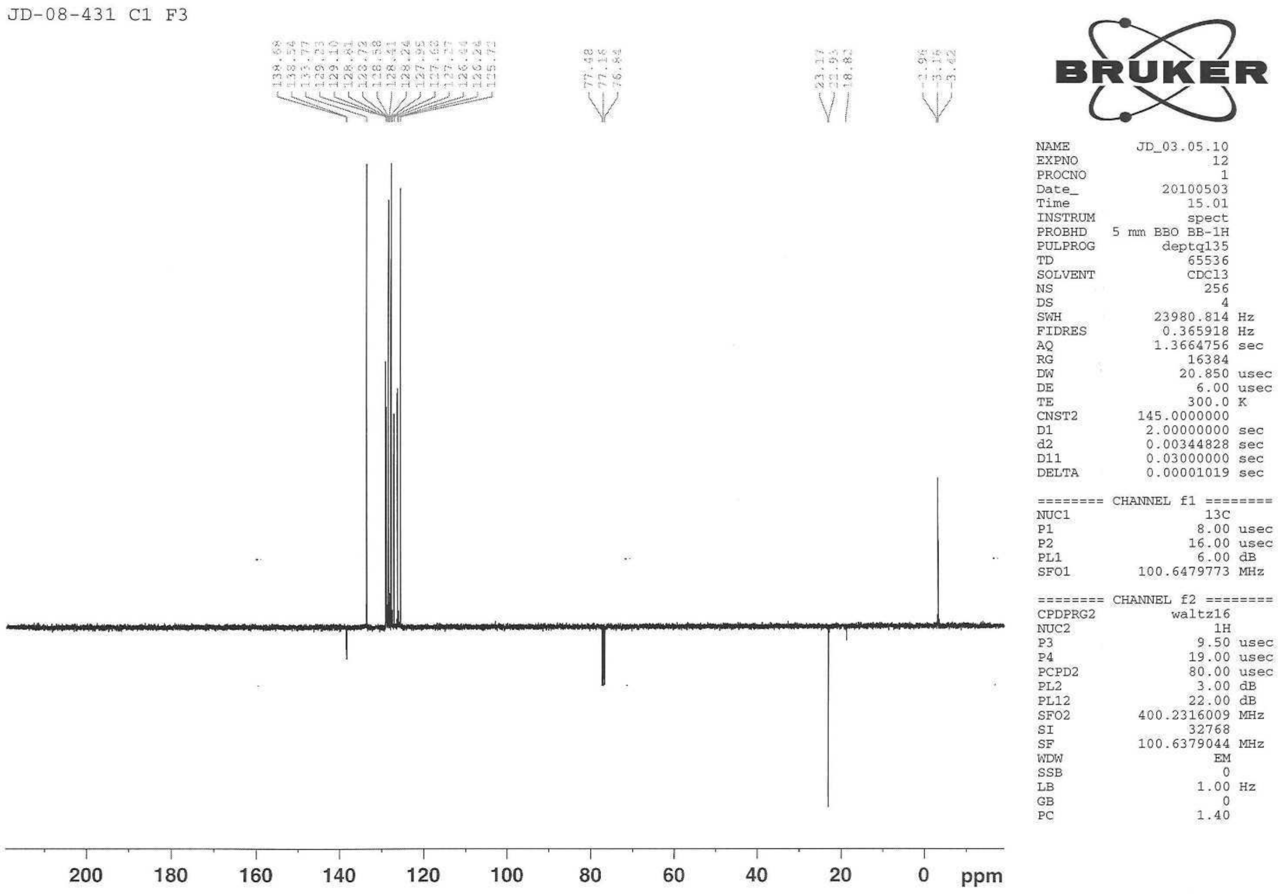

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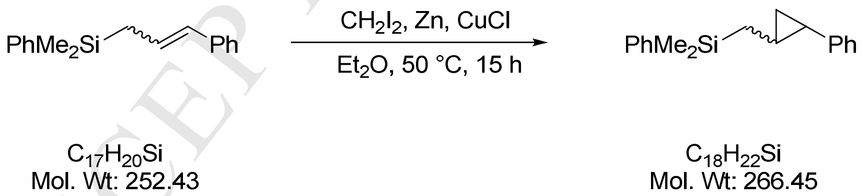
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

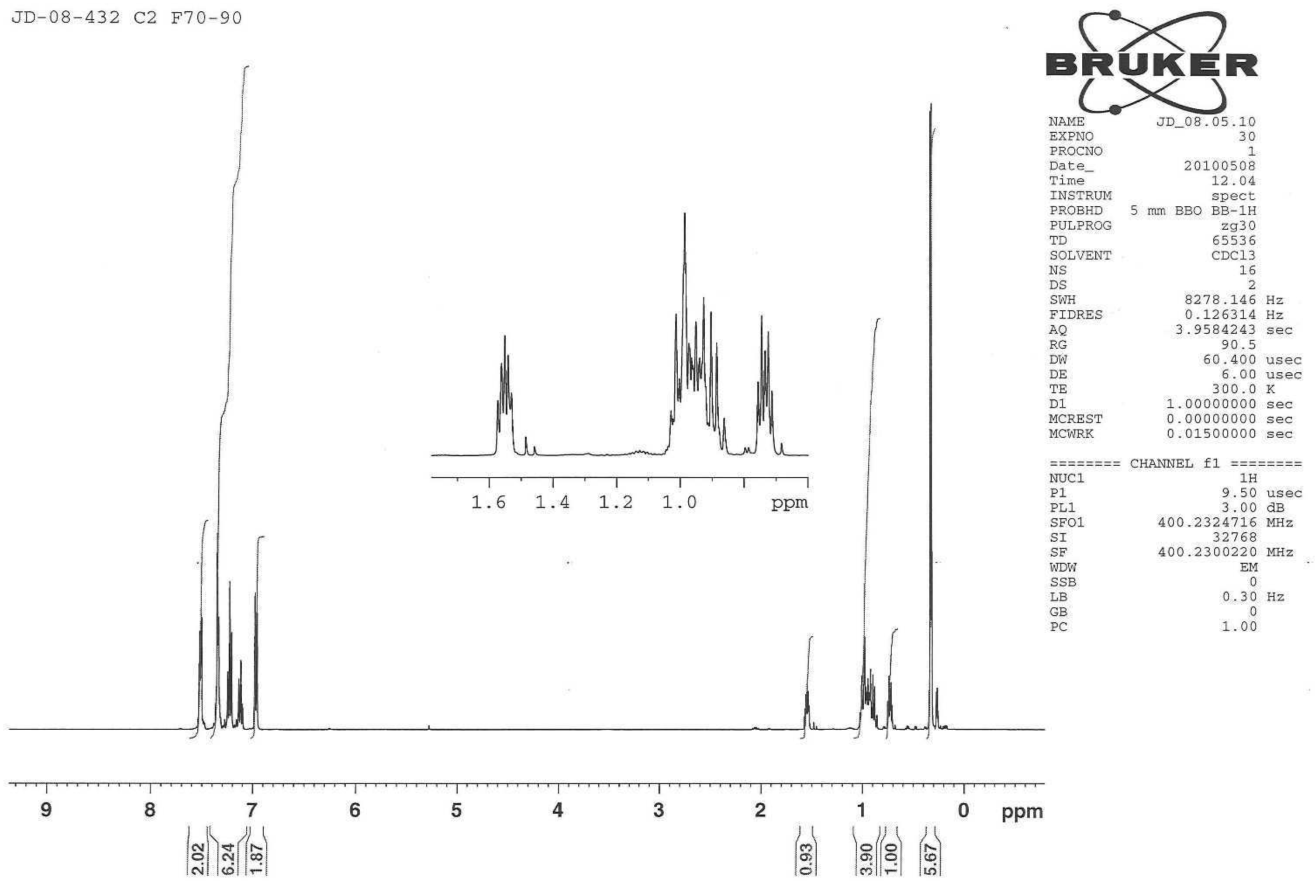
======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379044 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

(±)-Dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (40)



To a stirred suspension of zinc powder (3.96 g, 60.0 mmol) and copper chloride (5.94 g, 60.0 mmol) in anhydrous diethyl ether (90 mL), which had been heated at reflux temperature for 30 min and allowed to cool to room temperature, was added 3-dimethylphenylsilyl-1-phenyl-1-propene (1.57 g, 6.00 mmol) and diiodomethane (6.43 g, 1.93 mL, 24.0 mmol). The reaction was heated at reflux temperature for 48 h, cooled to room temperature and filtered through celite washing with diethyl ether (3 × 30 mL). The filtrate was washed with 1M HCl (2 x 25 mL) followed by 10% *w*/*v* aqueous sodium bicarbonate solution until pH 7. The combined aqueous layers were extracted with diethyl ether (3 x 30 mL) and the combined organic layers were washed with 10% *w*/*v* aqueous sodium thiosulphate solution (2 × 20 mL), brine (20 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield the impure product as a yellow oil (1.05 g). Purification by flash column chromatography using a mixture of 10% silver nitrate impregnated silica and standard silica (1 : 1) eluting with hexane gave the desired product (0.58 g, 2.20 mmol, 36%) as a colourless oil; R_f 0.26 [hexane]; ν_{max}(film)/cm^{-1} 3067 (C-H cyclopropyl), 2999, 2955, 2896, 1605 (Ar-H), 1427, 1248, 1113, 831 (Si-C); δ_H (400 MHz; CDCl$_3$) 0.33 (3H, s, SiMe), 0.34 (3H, s, SiMe), 0.71-0.76 (1H, m, C$\underline{H}_a$H$_b$ cyclopropyl), 0.86-1.04 (4H, m, overlapping signals SiC$\underline{H}_2$, CH and CH$_a\underline{H}_b$ cyclopropyl), 1.53-1.57 (1H, m, PhC$\underline{H}$ cyclopropyl), 6.77 (2H, d, *J* 7.8, 2 × *o*-CH Ph), 7.10-7.14 (1H, m, *p*-CH Ph), 7.23 (2H, t, *J* 7.8, 2 × *m*-CH Ph), 7.32-7.37 (3H, m, SiPh), 7.51-7.53 (2H, m, SiPh); δ_C (100.6 MHz; CDCl$_3$) −2.7 (SiMe), −2.6 (SiMe), 18.5 (CH$_2$ cyclopropyl), 19.7 (CH cyclopropyl), 21.6 (SiCH$_2$), 25.3 (PhC$\underline{H}$, cyclopropyl), 125.2 (*p*-CH, Ph), 125.5 (2 × *o*-CH, Ph), 127.9 (2 × *m*-CH, SiPh), 128.3 (2 × *m*-CH, Ph), 129.3 (*p*-CH, SiPh), 133.7 (2 × *o*-CH, SiPh), 139.4 (C, SiPh), 144.0 (C, Ph); LRMS (EI$^+$, *m/z*): 266 ([M]$^+$, 3%), 238 (7), 188 (11), 135 (100), 105 (9), 91 (8); HRMS (EI$^+$, *m/z*) 266.1487 [M]$^+$, C$_{18}$H$_{22}$Si requires 266.1485.



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PROCNO                  1
Date_            20100508
Time                12.04
INSTRUM             spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   90.5
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300220 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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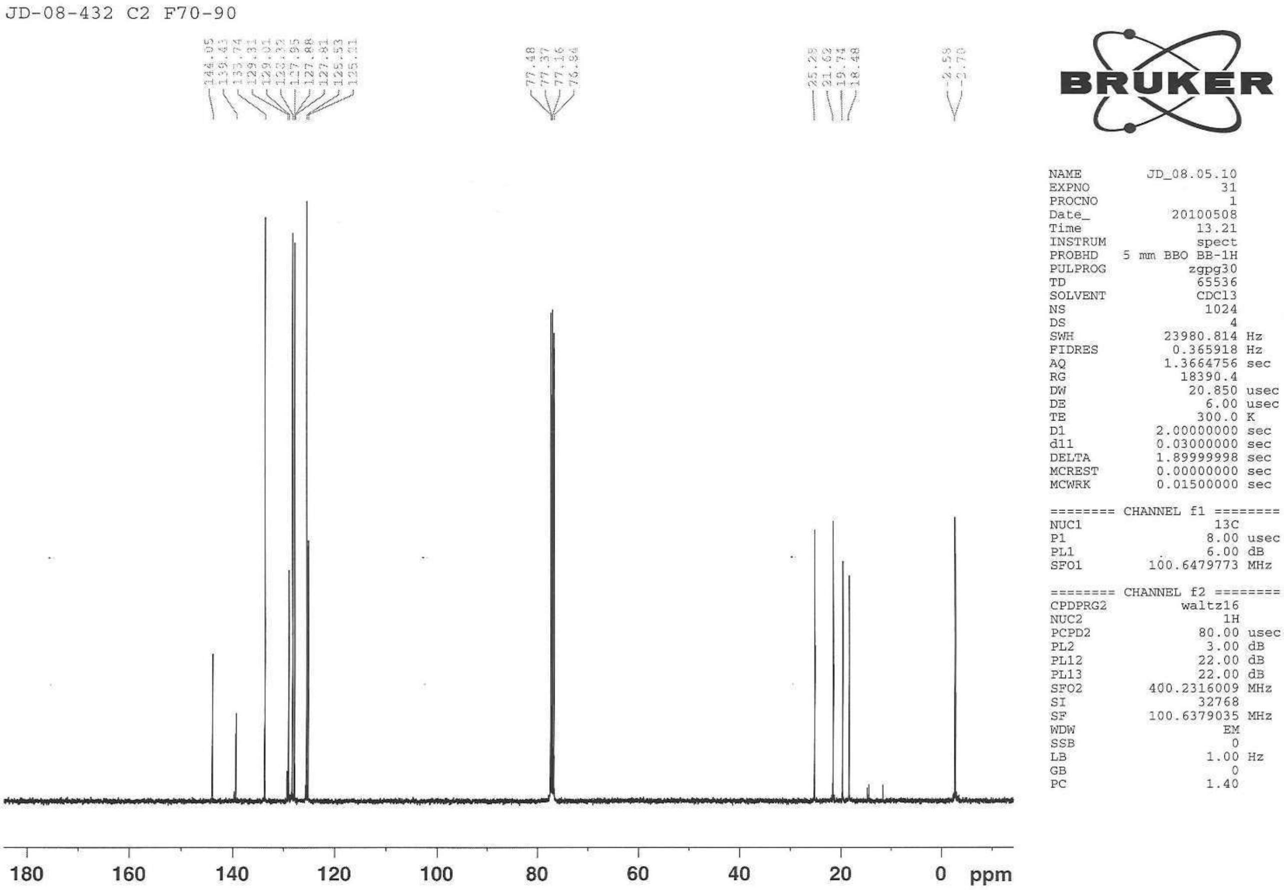

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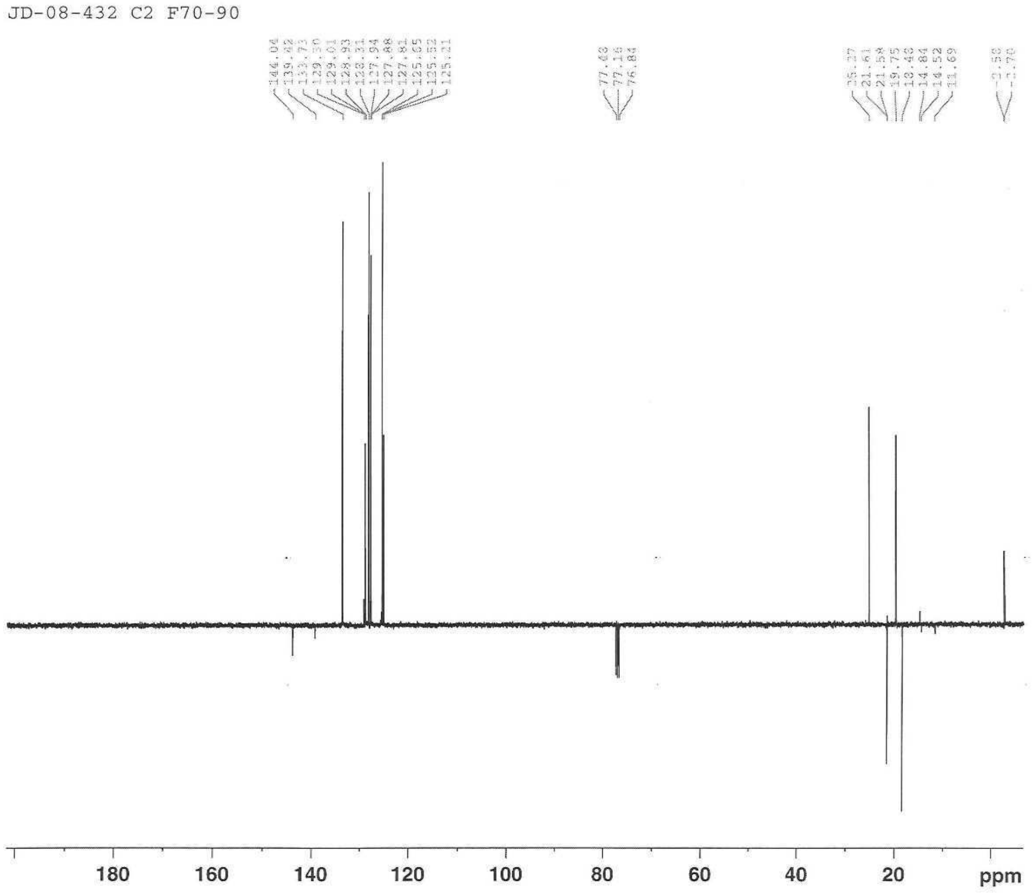
EXPNO                     31
PROCNO                     1
Date_               20100508
Time                   13.21
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG               zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                      8.00 usec
PL1                     6.00 dB
SFO1             100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     3.00 dB
PL12                   22.00 dB
PL13                   22.00 dB
SFO2             400.2316009 MHz
SI                     32768
SF               100.6379035 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



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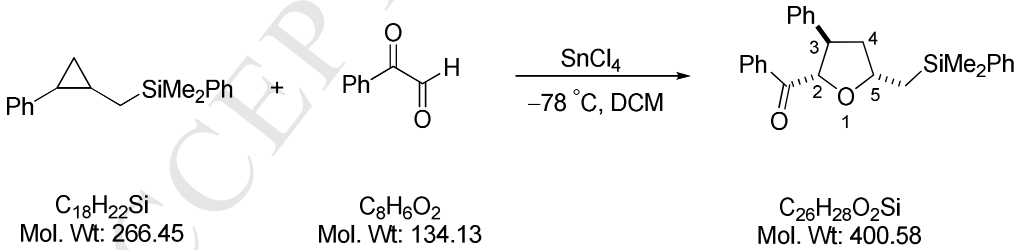
NAME          JD_08.05.10
EXPNO                  32
PROCNO                  1
Date_            20100508
Time                13.37
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG          deptq135
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

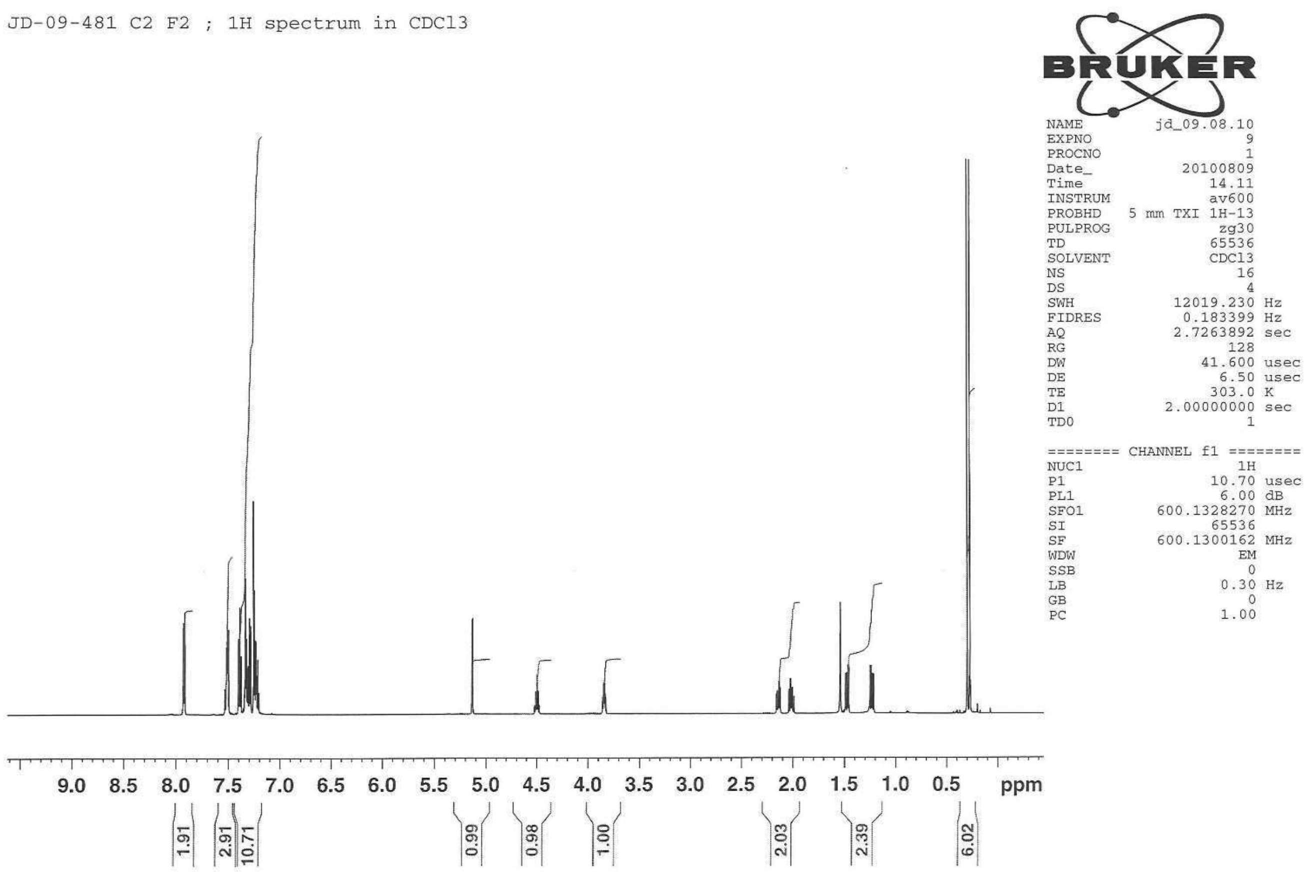
======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379039 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

(±)-(5-((dimethyl(phenyl)silyl)methyl)-3-phenyltetrahydrofuran-2-yl)(phenyl)methanone (41a)



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) in anhydrous DCM (3 mL) at −78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.17 g, 0.08 mL, 0.66 mmol) in anhydrous DCM (3 mL). The resulting mixture was stirred at −78 °C for 5 min followed by the dropwise addition of a solution of dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (0.16 g, 0.60 mmol) in anhydrous DCM (3 mL). The reaction was stirred at −78 °C and monitored by TLC, after 5 h the reaction was quenched by the addition of wet acetone (5 mL) and allowed to warm to 0 °C and poured on to H_2O (10 mL). The organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.25 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution 100% hexane – 20% diethyl ether : hexane] followed by flash column chromatography [silica gel, gradient elution 60% dichloromethane : hexane] afforded the desired product as single diastereoisomer (0.02 g, 0.04 mmol, 7%) as a colourless oil; R_f 0.48 [60% dichloromethane : hexane]; δ_H (600 MHz; $CDCl_3$); 0.28 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 1.24 (1H, dd, *J* 14.3 and 8.0, SiC$\underline{H}_a$H$_b$), 1.48 (1H, dd, *J* 14.3 and 6.5, SiH$_a\underline{H}_b$), 2.01 (1H, app dt, *J* 12.7 and 8.7, C$\underline{H}_a$H$_b$ C-4 THF), 2.14 (1H, ddd, *J* 12.6 6.3 and 4.8, CH$_a\underline{H}_b$ C-4 THF), 3.84 (1H, app dt, *J* 8.9 and 5.1, CH C-3 THF), 4.50 (1H, app tt, *J* 7.8 and 6.5, CH C-5 THF), 5.14 (1H, d, *J* 5.5, CH C-2 THF), 7.20-7.41 (10H, m, Ar), 7.50-7.53 (3H, m, Ar), 7.92-7.93 (2H, m, Ar); δ_C (100.6 MHz; $CDCl_3$) −2.3 ($SiCH_3$), −2.0 ($SiCH_3$), 24.2 ($SiCH_2$), 42.5 (CH_2 C-4 THF), 47.4 (CH C-3 THF), 79.3 (CH C-5 THF), 86.6 (CH C-2 THF), 126.9 (CH, Ar), 127.6 (CH, Ar), 127.9 (CH, Ar), 128.5 (CH, Ar), 128.9 (CH, Ar), 129.1 (CH, Ar), 129.3 (CH, Ar), 133.3 (CH, Ar), 133.7 (CH, Ar), 135.6 (C, Ar), 139.0 (C, Ar), 142.9 (C, Ar), 197.5 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 295 ([M-PhCO]$^+$, 12%), 277 (4), 239 (5), 135 (100), 105 (13), 91 (10), 77 (15); HRMS (ESI, *m/z*) 418.2195 [M+NH$_4$]$^+$, $C_{26}H_{32}O_2NSi$ requires 418.2197.



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EXPNO                   9
PROCNO                  1
Date_            20100809
Time                14.11
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      4
SWH             12019.230 Hz
FIDRES           0.183399 Hz
AQ              2.7263892 sec
RG                    128
DW                 41.600 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.70 usec
PL1                  6.00 dB
SFO1          600.1328270 MHz
SI                  65536
SF            600.1300162 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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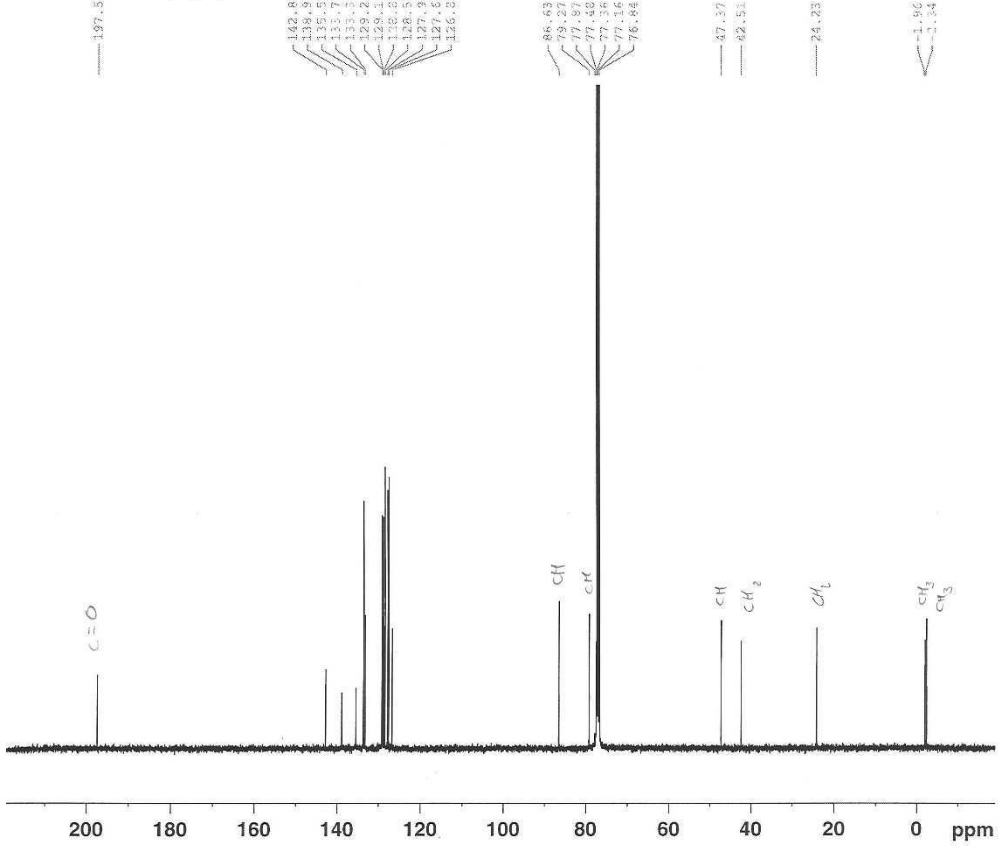
JD-09-481 C2 F2
C13CPD CDCl3 /opt/xwinnmr bruker 15



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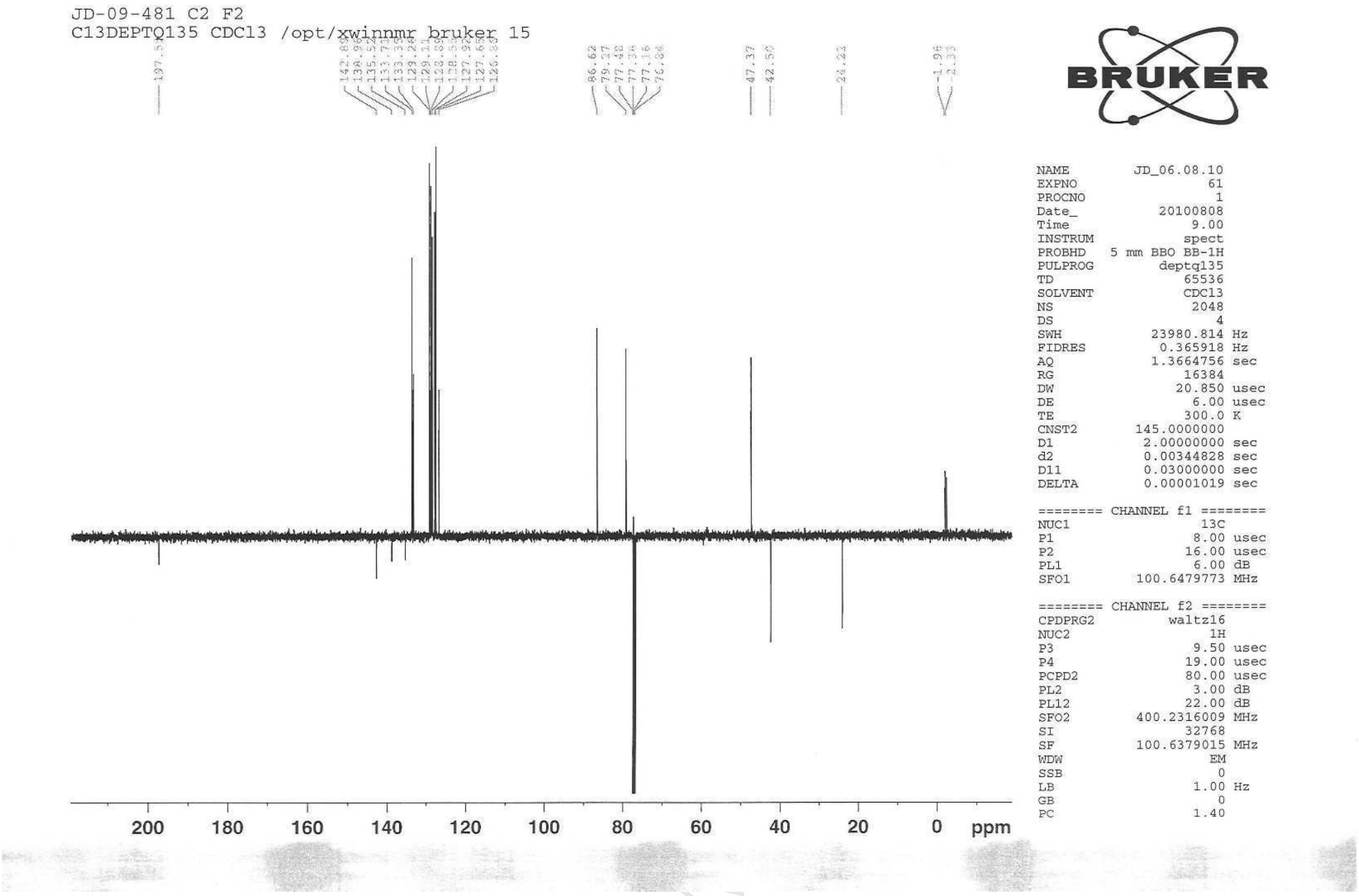
NAME          JD_06.08.10
EXPNO                  60
PROCNO                  1
Date_            20100808
Time                 7.02
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  8192
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                 6.00 dB
SFO1         100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               22.00 dB
PL13               22.00 dB
SFO2         400.2316009 MHz
SI                 32768
SF           100.6379014 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



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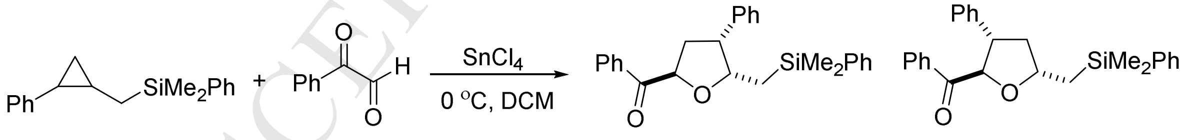
JD-09-481 C2 F2
C13DEPTQ135 CDCl3 /opt/xwinnmr bruker 15
```

```
NAME          JD_06.08.10
EXPNO                  61
PROCNO                  1
Date_            20100808
Time                 9.00
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG          deptq135
TD                  65536
SOLVENT             CDCl3
NS                   2048
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
D11            0.03000000 sec
DELTA          0.00001019 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
P2                  16.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
P3                   9.50 usec
P4                  19.00 usec
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379015 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

(±)-(5-((dimethyl(phenyl)silyl)methyl)-4-phenyltetrahydrofuran-2-yl)(phenyl)methanone (42) and (±)-(5-((dimethyl(phenyl)silyl)methyl)-3-phenyltetrahydrofuran-2-yl)(phenyl)methanone (41b)



$C_{18}H_{22}Si$
Mol. Wt: 266.46

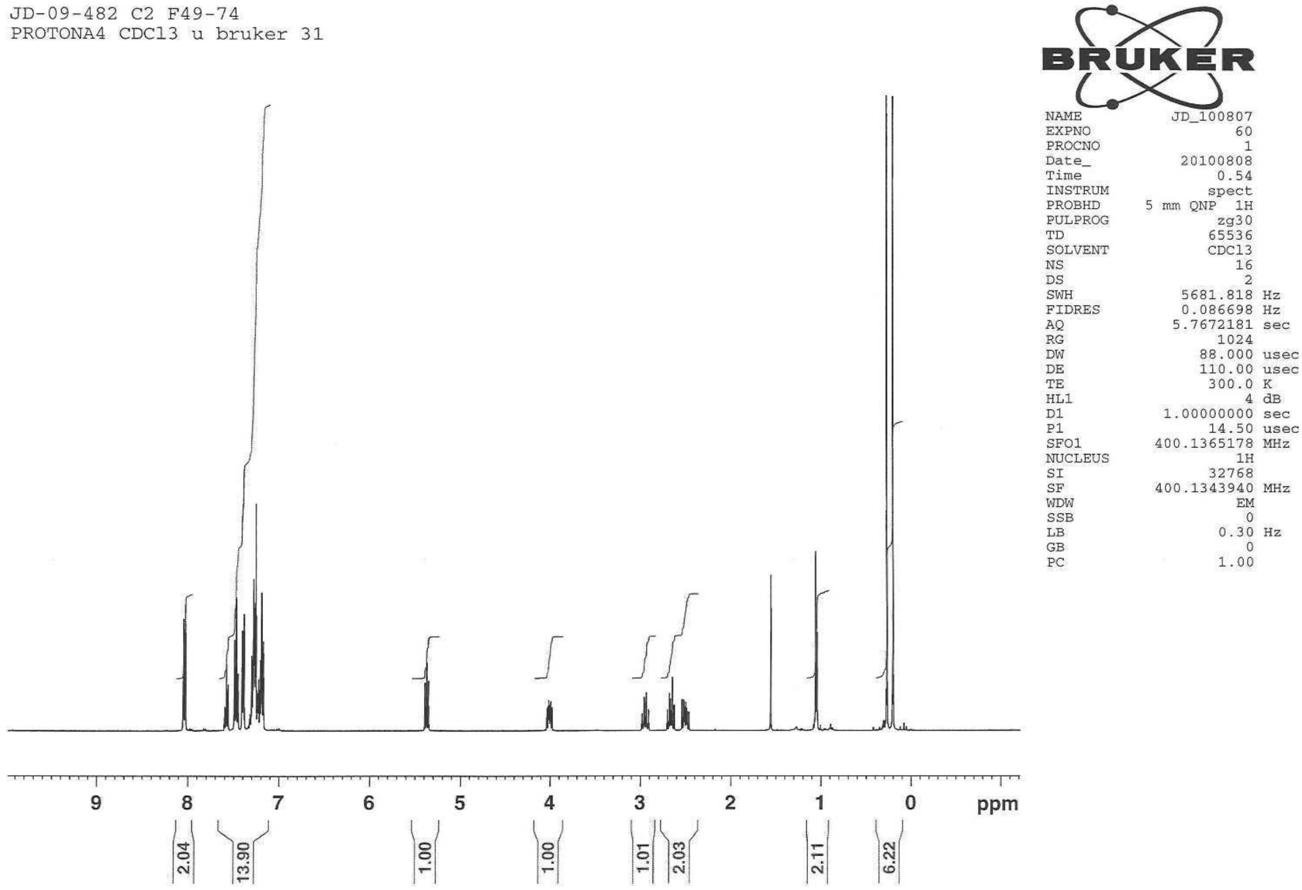
$C_8H_6O_2$
Mol. Wt: 134.13

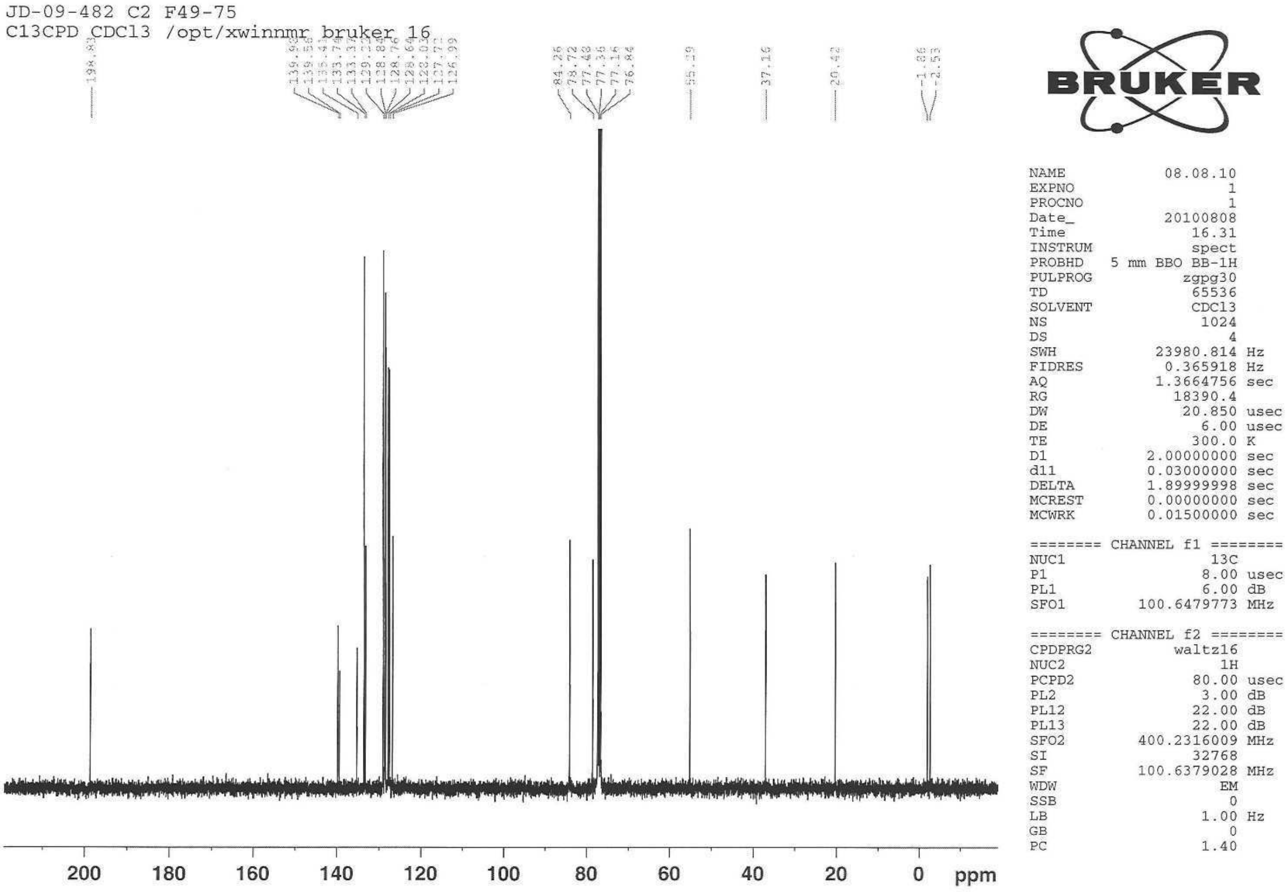
42
$C_{26}H_{28}O_2Si$
Mol. Wt: 400.58

41b
$C_{26}H_{28}O_2Si$
Mol. Wt: 400.58

To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (0.16 g, 0.60 mmol) in anhydrous DCM (6 mL) at 0 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.01 g, 0.04 mL, 0.36 mmol) in anhydrous DCM (3 mL). The reaction was stirred at 0 °C and monitored by TLC. After 3 h the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.257 g) as a yellow oil.

Purification by flash column chromatography [silica gel, 50 % dichloromethane : hexane] afforded product **42** (yield 0.024 g, 0.06 mmol, 10 %) as a colourless oil; R_f 0.48 [50 % dichloromethane : hexane]; δ_H (400 MHz; $CDCl_3$) 0.21 (3H, s, $SiCH_3$), 0.28 (3H, s, $SiCH_3$), 1.04-1.06 (2H, m, $SiCH_2$), 2.50 (1H, ddd, *J* 13.0 10.6 and 7.2, C$\underline{H}_a$H$_b$ C-3 THF), 2.67 (1H, dt, *J* 13.1 and 8.4, CH$_a\underline{H}_b$ C-3 THF), 2.95 (1H, q, *J* 9.4, CH C-4 THF), 4.00 (1H, ddd, J 9.4 7.3 and 5.9, CH C-5 THF), 5.38 (1H, dd, *J* 8.1 and 7.3, CH C-2 THF), 7.17-7.61 (13H, m, Ar), 8.04 (2H, app dd, *J* 8.1 and 0.9, Ar); δ_C (100.6 MHz; $CDCl_3$) -2.5 ($SiCH_3$), -1.9 ($SiCH_3$), 20.4 ($SiCH_2$), 37.2 (CH_2 C-3 THF) 55.3 (CH, C-4 THF), 78.7 (CH, C-2 THF), 84.3 (CH C-5 THF), 127.0 (CH, Ph), 127.7 (CH, Ph), 128.8 (CH, Ph), 129.2 (CH, Ph), 133.4 (CH, Ph), 133.7 (CH, Ph), 135.4 (C, Ph), 139.6 (C, Ph), 140.0 (C, Ph), 198.9 (C=O); LRMS (EI$^+$, *m/z*): M$^+$ not visible, 323 ([M-Ph]$^+$, 1 %), 296 (10), 239 (4), 135 (60), 117 (100), 105 (40), 91 (10), 77 (21); HRMS (ESP, *m/z*) 418.2196 [M+NH_4]$^+$, $C_{26}H_{282}NSi$ requires 418.2197.





JD-09-482 C2 F49-75
C13CPD CDCl3 /opt/xwinnmr bruker 16

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EXPNO                   1
PROCNO                  1
Date_            20100808
Time                16.31
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379028 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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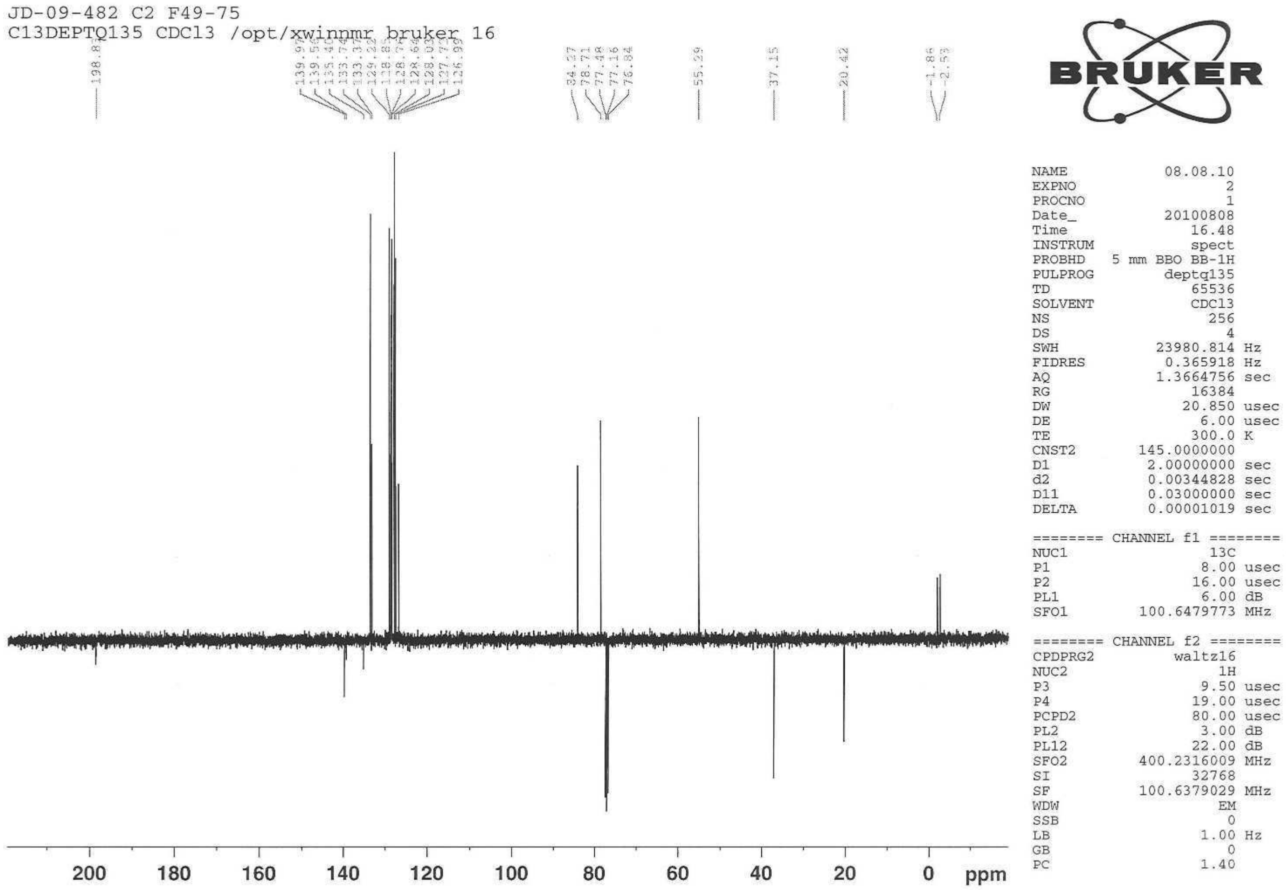
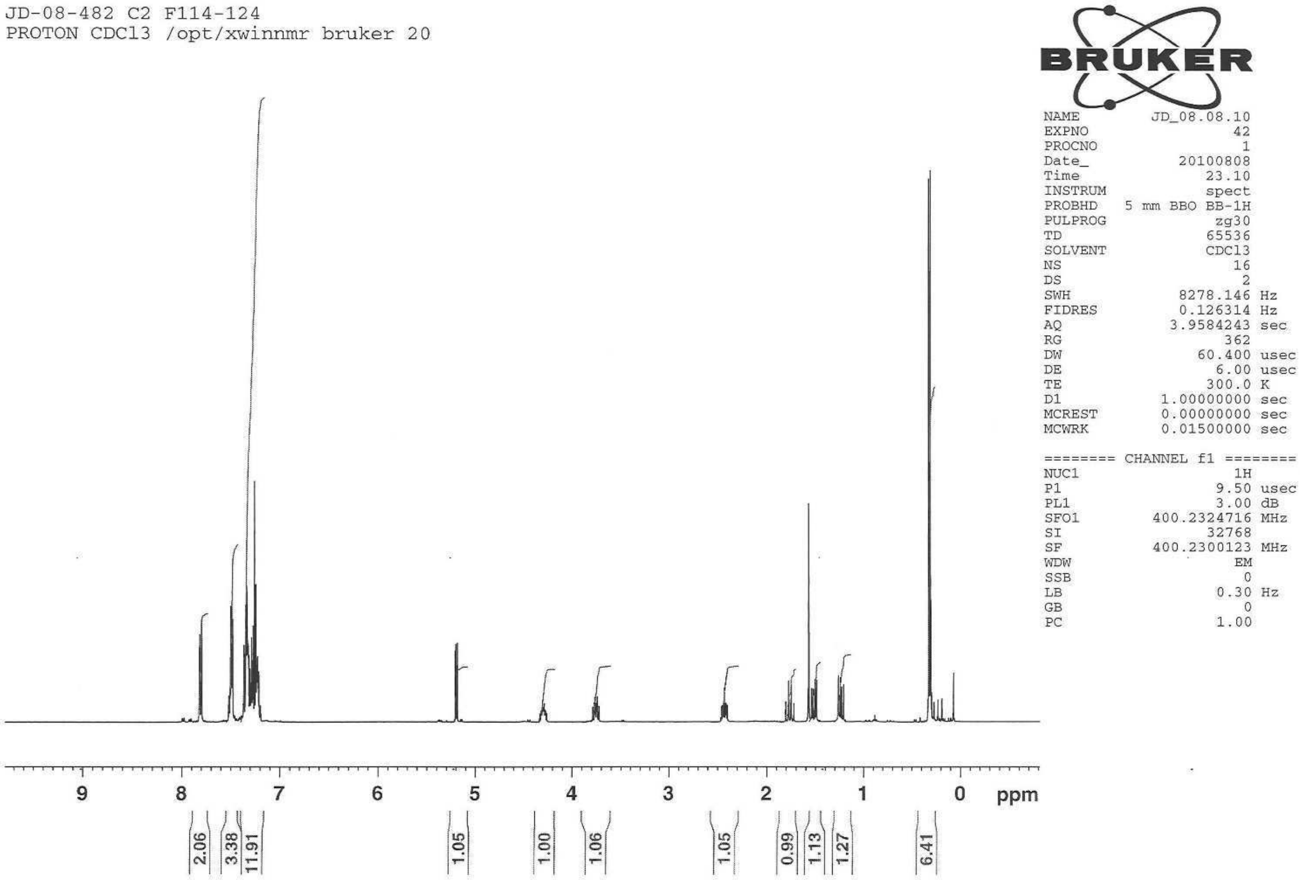


```
NAME              08.08.10
EXPNO                    2
PROCNO                   1
Date_             20100808
Time                 16.48
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG           deptq135
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   300.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
D11             0.03000000 sec
DELTA           0.00001019 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
P2                   16.00 usec
PL1                   6.00 dB
SFO1           100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
P3                    9.50 usec
P4                   19.00 usec
PCPD2                80.00 usec
PL2                   3.00 dB
PL12                 22.00 dB
SFO2           400.2316009 MHz
SI                   32768
SF             100.6379029 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

(±)-(5-((dimethyl(phenyl)silyl)methyl)-3-phenyltetrahydrofuran-2-yl)(phenyl)methanone (41b) (0.034 g, 0.09 mmol, 14 %) is a colourless oil; R_f 0.35 [50 % dichloromethane : hexane]; δ_H (600 MHz; $CDCl_3$) 0.31 (3H, s, $SiCH_3$), 0.33 (3H, s, $SiCH_3$), 1.24 (1H, dd, *J* 14.3 and 8.0, $SiC\underline{H}_aH_b$), 1.52 (1H, dd, *J* 14.2 and 6.2, $SiCH_a\underline{H}_b$), 1.78 (1H, app dt, *J* 12.2 and 10.3, $C\underline{H}_aH_b$ C-4 THF), 2.44 (1H, ddd, *J* 12.3 7.8 and 4.7, $CH_a\underline{H}_b$ C-4 THF), 3.78 (1H, dt, *J* 10.3 and 7.4, CH C-3 THF), 4.29 (1H, dddd, *J* 10.3 7.7 6.4 and 4.8, CH C-5 THF), 5.19 (1H, d, *J* 6.8, CH C-2 THF), 7.20-7.39 (10H, m, Ar), 7.48-7.52 (3H, m, Ar), 7.30 (2H, app dd, *J* 8.3 and 1.0, Ar); δ_C (100.6 MHz; $CDCl_3$) -2.2 ($SiCH_3$), -2.0 ($SiCH_3$), 23.2 ($SiCH_2$), 45.2 (CH_2 C-4 THF) 48.3 (CH, C-4 THF), 79.3 (CH, C-5 THF), 86.1 (CH C-2 THF), 126.9 (CH, Ph), 127.8 (CH, Ph), 127.9 (CH, Ph), 128.4 (CH, Ph), 128.9 (CH, Ph), 129.1 (CH, Ph), 129.3 (CH, Ph), 133.3 (CH, Ph), 133.7 (CH, Ph), 135.4 (C, Ph), 138.9 (C, Ph), 142.6 (C, Ph), 198.5 (C=O); LRMS (EI^+, *m/z*): M^+ not visible, 295 ($[M\text{-}PhCO]^+$, 18 %), 277 (4), 239 (5), 135 (100), 105 (19), 91 (8), 77 (14); HRMS (ESI, *m/z*) 418.2190 $[M+NH_4]^+$, $C_{26}H_{32}O_2NSi$ requires 418.2197.



```
JD-08-482 C2 F114-124
PROTON CDCl3 /opt/xwinnmr bruker 20
```

```
NAME          JD_08.08.10
EXPNO                  42
PROCNO                  1
Date_            20100808
Time                23.10
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    362
DW                 60.400 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.50 usec
PL1                  3.00 dB
SFO1          400.2324716 MHz
SI                  32768
SF            400.2300123 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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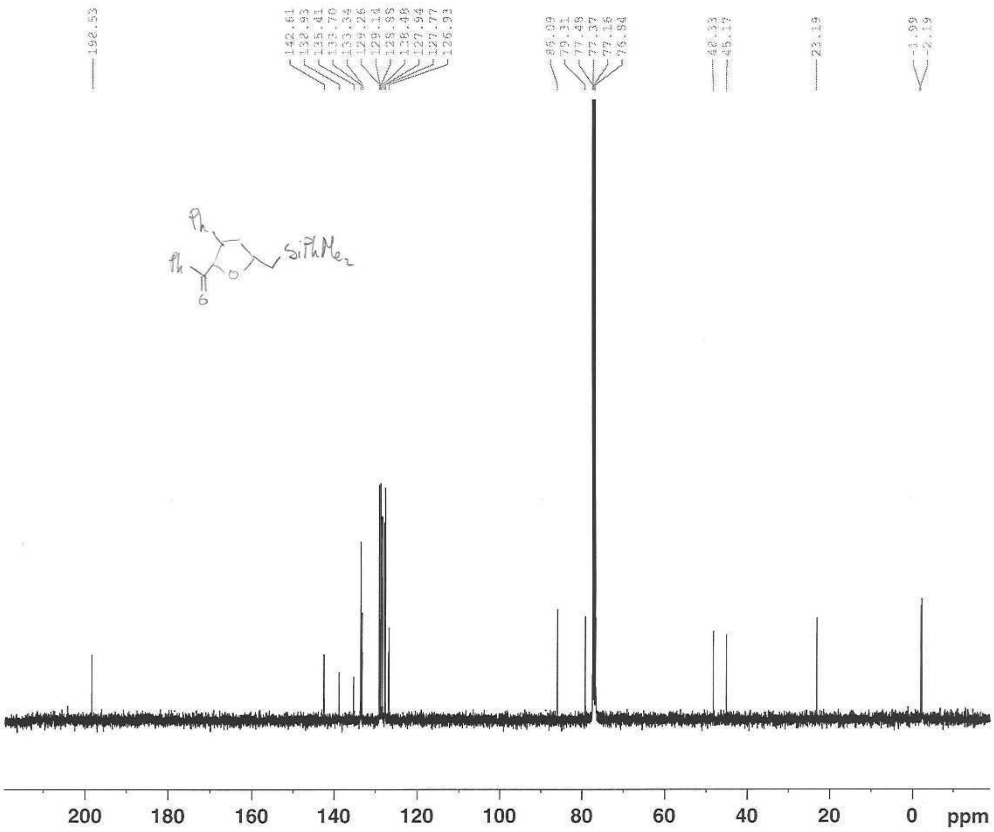
JD-08-482 C2 F114-124
C13CPD CDCl3 /opt/xwinnmr bruker 20



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NAME          JD_08.08.10
EXPNO                  40
PROCNO                  1
Date_            20100808
Time                22.50
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                10321.3
DW                 20.850 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.00 usec
PL1                  6.00 dB
SFO1          100.6479773 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          400.2316009 MHz
SI                  32768
SF            100.6379013 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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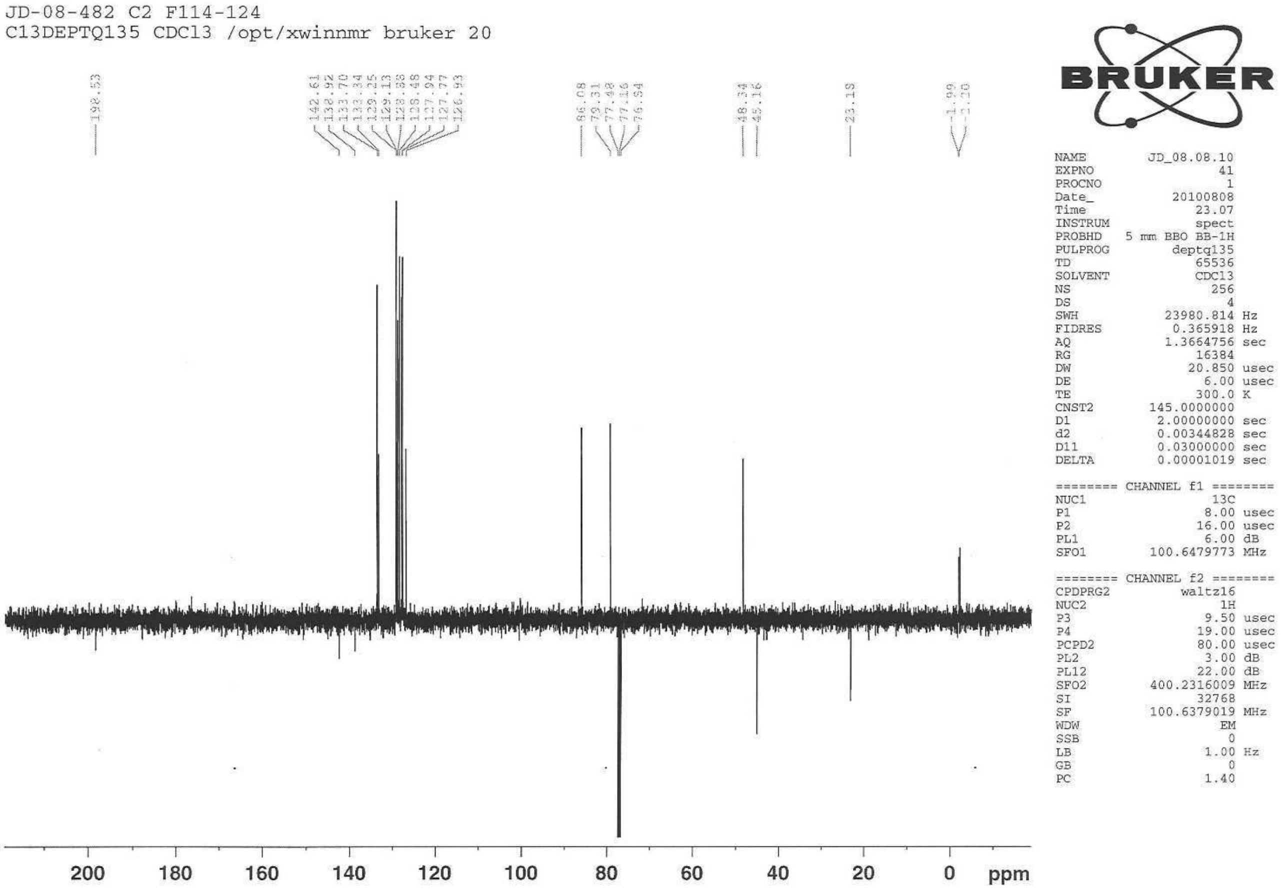
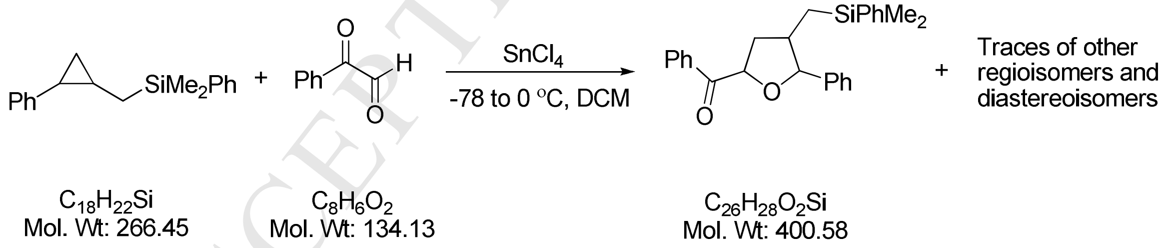
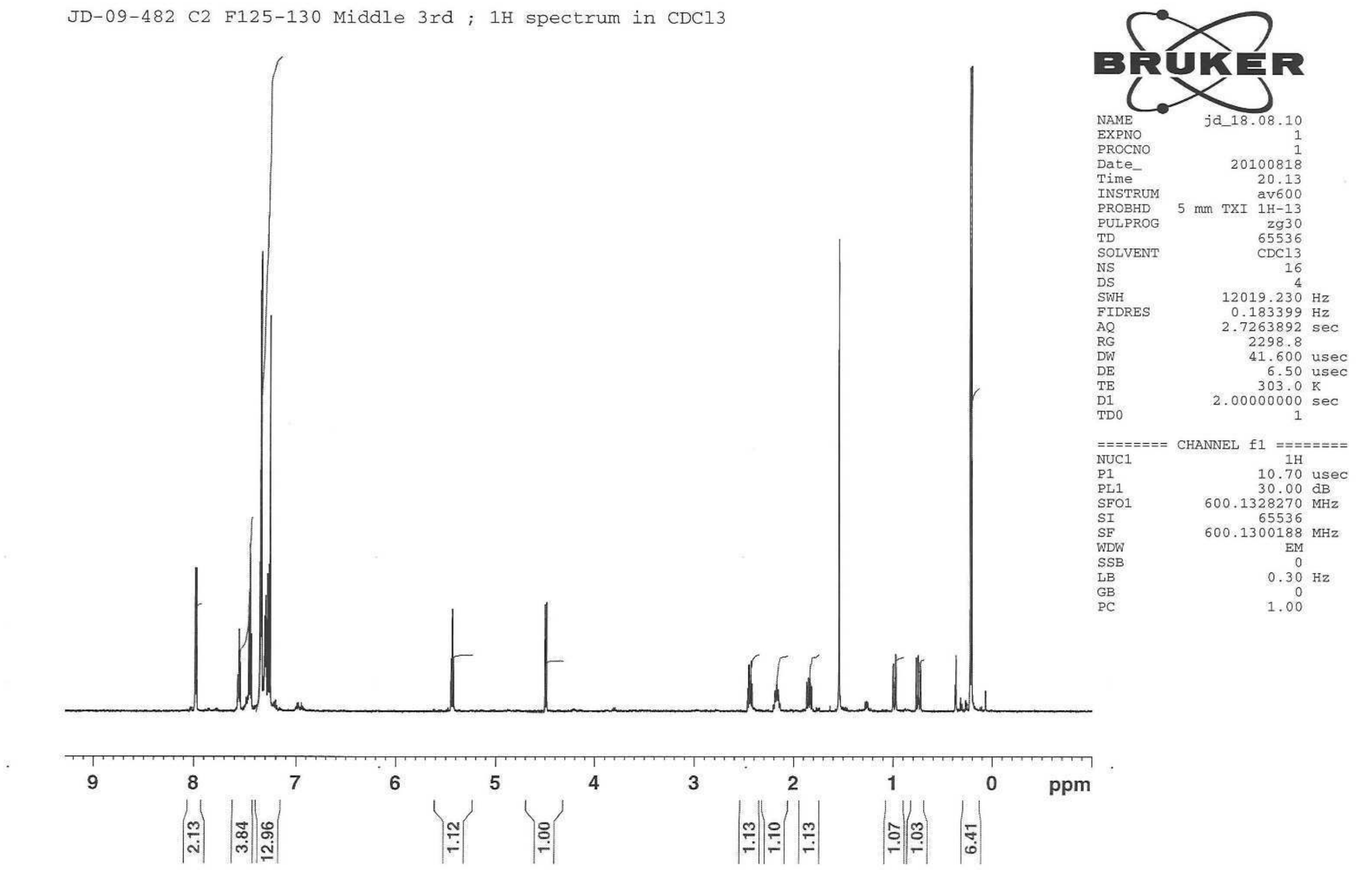


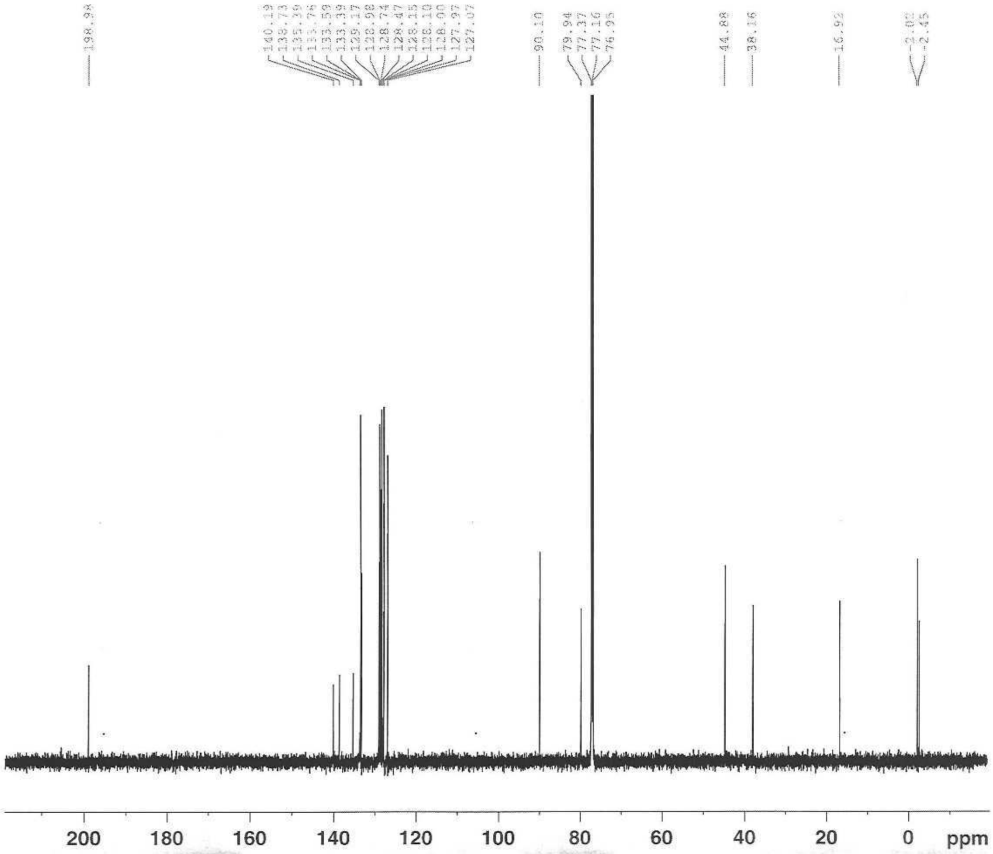
(±)-(4-((dimethyl(phenyl)silyl)methyl)-5-phenyltetrahydrofuran-2-yl)(phenyl)methanone (43)



To a stirred solution of freshly distilled phenyl glyoxal (0.12 g, 0.90 mmol) and dimethyl(phenyl)((2-phenylcyclopropyl)methyl)silane (0.16 g, 0.60 mmol) in anhydrous DCM (6 mL) at -78 °C and under an atmosphere of argon was added, dropwise, a solution of tin tetrachloride (0.01 g, 0.04 mL, 0.36 mmol) in anhydrous DCM (3 mL). The reaction was stirred and allowed to warm to 0 °C and monitored by TLC. After 2 h at 0 °C the reaction was quenched by the addition of water (5 mL), the organic layer was separated and the aqueous layer further extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL), separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the impure product (0.219 g) as a yellow oil. Purification by flash column chromatography [silica gel, gradient elution, 100 % hexane – 10 % diethyl ether : hexane] followed by preparative TLC [60 % dichloromethane : hexane] afforded product (yield 0.007 g, 0.02 mmol, 3 %) as a colourless oil; R_f 0.19 [60 % dichloromethane : hexane]; δ_H (400 MHz; $CDCl_3$) 0.21 (3H, s, $SiCH_3$), 0.23 (3H, s, $SiCH_3$), 0.75 (1H, dd, *J* 14.7 and 11.3, $Si\underline{CH_a}H_b$), 0.99 (1H, dd, *J* 14.7 and 2.8, SiCH$_a\underline{H}_b$), 1.85 (1H, ddd, *J* 12.3 10.8 and 8.7, C$\underline{H}_a$H$_b$ C-3 THF), 2.18 (1H, m, CH C-4 THF), 2.45 (1H, dt, *J* 12.6 and 7.4, CH$_a\underline{H}_b$ C-3 THF), 4.50 (1H, d, *J* 9.1, CH C-5 THF), 5.44 (1H, t, *J* 8.0, CH C-2 THF), 7.25-7.56 (13H, m, Ar), 7.98 (2H, app d, *J* 8.1, Ar); δ_C (100.6 MHz; CDCl$_3$) -2.4 (SiCH$_3$), -2.0 (SiCH$_3$), 16.9 (SiCH$_2$), 38.2 (CH$_2$ C-3 THF) 44.9 (CH, C-4 THF), 79.9 (CH, C-2 THF), 90.1 (CH, C-5 THF), 127.1 (CH, Ph), 128.0 (CH, Ph), 128.1 (CH, Ph), 128.5 (CH, Ph), 128.7 (CH, Ph), 129.0 (CH, Ph), 129.2 (CH, Ph), 133.4 (CH, Ph), 133.6 (CH, Ph), 135.4 (C, Ph), 138.7 (C, Ph), 140.2 (C, Ph), 199.0 (C=O).



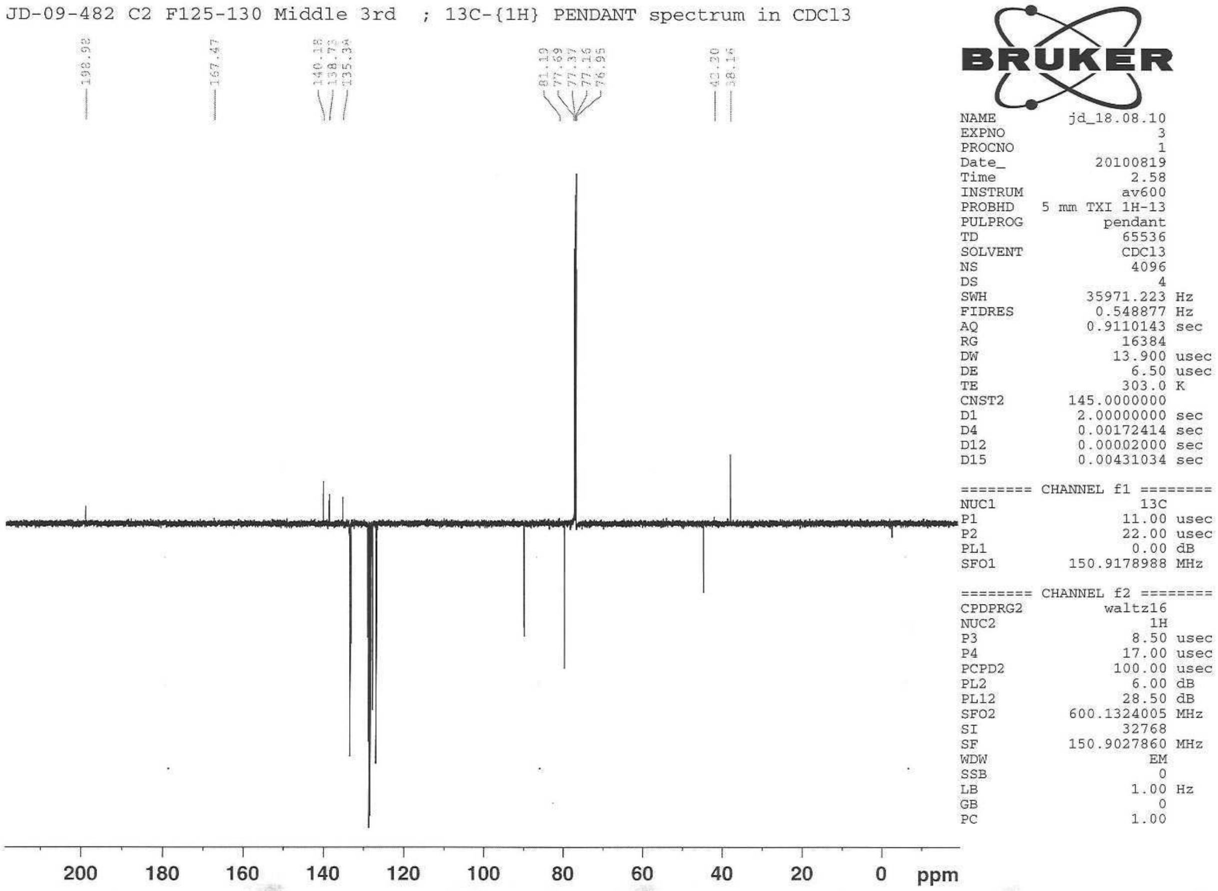
JD-09-482 C2 F125-130 Middle 3rd ; 13C-{1H} spectrum in CDCl3



```
NAME          jd_18.08.10
EXPNO                   2
PROCNO                  1
Date_            20100818
Time                20.19
INSTRUM             av600
PROBHD   5 mm TXI 1H-13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   4096
DS                      4
SWH             35971.223 Hz
FIDRES           0.548877 Hz
AQ              0.9110143 sec
RG                    362
DW                 13.900 usec
DE                   6.50 usec
TE                  303.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.00 usec
PL1                  0.00 dB
SFO1          150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                  6.00 dB
PL12                25.40 dB
PL13                25.40 dB
SFO2          600.1324005 MHz
SI                  32768
SF            150.9027857 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```



```
NAME           jd_18.08.10
EXPNO                    3
PROCNO                   1
Date_             20100819
Time                  2.58
INSTRUM              av600
PROBHD   5 mm TXI 1H-13
PULPROG            pendant
TD                   65536
SOLVENT              CDCl3
NS                    4096
DS                       4
SWH              35971.223 Hz
FIDRES            0.548877 Hz
AQ               0.9110143 sec
RG                   16384
DW                  13.900 usec
DE                    6.50 usec
TE                   303.0 K
CNST2          145.0000000
D1              2.00000000 sec
D4              0.00172414 sec
D12             0.00002000 sec
D15             0.00431034 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.00 usec
P2                   22.00 usec
PL1                   0.00 dB
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
P3                    8.50 usec
P4                   17.00 usec
PCPD2               100.00 usec
PL2                   6.00 dB
PL12                 28.50 dB
SFO2        600.1324005 MHz
SI                   32768
SF          150.9027860 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.00
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