Supporting information

Brønsted acid catalyzed 1,2-silyl shift in propargyl silanes – synthesis of silyl dienes and silyl indenes

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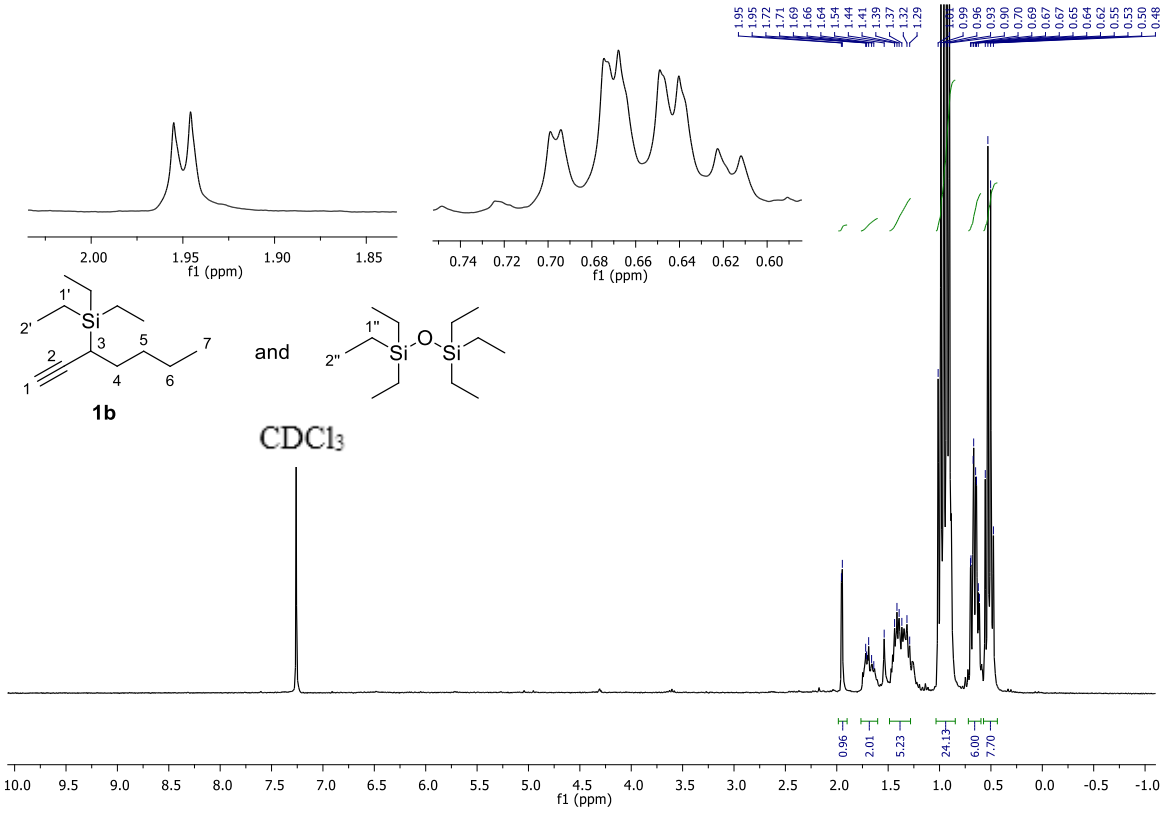
Contents

1. NMR spectra of starting materials

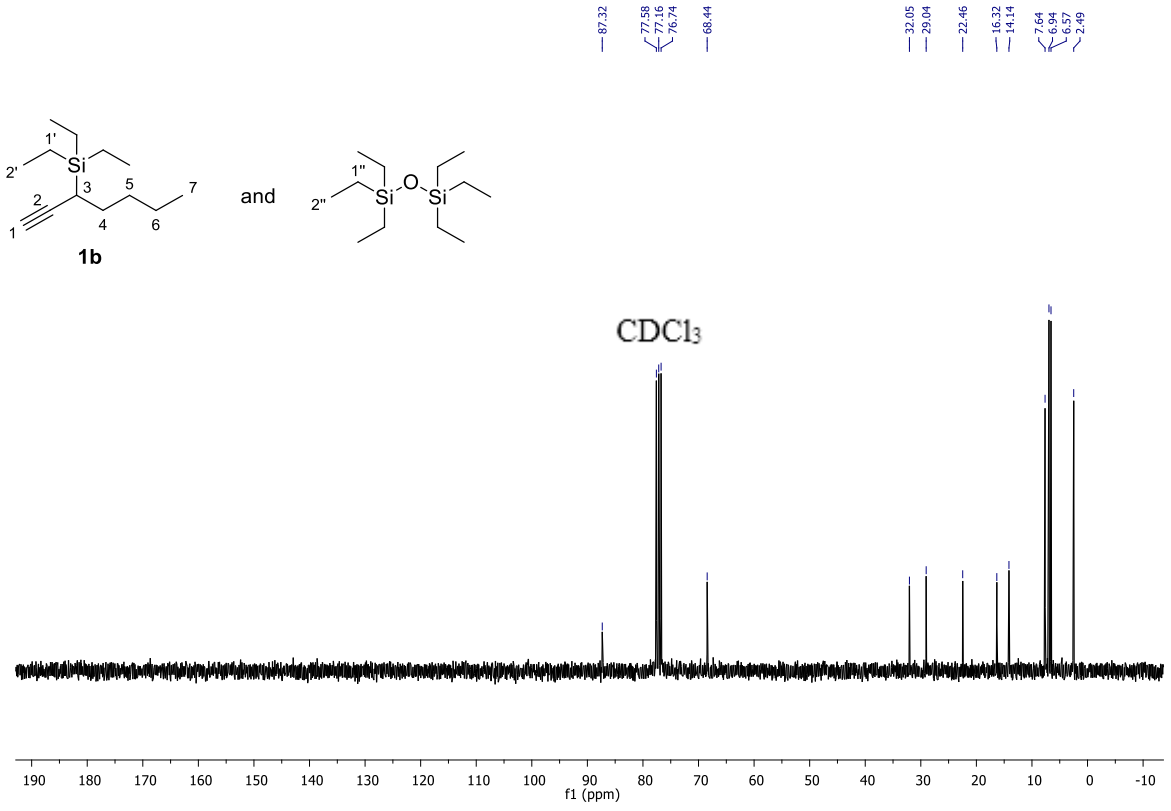
1.1. Terminal propargyl silanes

Hept-1-yn-3-il triethyl silane **1b**

^{1}H NMR (300 MHz, $CDCl_3$)

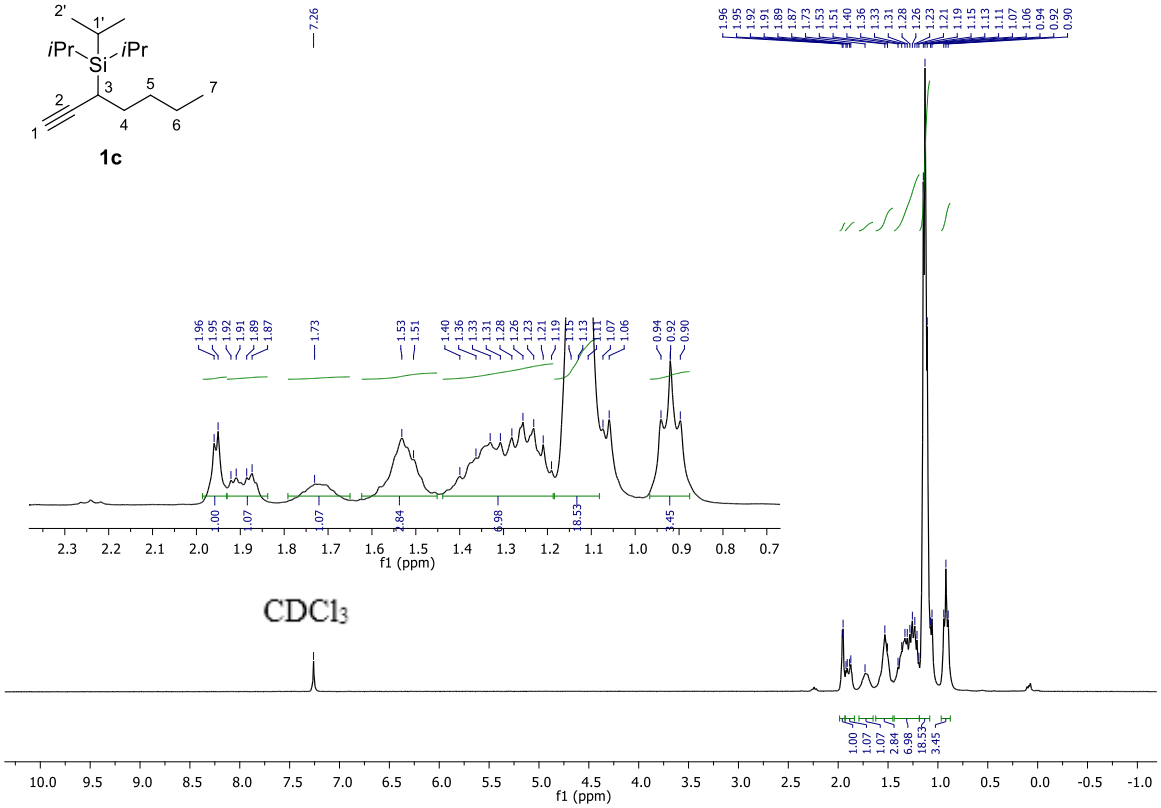


^{13}C NMR (75.5 MHz, $CDCl_3$)

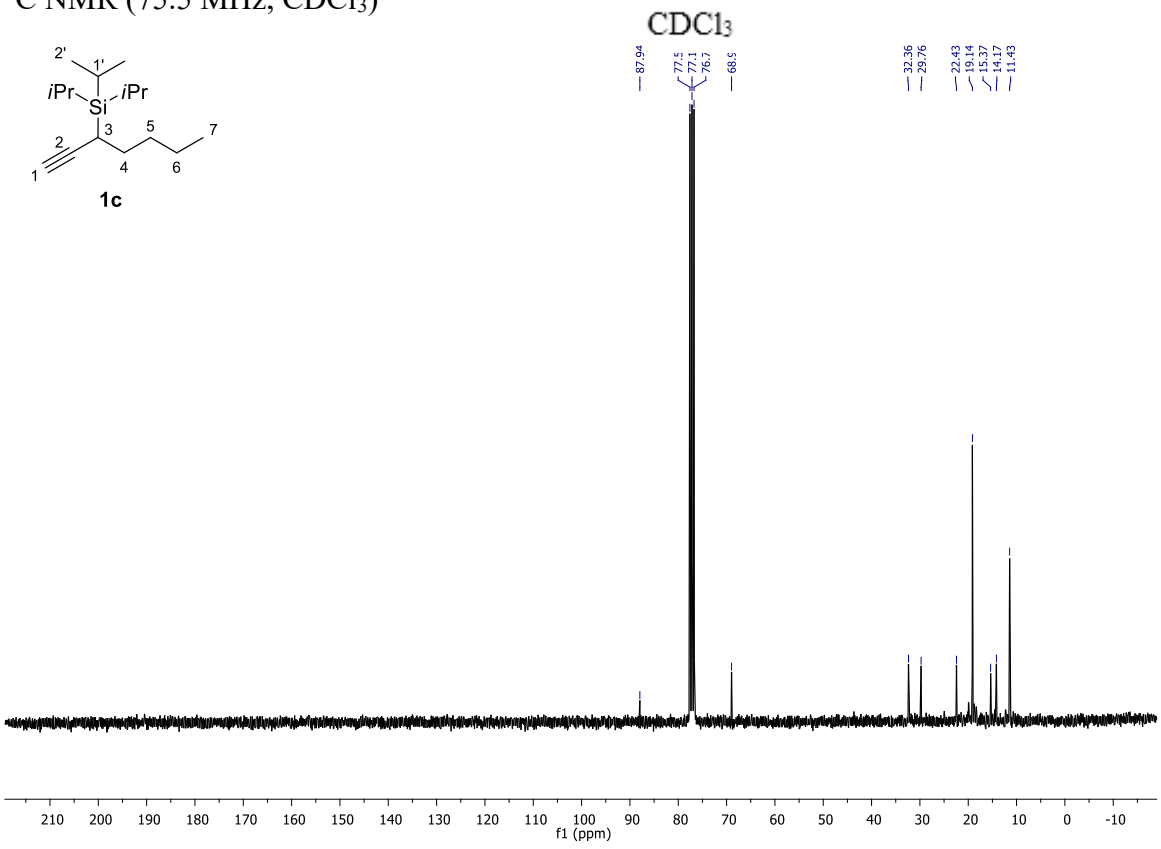


Hept-1-yn-3-yltriisopropylsilane **1c**

^{1}H NMR (300 MHz, $CDCl_3$)

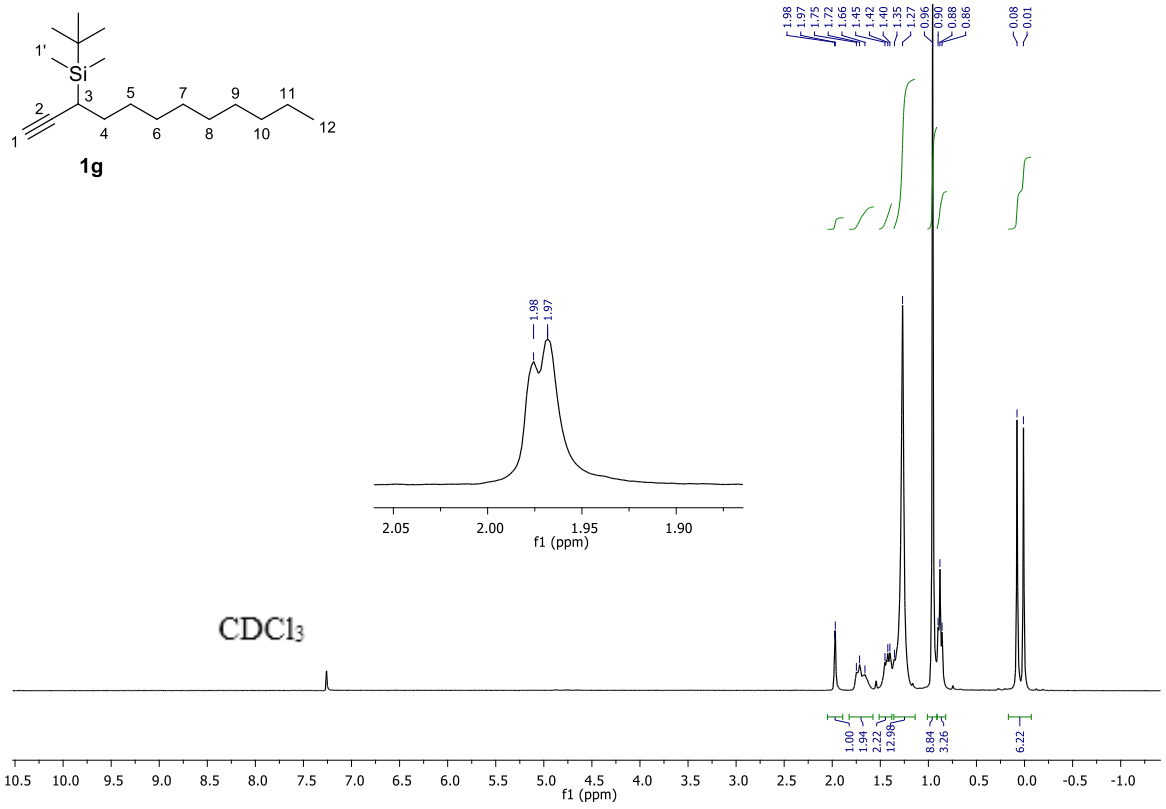


^{13}C NMR (75.5 MHz, $CDCl_3$)

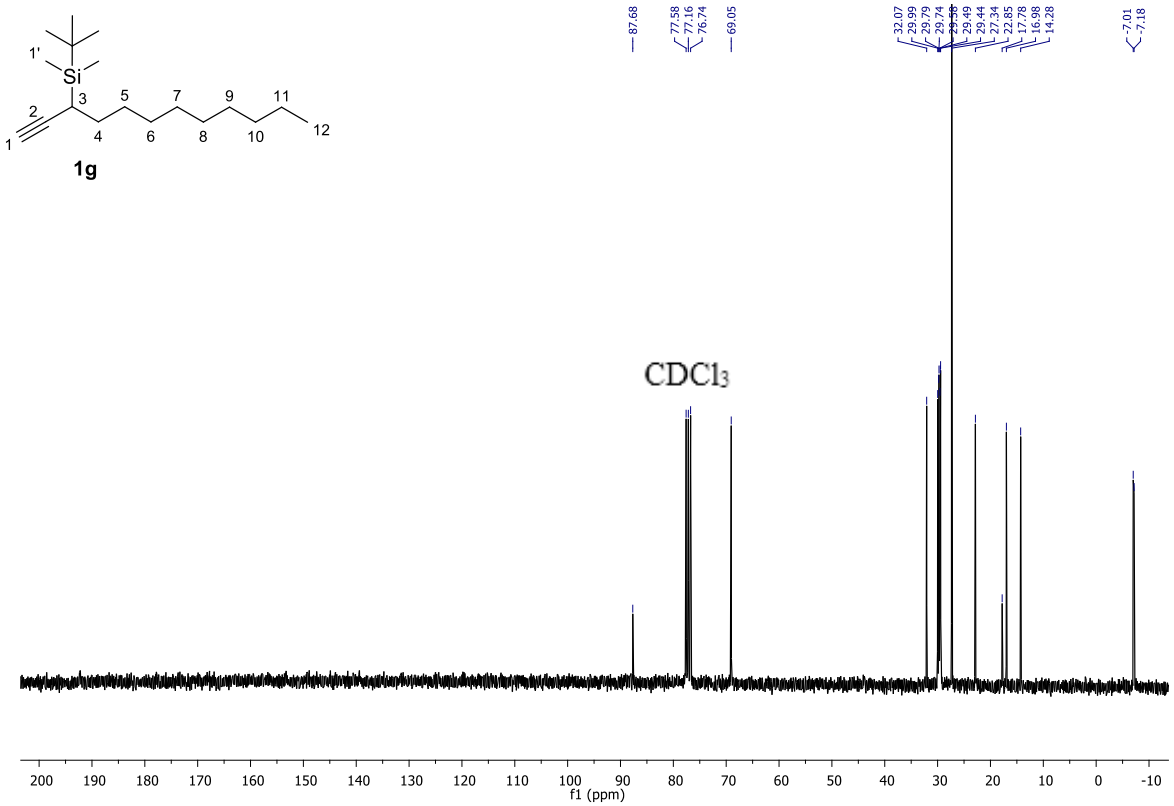


Tert-butyl dodec-1-yn-3-il dimethyl silane **1g**

^{1}H NMR (300 MHz, $CDCl_3$)

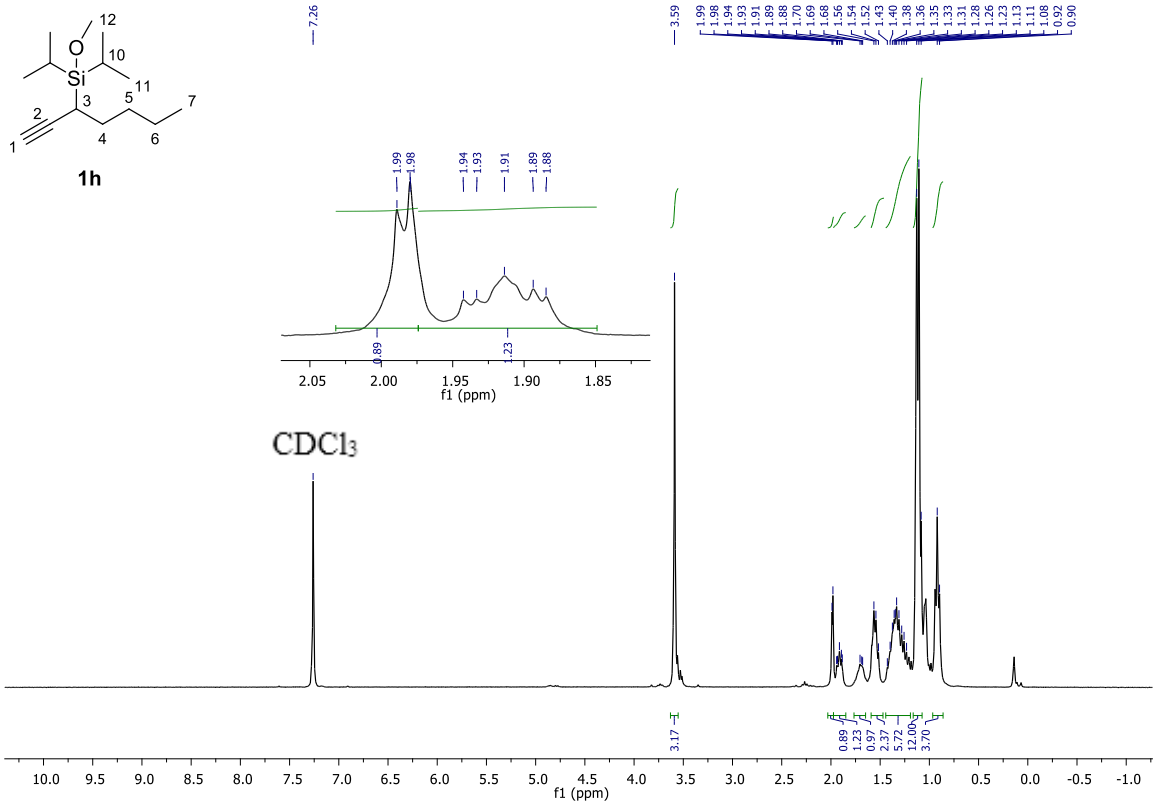


^{13}C NMR (75.5 MHz, $CDCl_3$)

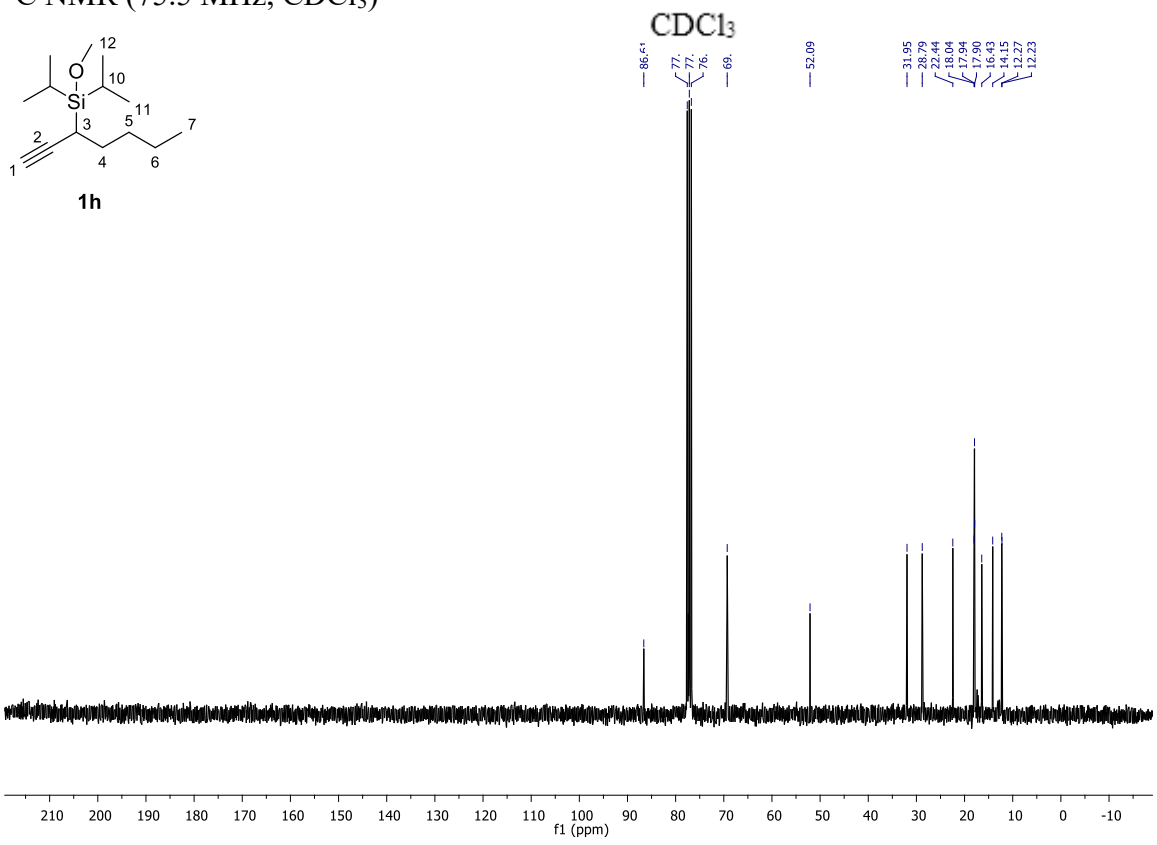


Hept-1-yn-3-yldiisopropyl(methoxy)silane **1h**

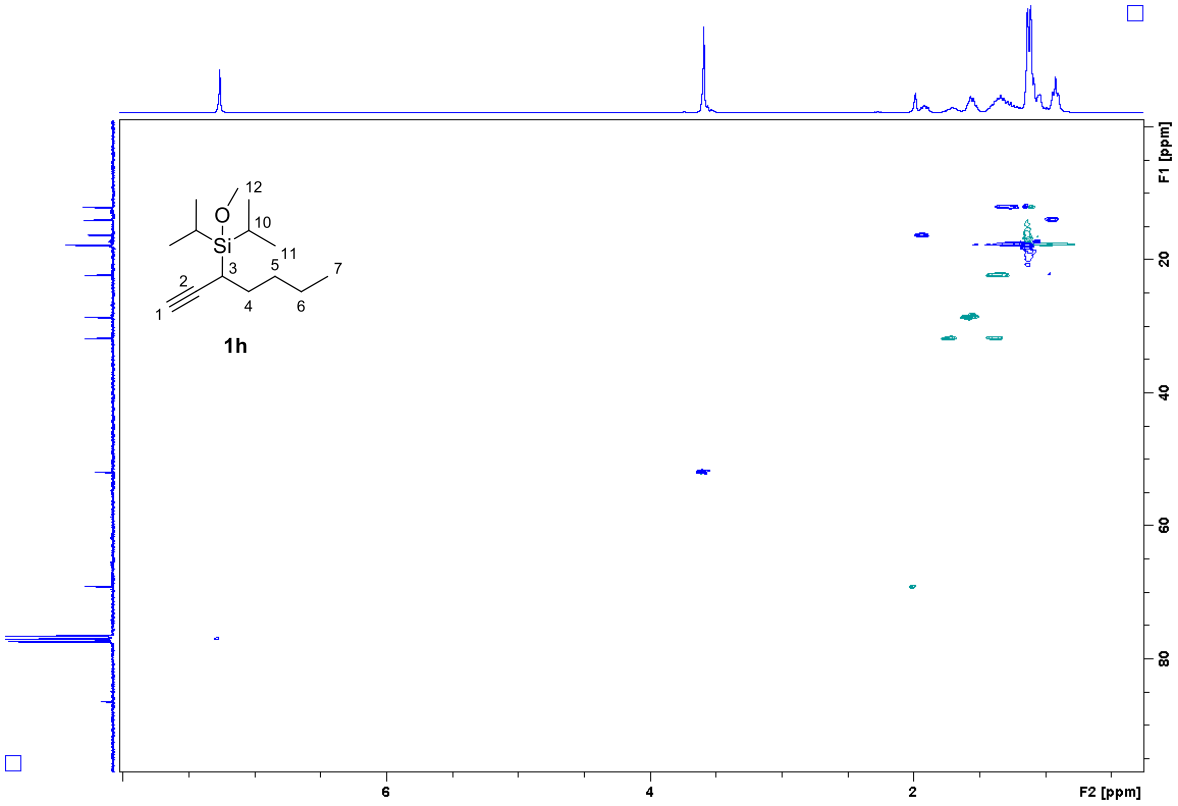
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)



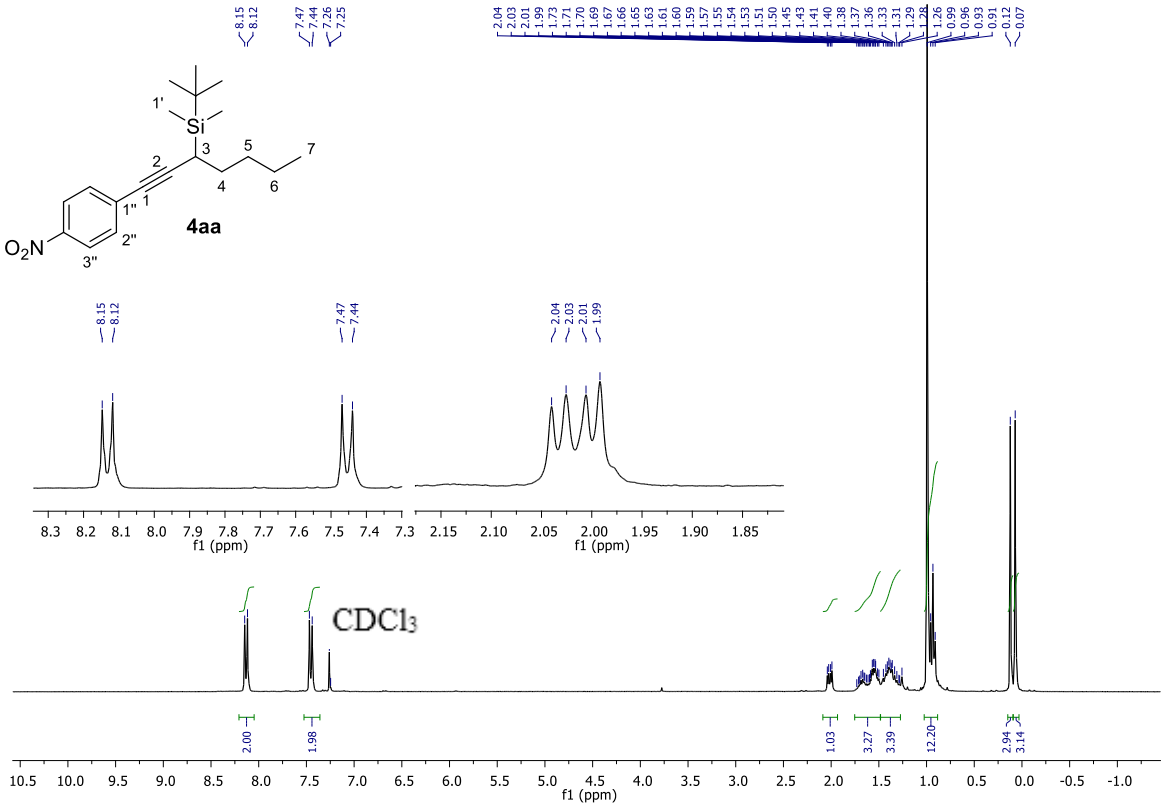
2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)



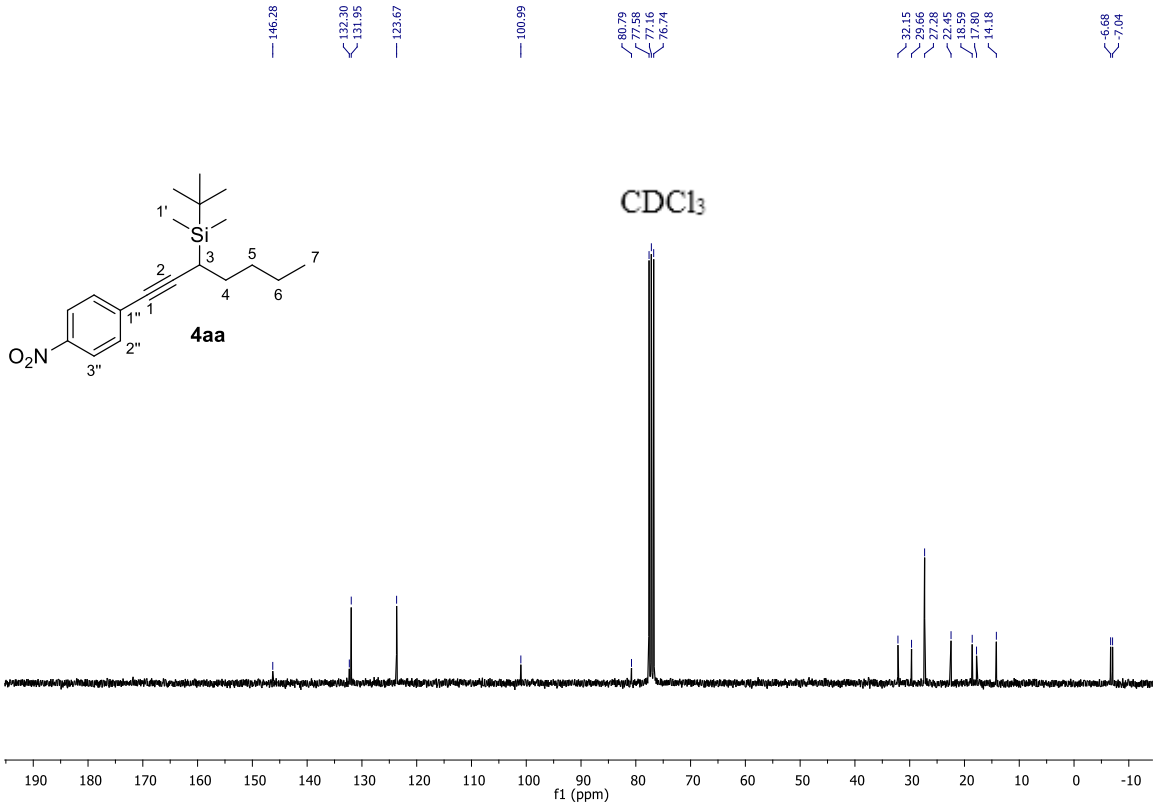
1.2. 1-Aryl propargyl silanes

Tert-butyldimethyl(1-(4-nitrophenyl)hept-1-yn-3-yl)silane **4aa**

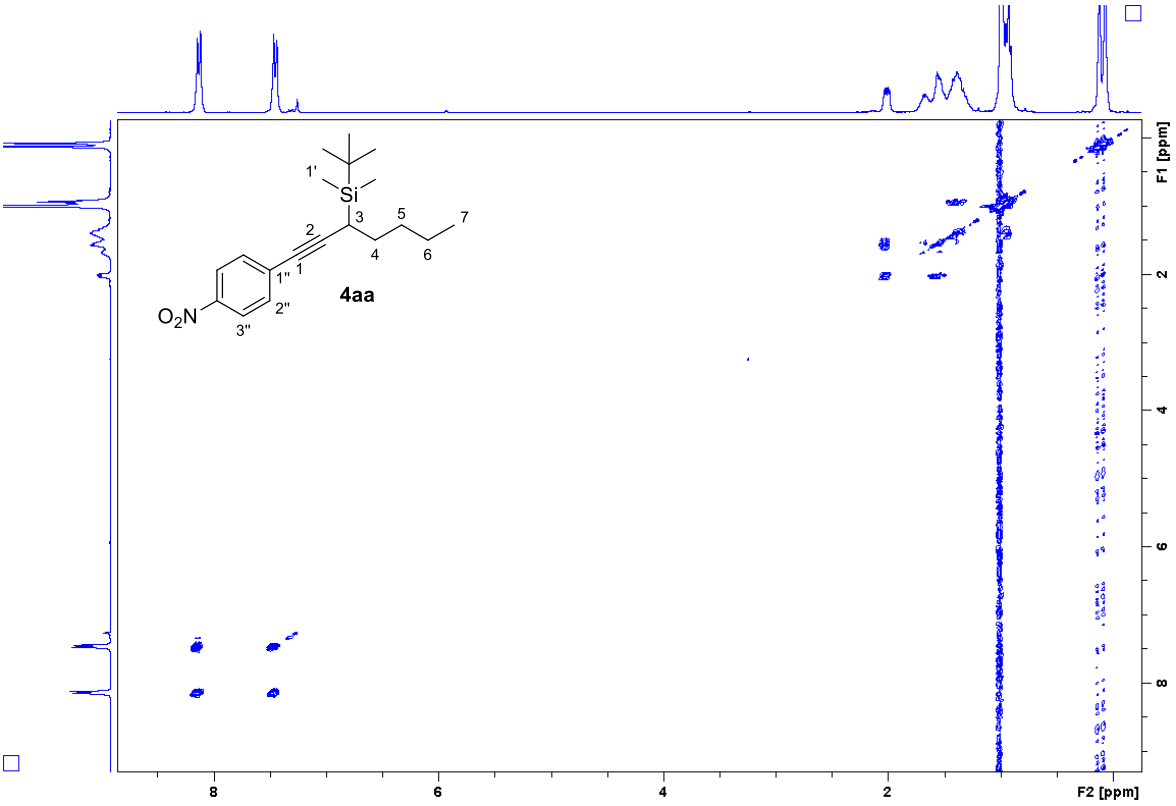
^{1}H NMR (300 MHz, $CDCl_3$)



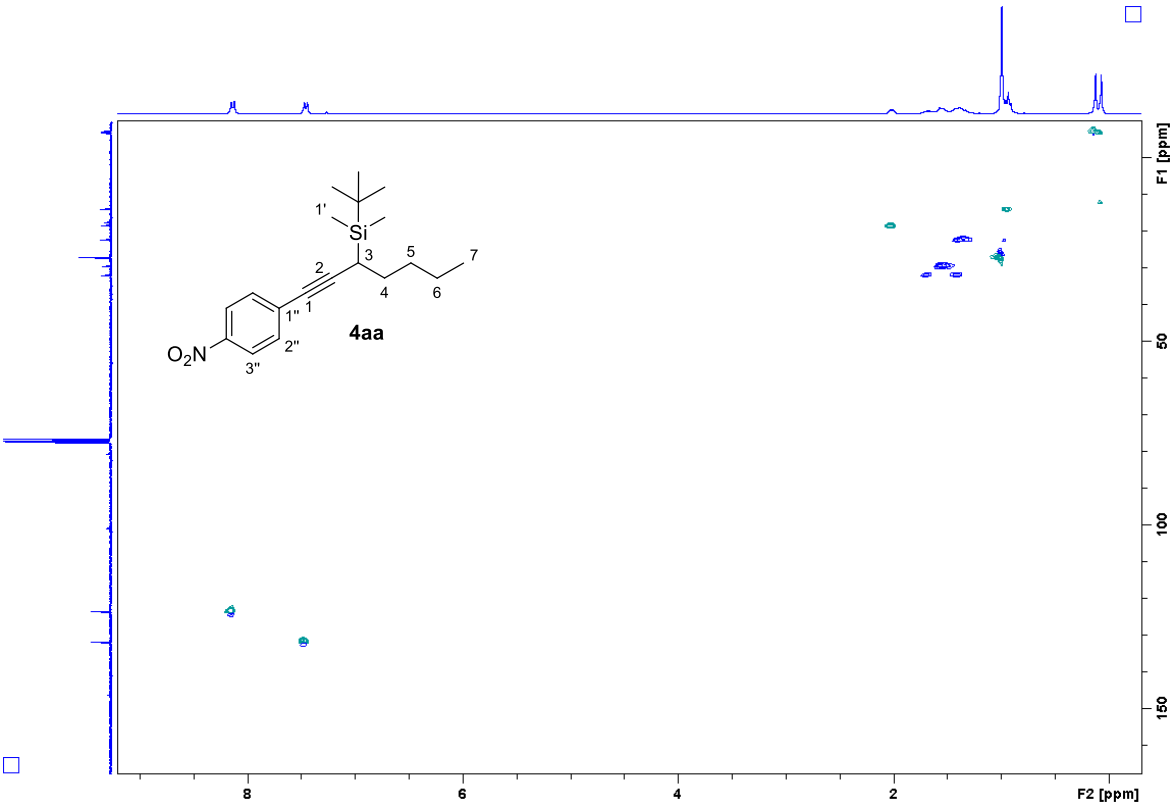
^{13}C NMR (75.5 MHz, $CDCl_3$)



2D ^{1}H-^{1}H COSY NMR ($CDCl_3$)

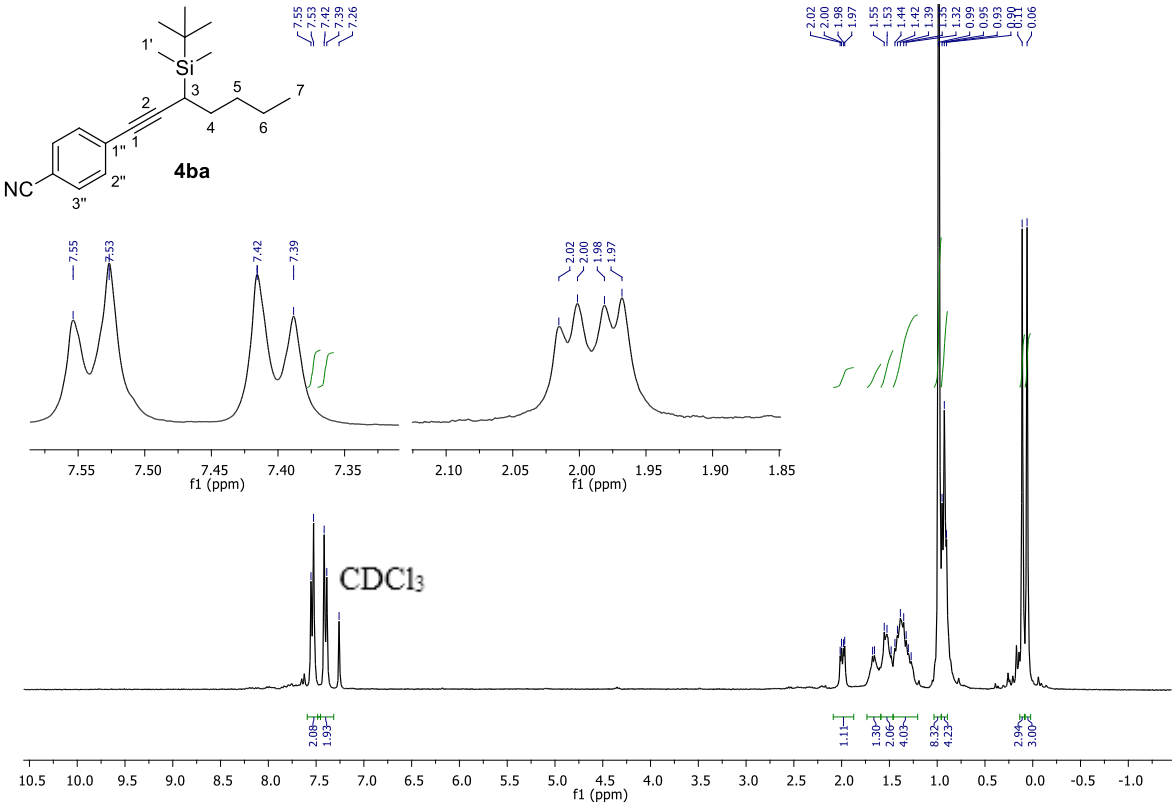


2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

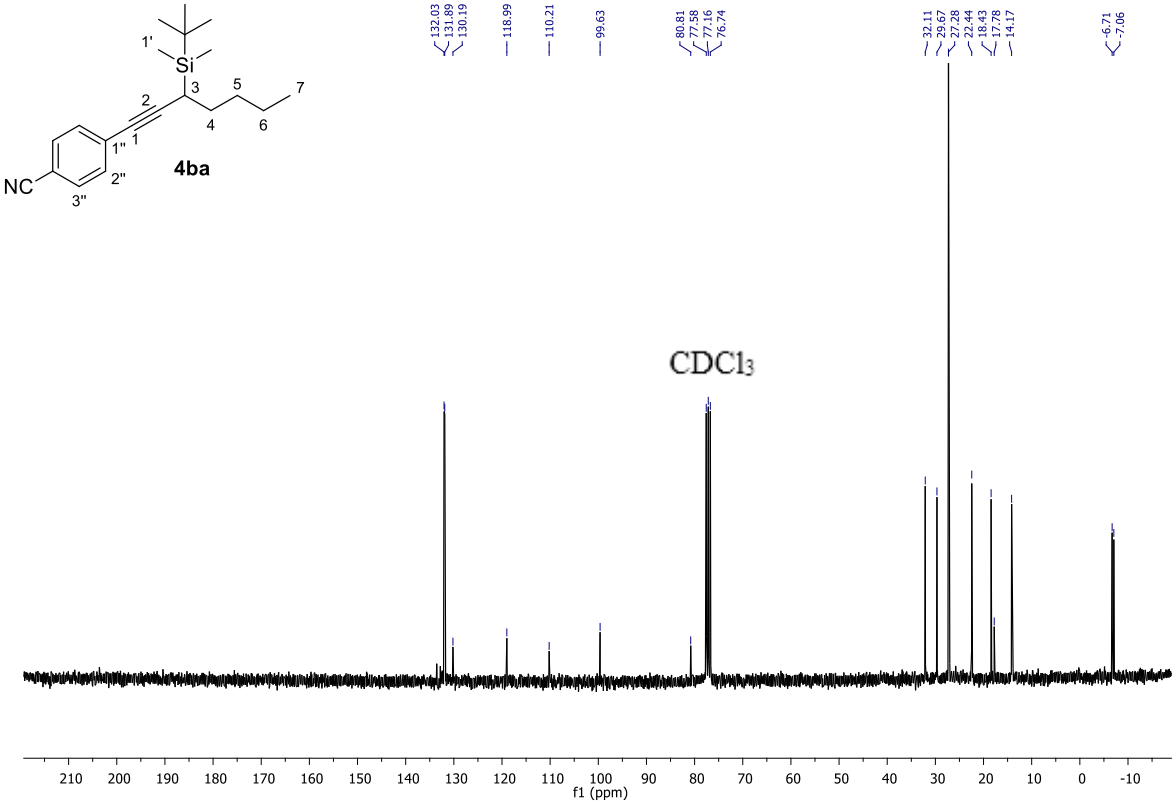


4-(3-(*Tert*-butyldimethylsilyl)hept-1-yn-1-yl)benzonitrile **4ba**

^{1}H NMR (300 MHz, $CDCl_3$)

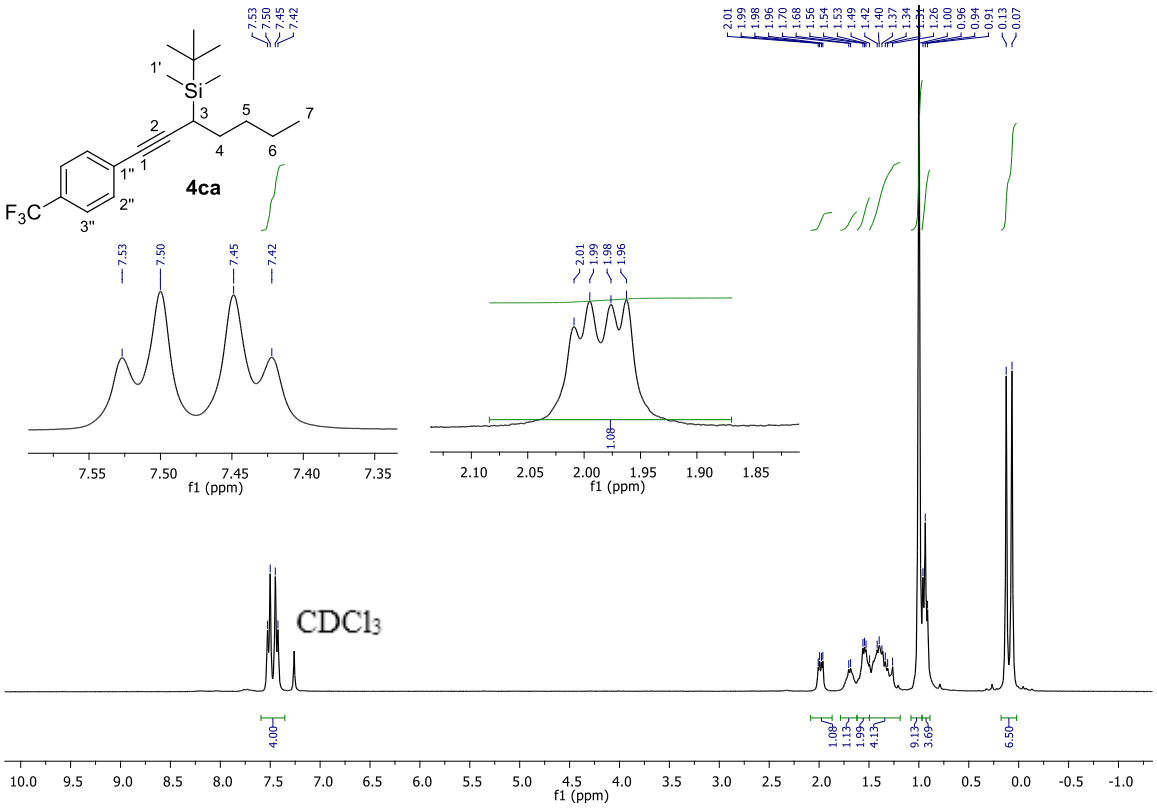


^{13}C NMR (75.5 MHz, $CDCl_3$)

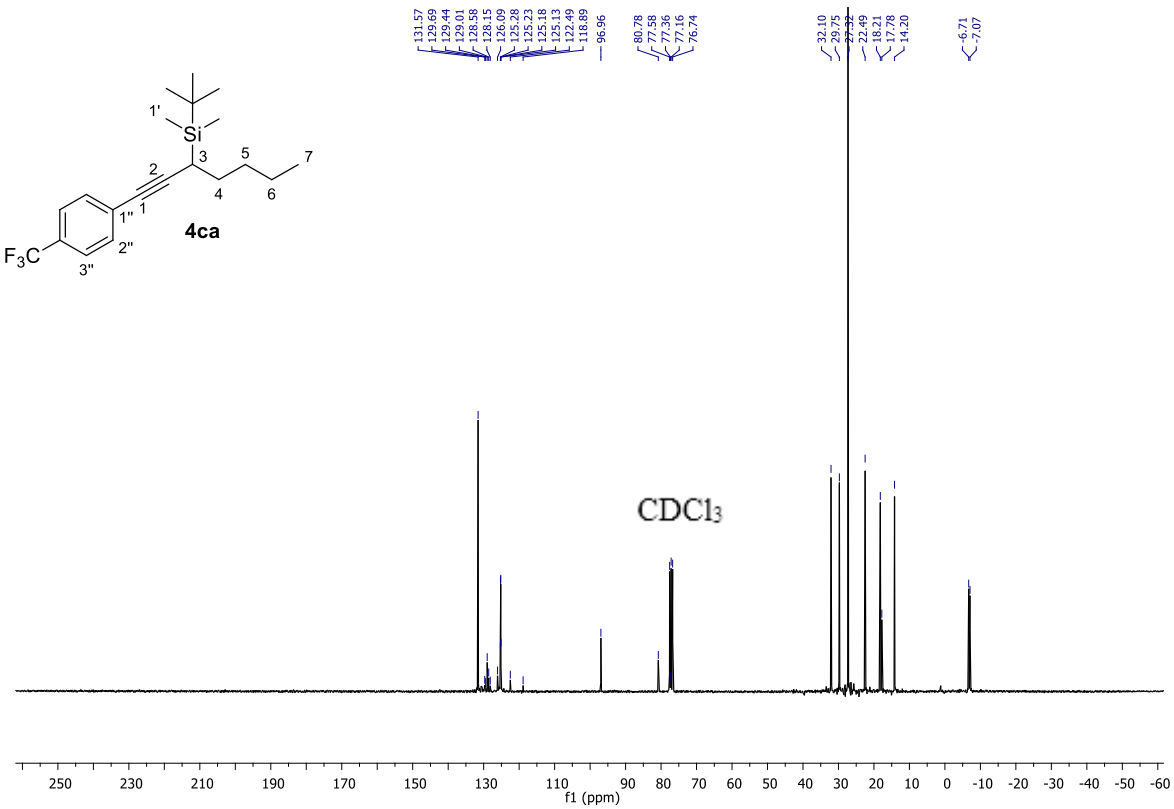


Tert-butyldimethyl(1-(4-(trifluoromethyl)phenyl)hept-1-yn-3-yl)silane **4ca**

^{1}H NMR (300 MHz, $CDCl_3$)

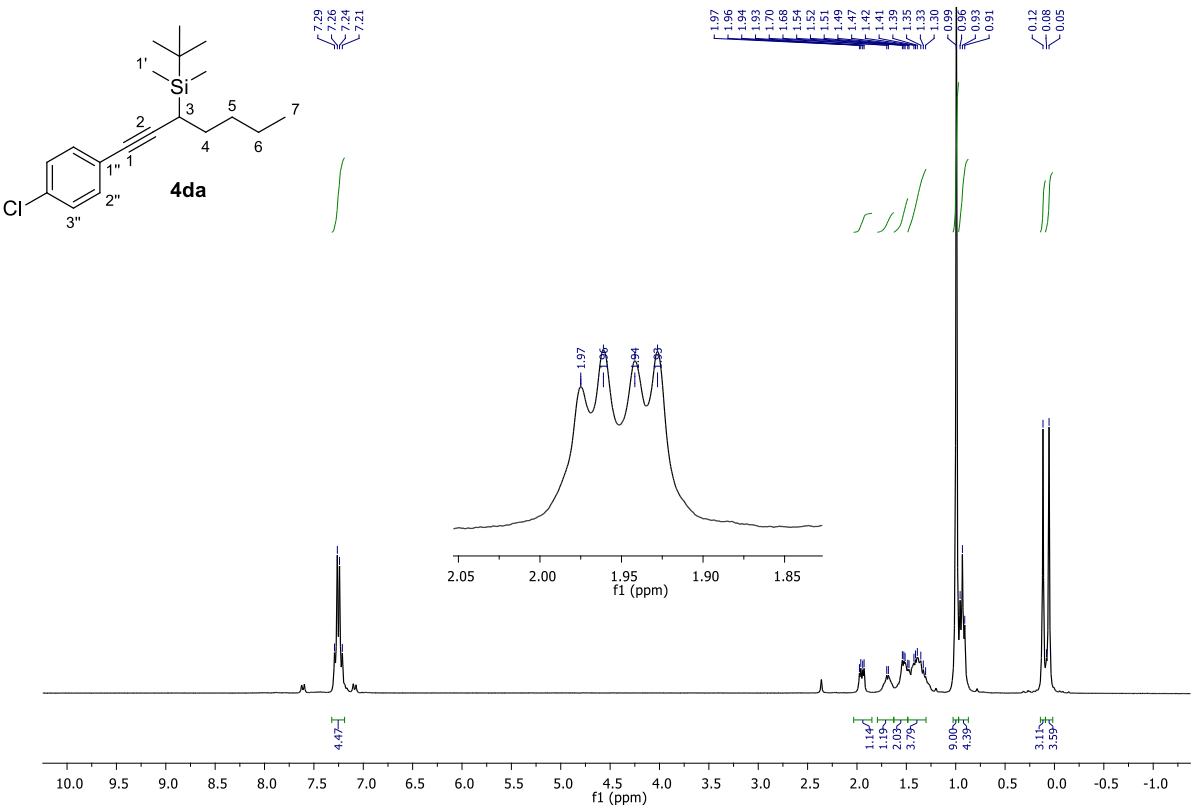


^{13}C NMR (75.5 MHz, $CDCl_3$)

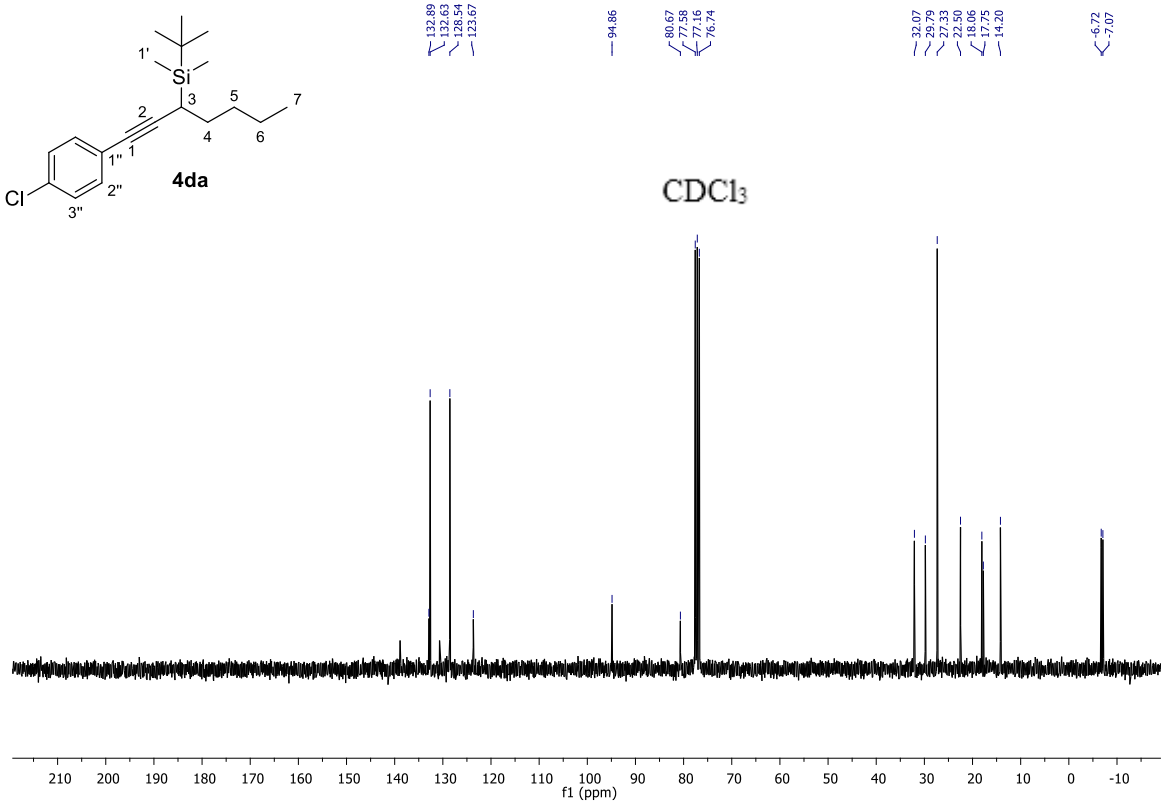


Tert-butyl(1-(4-chlorophenyl)hept-1-yn-3-yl)dimethylsilane **4da**

^{1}H NMR (300 MHz, $CDCl_3$)

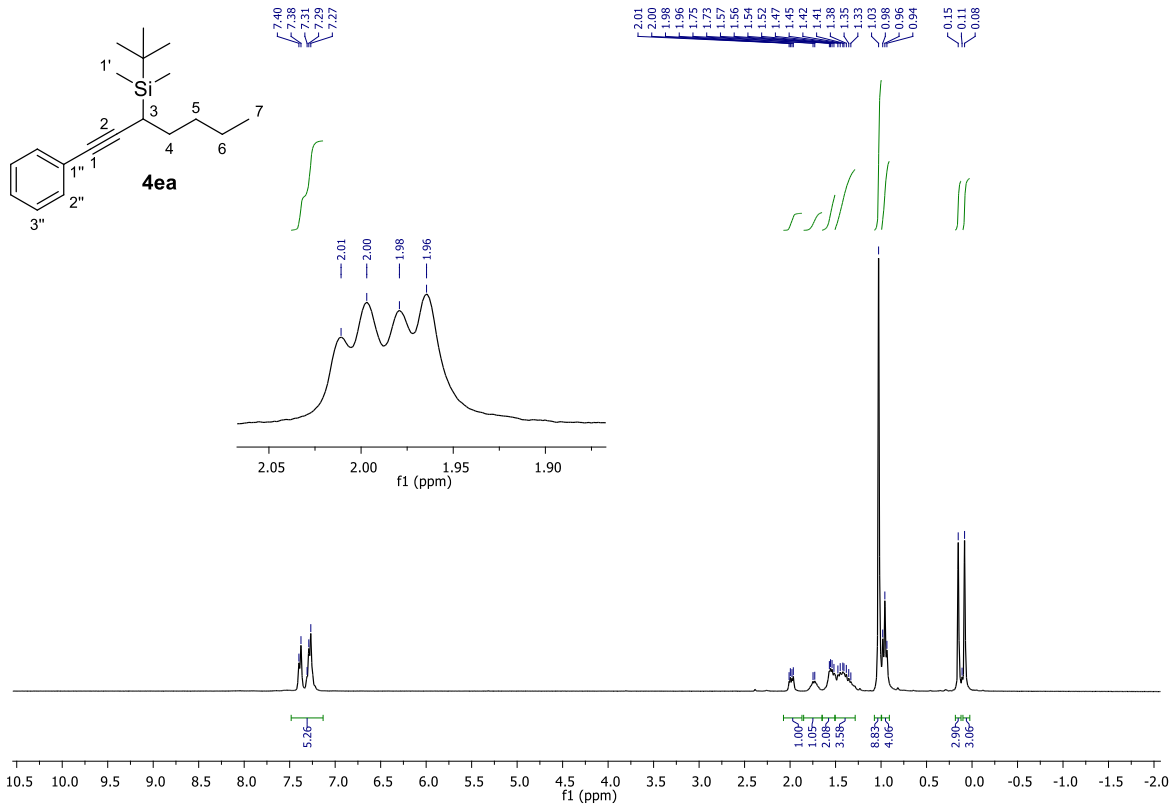


^{13}C NMR (75.5 MHz, $CDCl_3$)

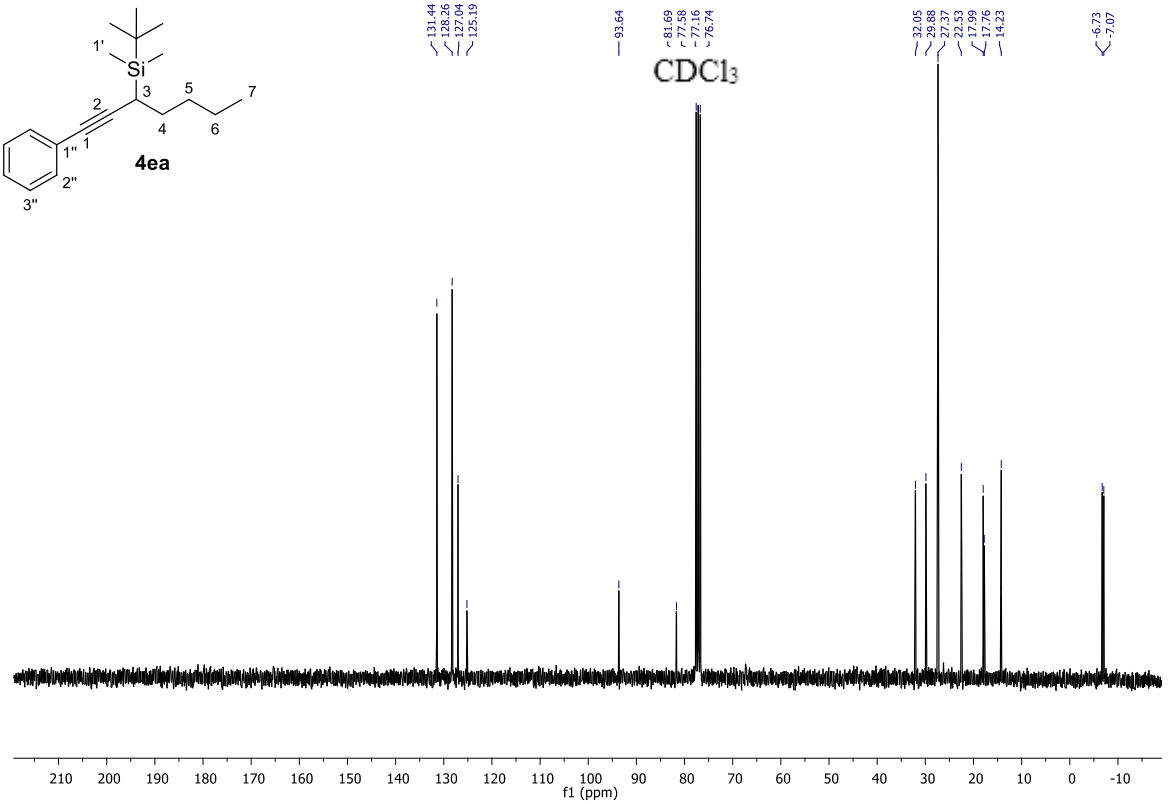


Tert-butyldimethyl(1-phenylhept-1-yn-3-yl)silane **4ea**

^{1}H NMR (300 MHz, $CDCl_3$)

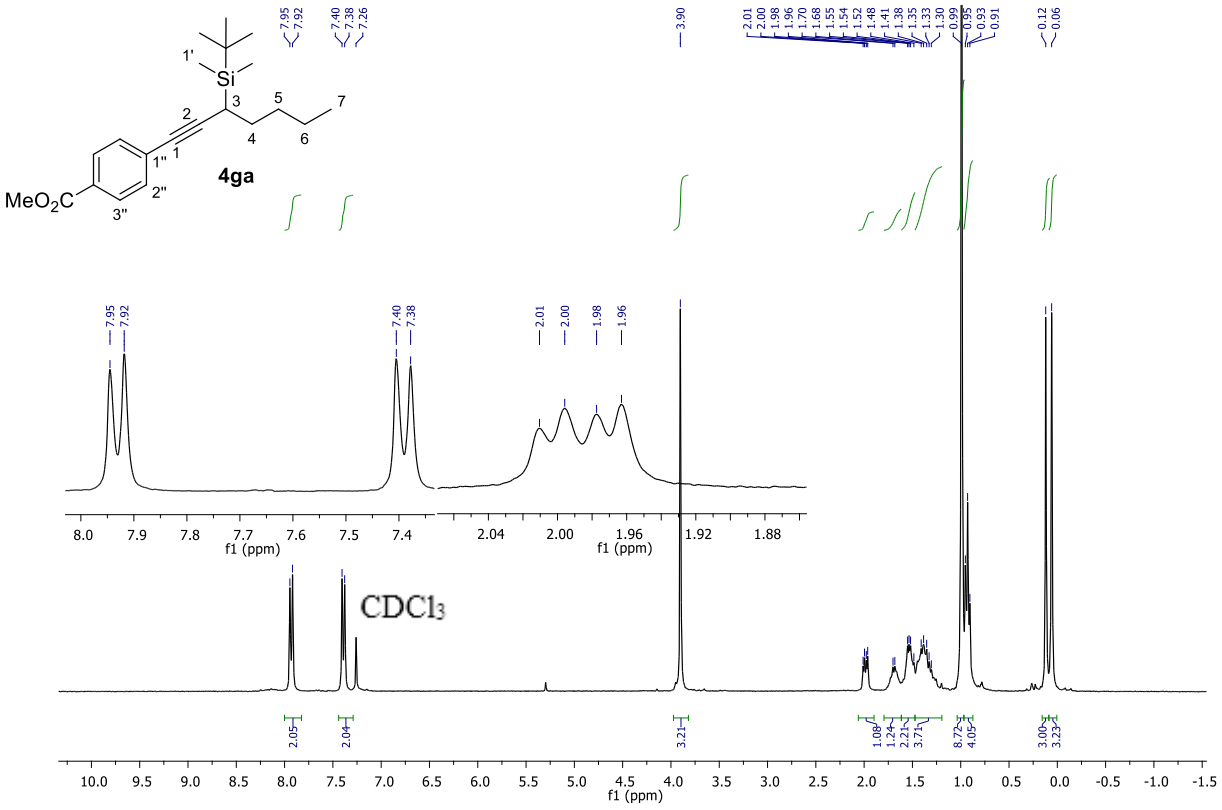


^{13}C NMR (75.5 MHz, $CDCl_3$)

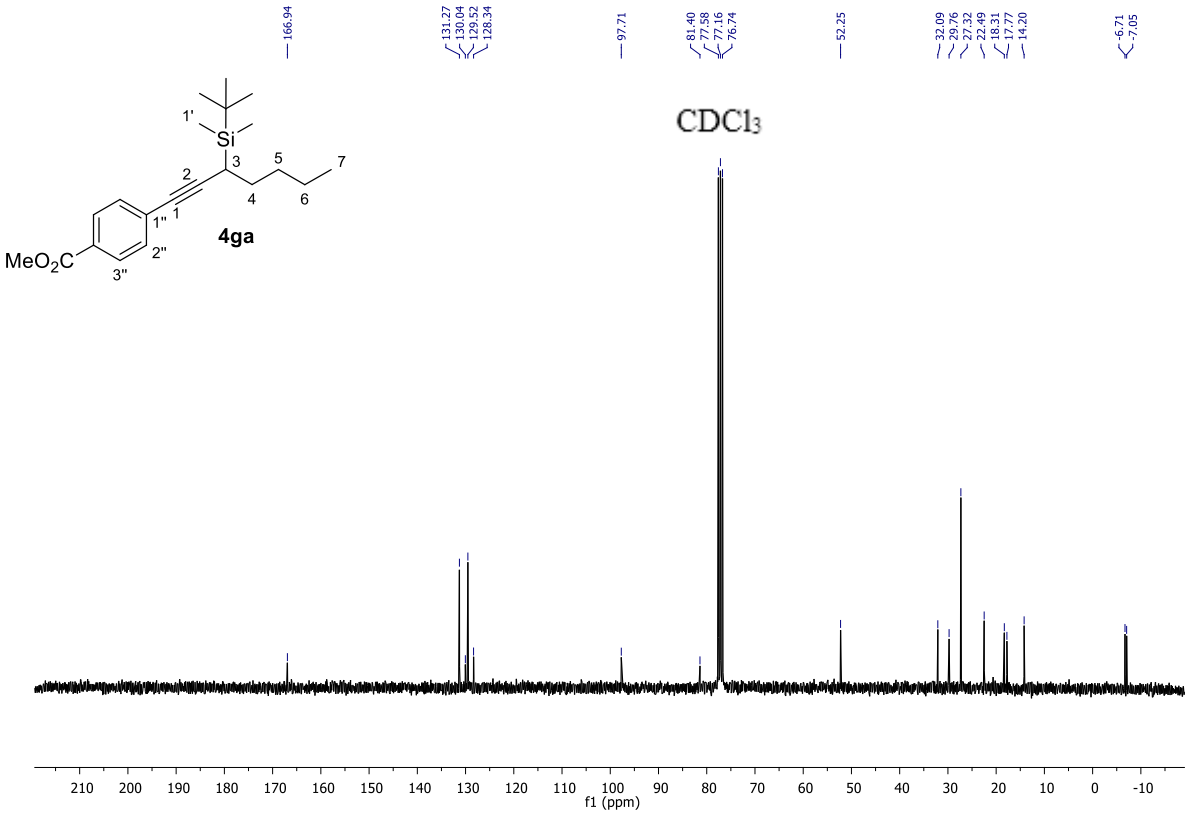


Methyl 4-(3-(tert-butyldimethylsilyl)hept-1-yn-1-yl)benzoate **4ga**

^{1}H NMR (300 MHz, $CDCl_3$)

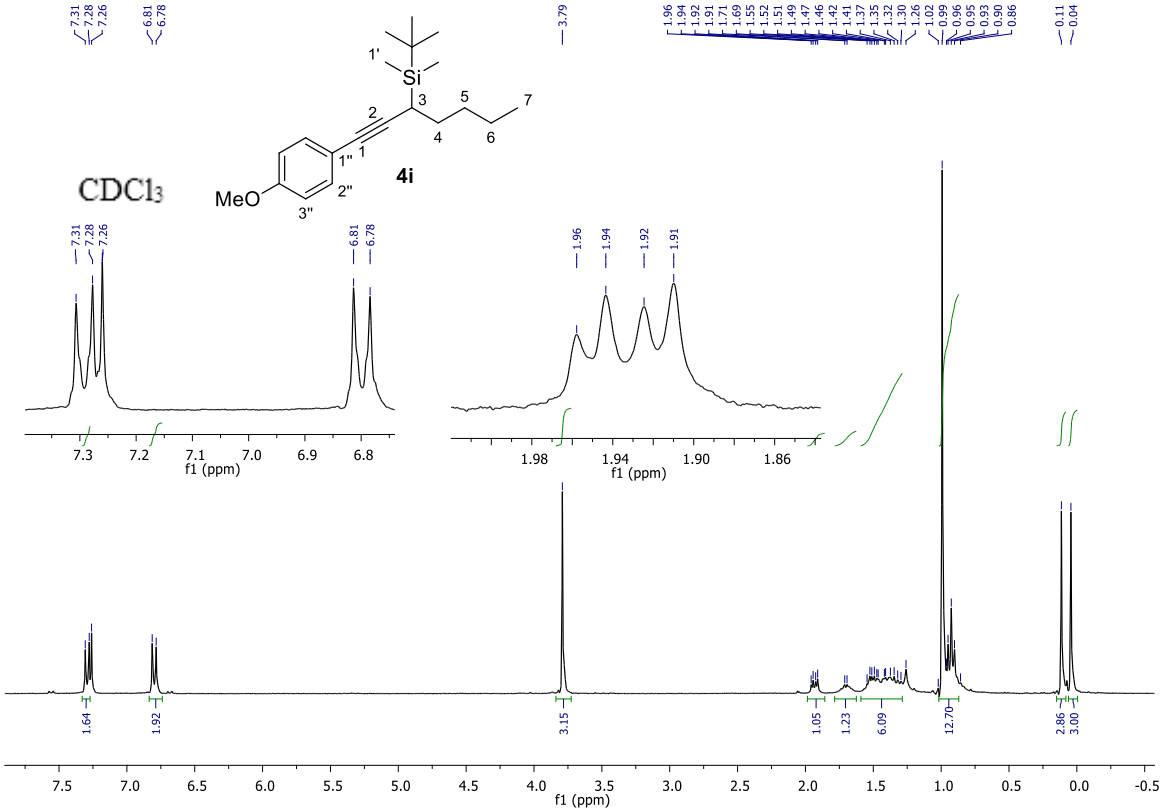


^{13}C NMR (75.5 MHz, $CDCl_3$)

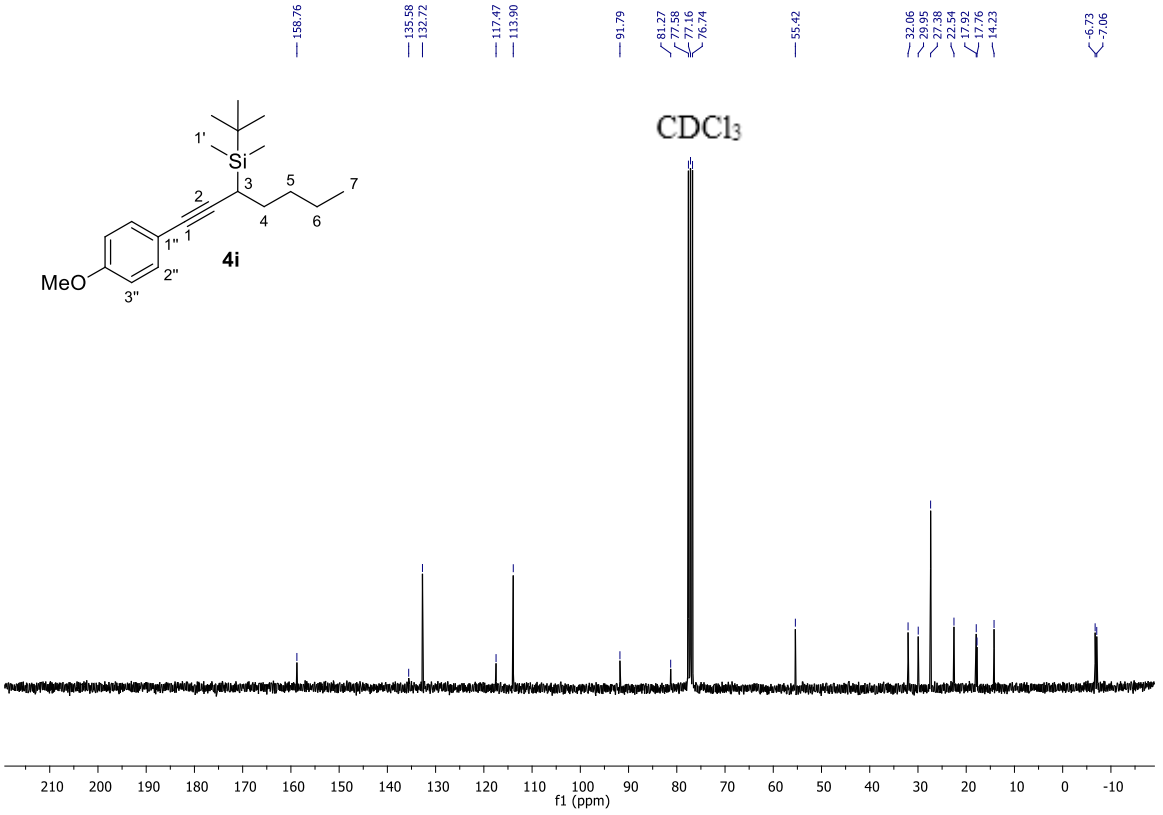


Tert-butyl(1-(4-methoxyphenyl)hept-1-yn-3-yl)dimethylsilane **4i**

^{1}H NMR (300 MHz, $CDCl_3$)

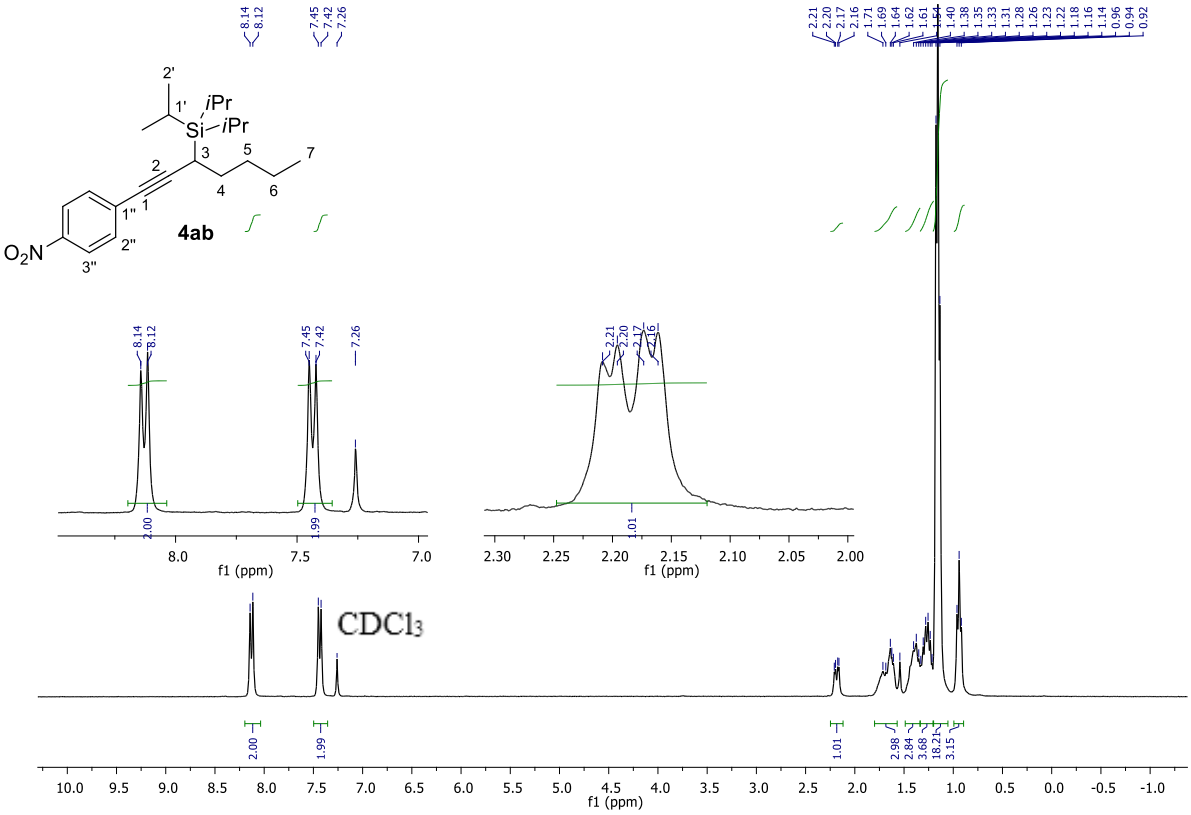


^{13}C NMR (75.5 MHz, $CDCl_3$)

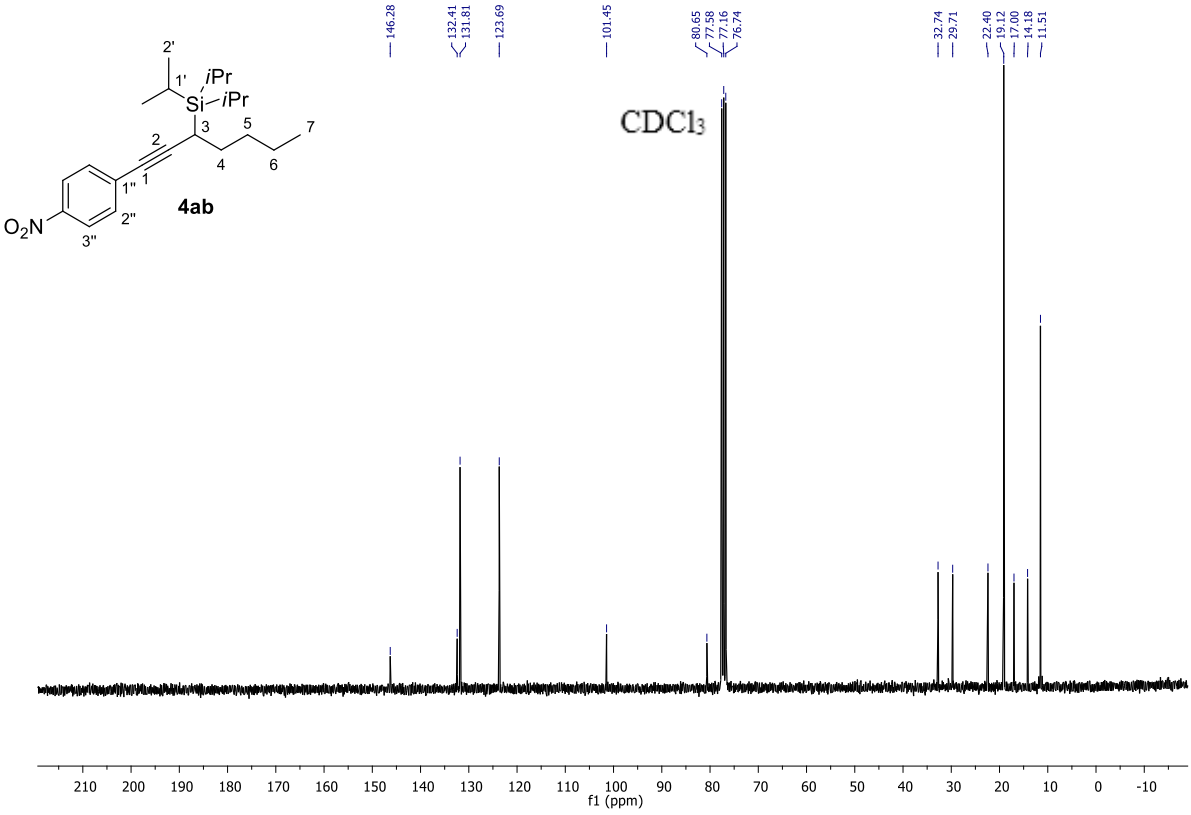


Triisopropyl(1-(4-nitrophenyl)hept-1-yn-3-yl)silane **4ab**

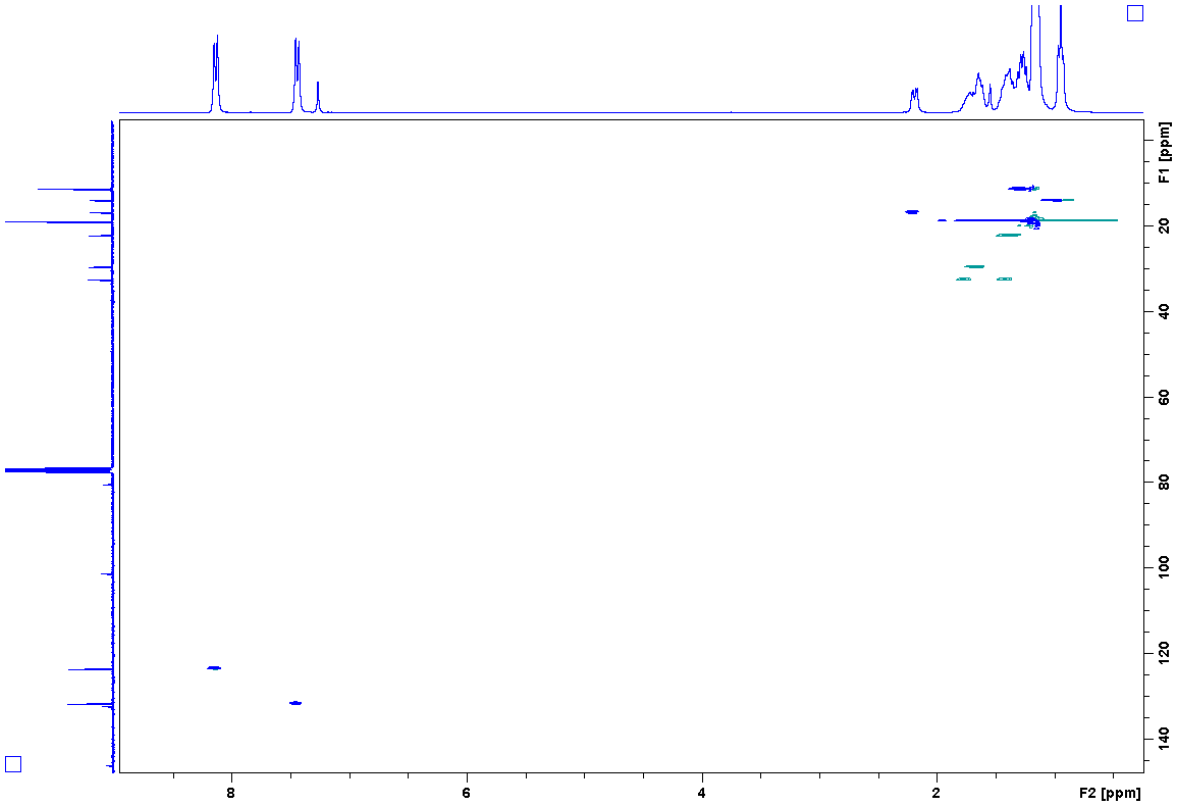
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

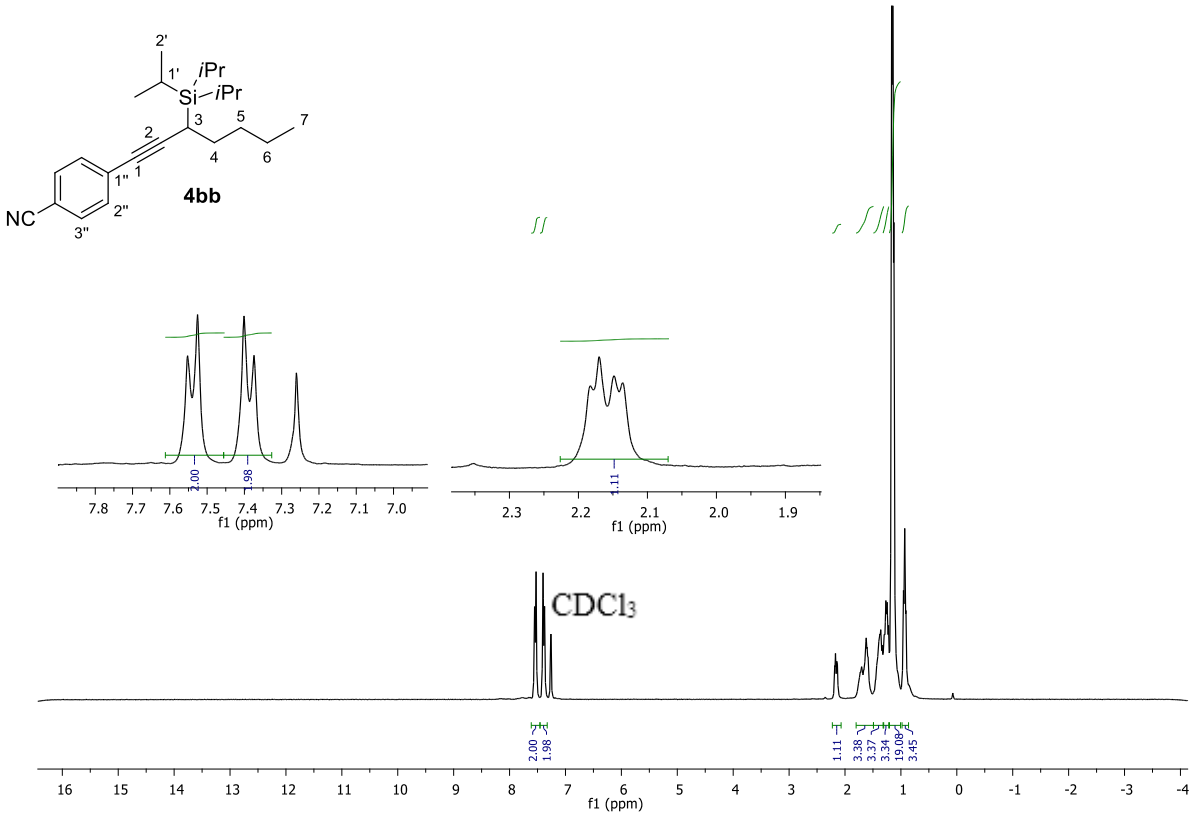


2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

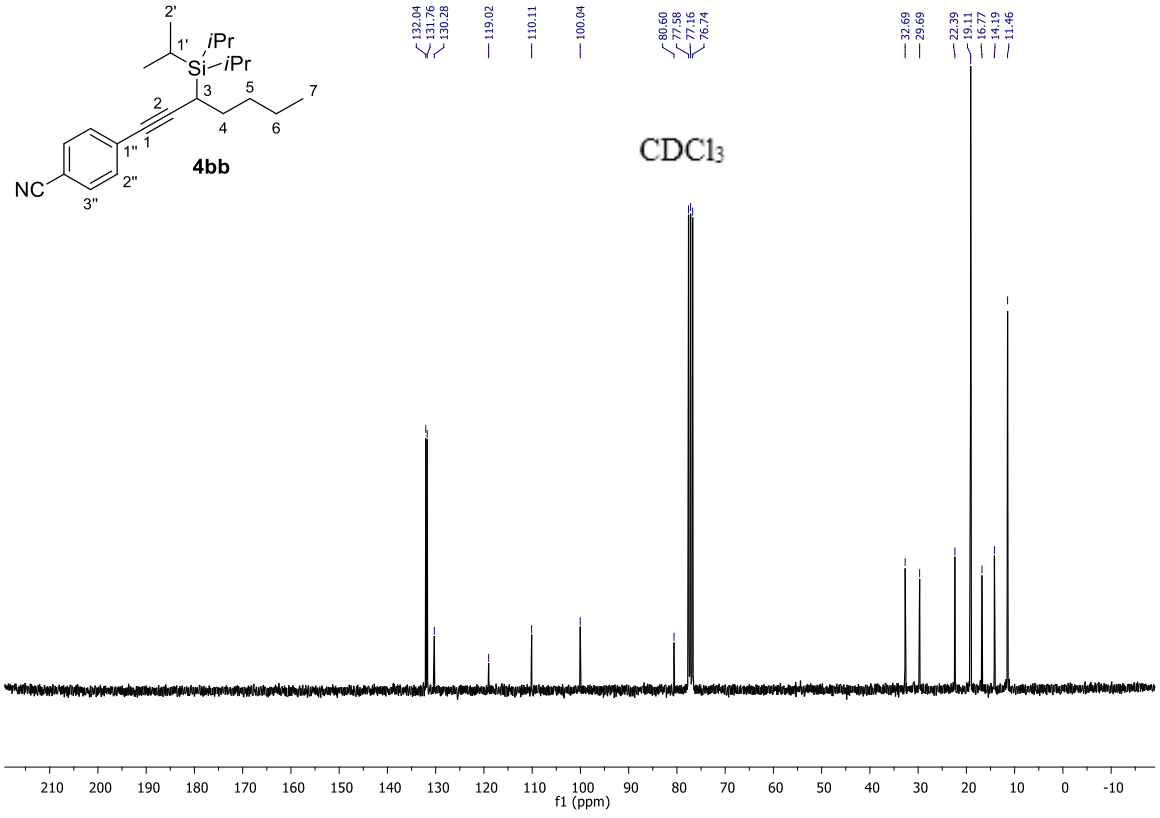


4-(3-(Triisopropylsilyl)hept-1-yn-1-yl)benzonitrile **4bb**

^{1}H NMR (300 MHz, $CDCl_3$)

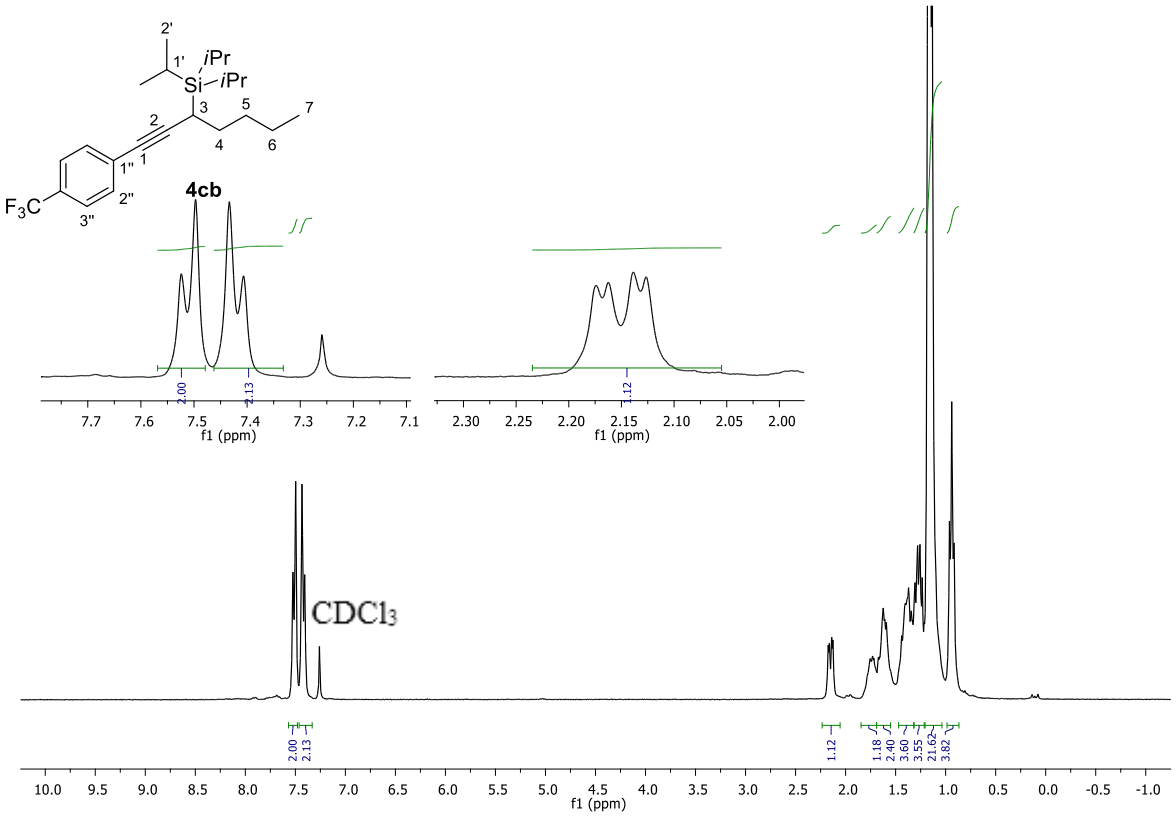


^{13}C NMR (75.5 MHz, $CDCl_3$)

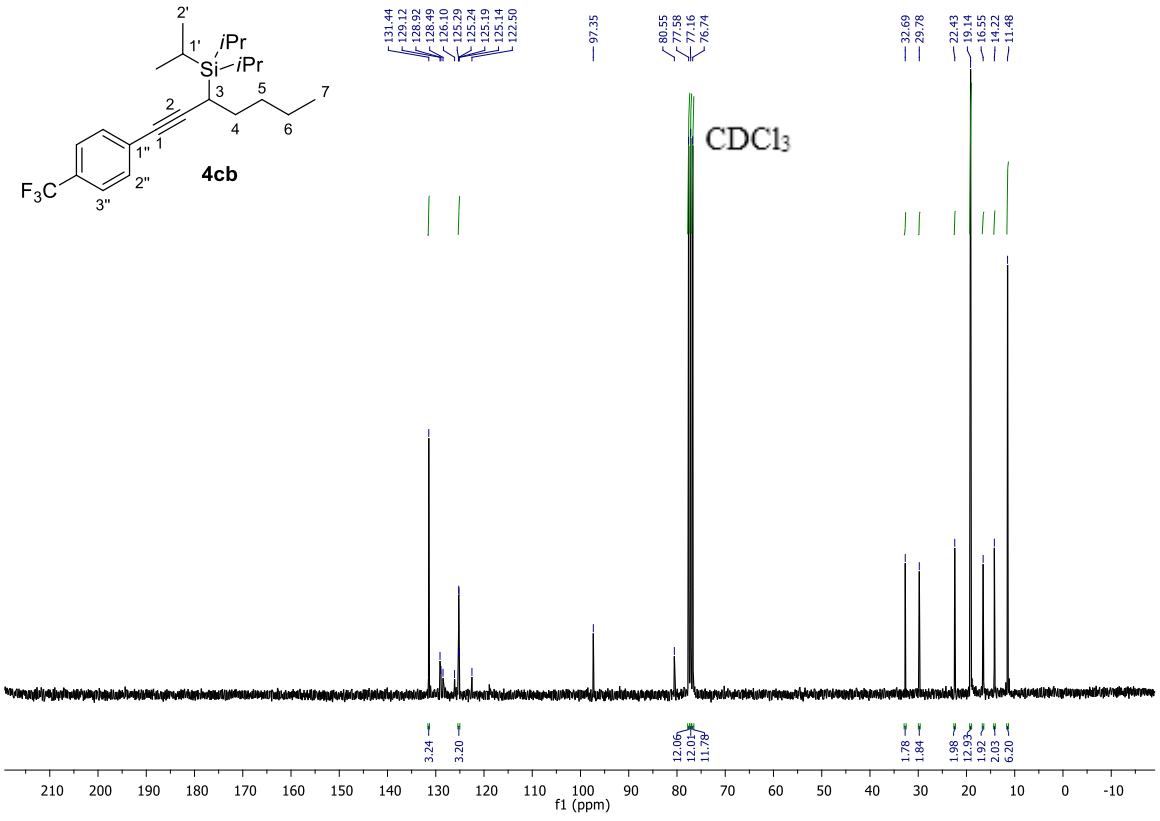


Triisopropyl(1-(4-(trifluoromethyl)phenyl)hept-1-yn-3-yl)silane **4cb**

^{1}H NMR (300 MHz, $CDCl_3$)

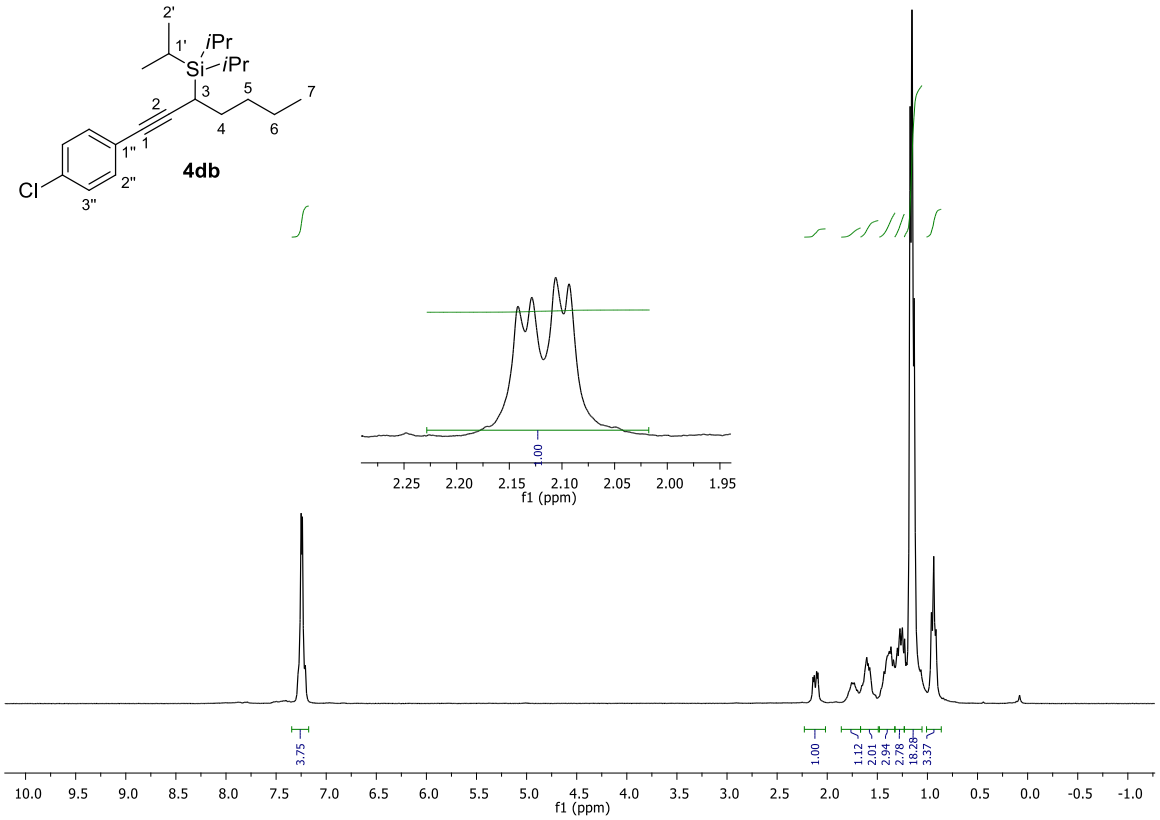


^{13}C NMR (75.5 MHz, $CDCl_3$)

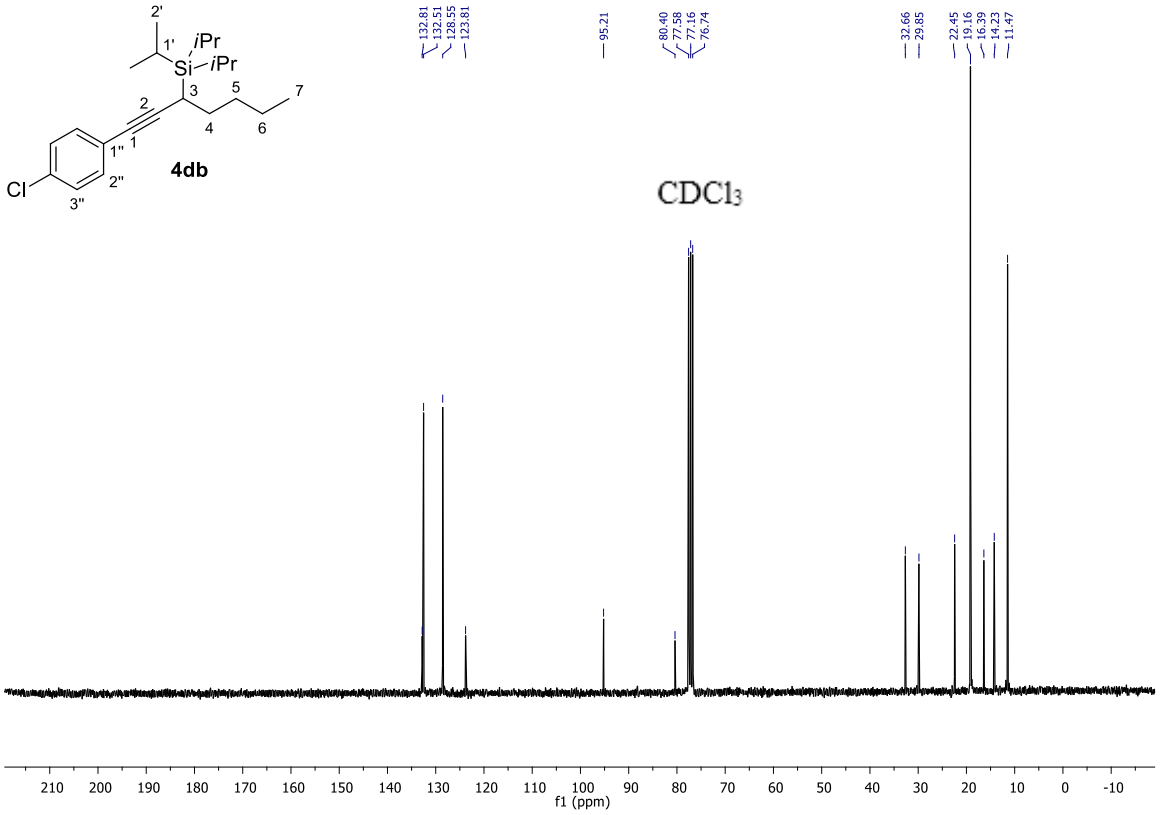


(1-(4-Chlorophenyl)hept-1-yn-3-yl)triisopropylsilane **4db**

^{1}H NMR (300 MHz, $CDCl_3$)

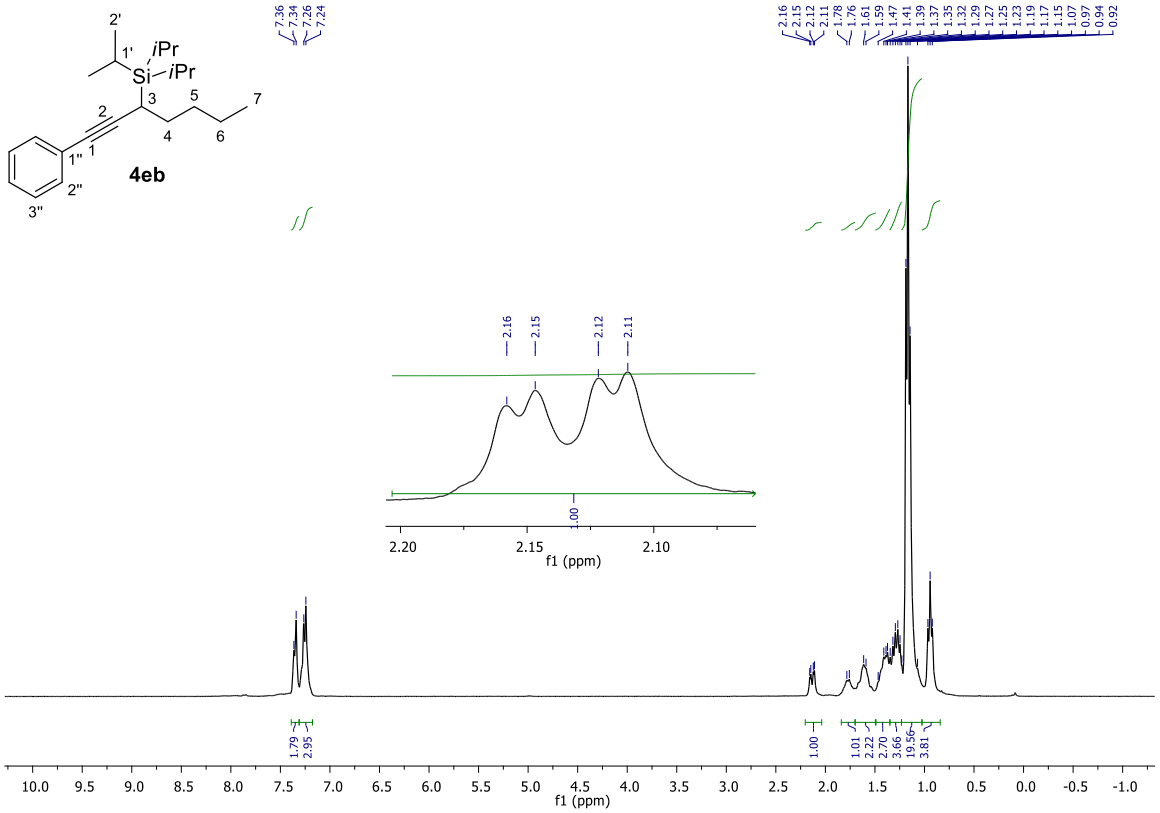


^{13}C NMR (75.5 MHz, $CDCl_3$)

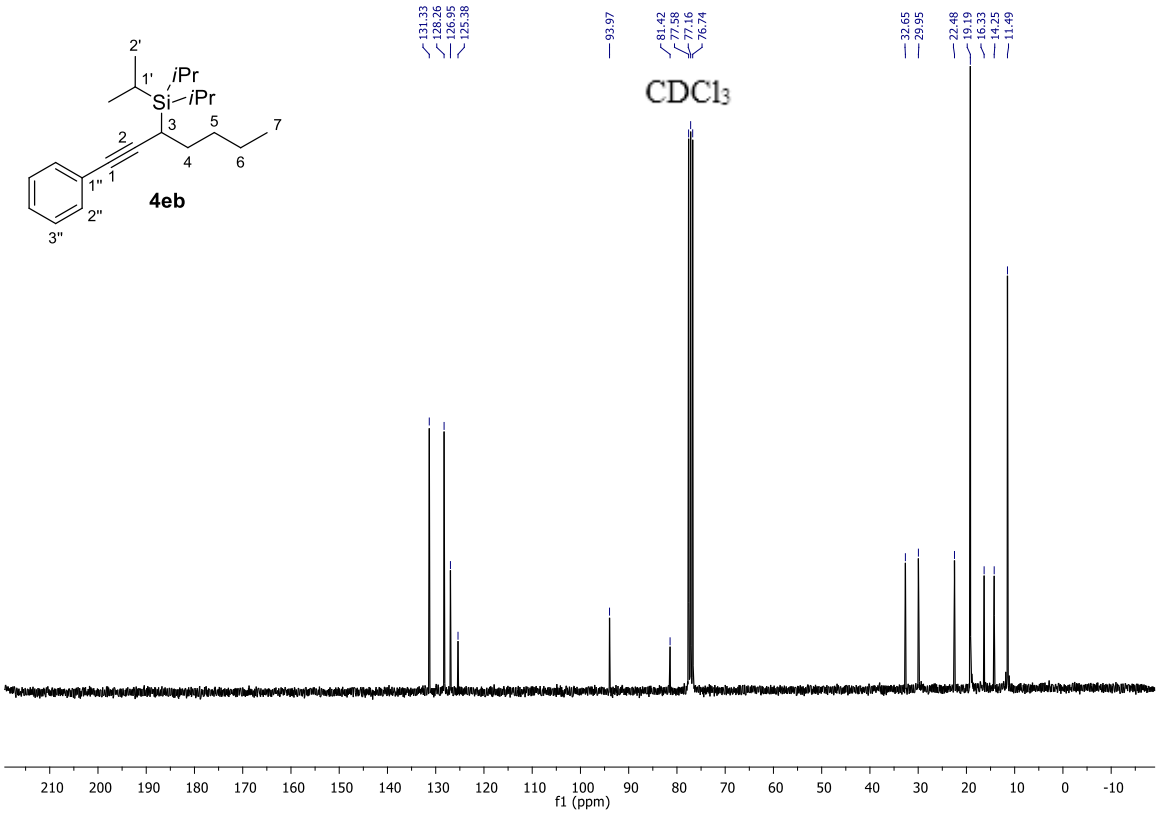


Triisopropyl(1-phenylhept-1-yn-3-yl)silane **4eb**

^{1}H NMR (300 MHz, $CDCl_3$)

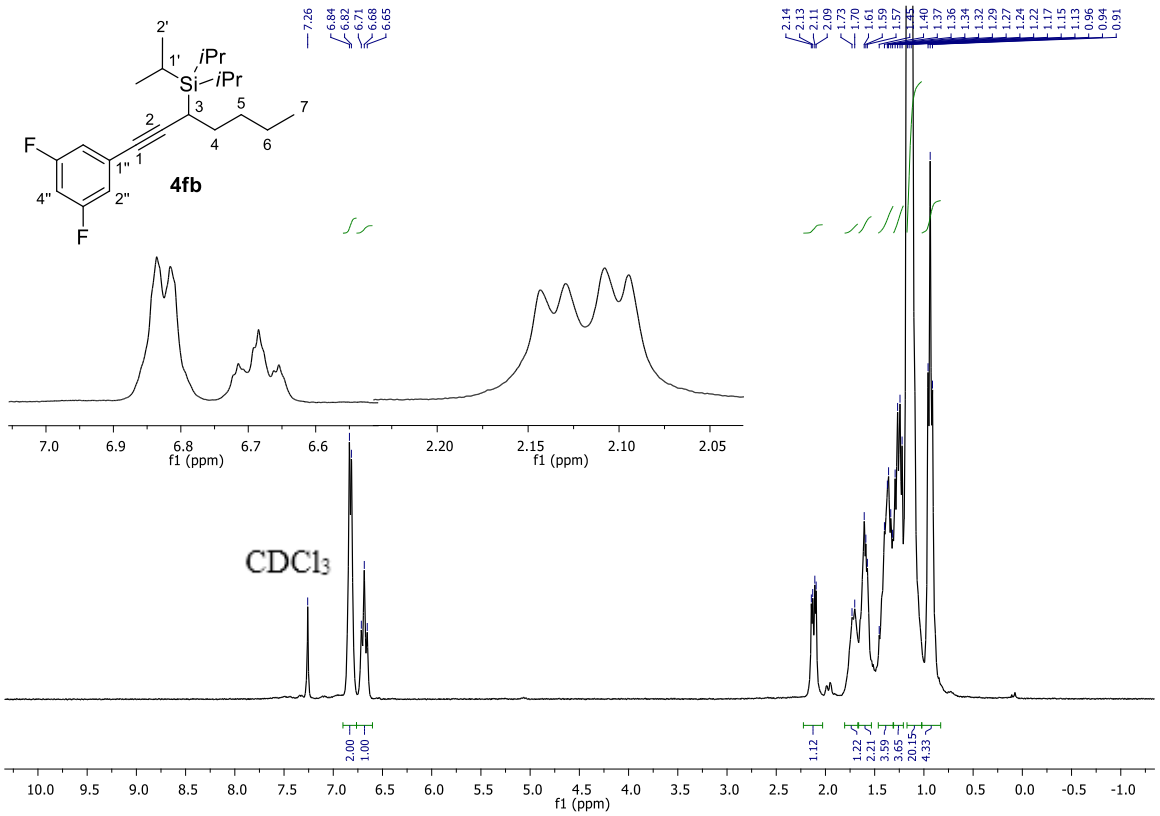


^{13}C NMR (75.5 MHz, $CDCl_3$)

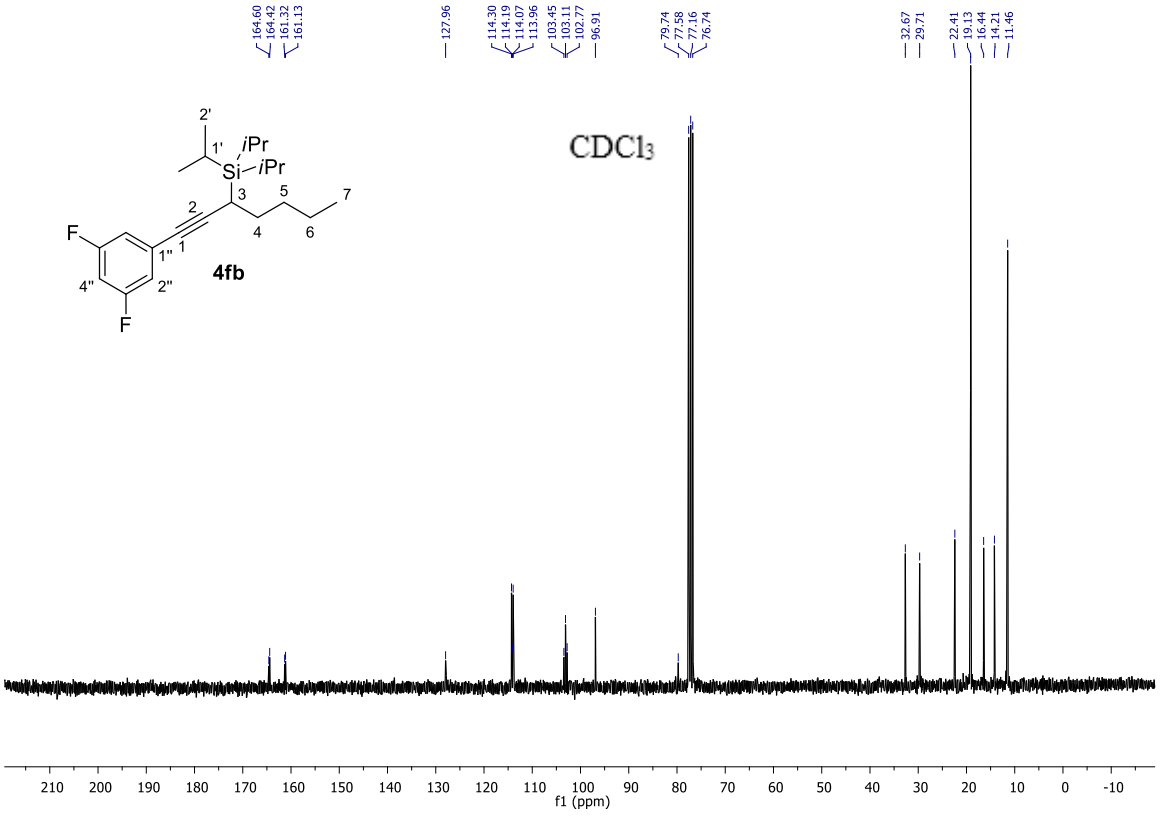


(1-(3,5-Difluorophenyl)hept-1-yn-3-yl)triisopropylsilane **4fb**

^{1}H NMR (300 MHz, $CDCl_3$)

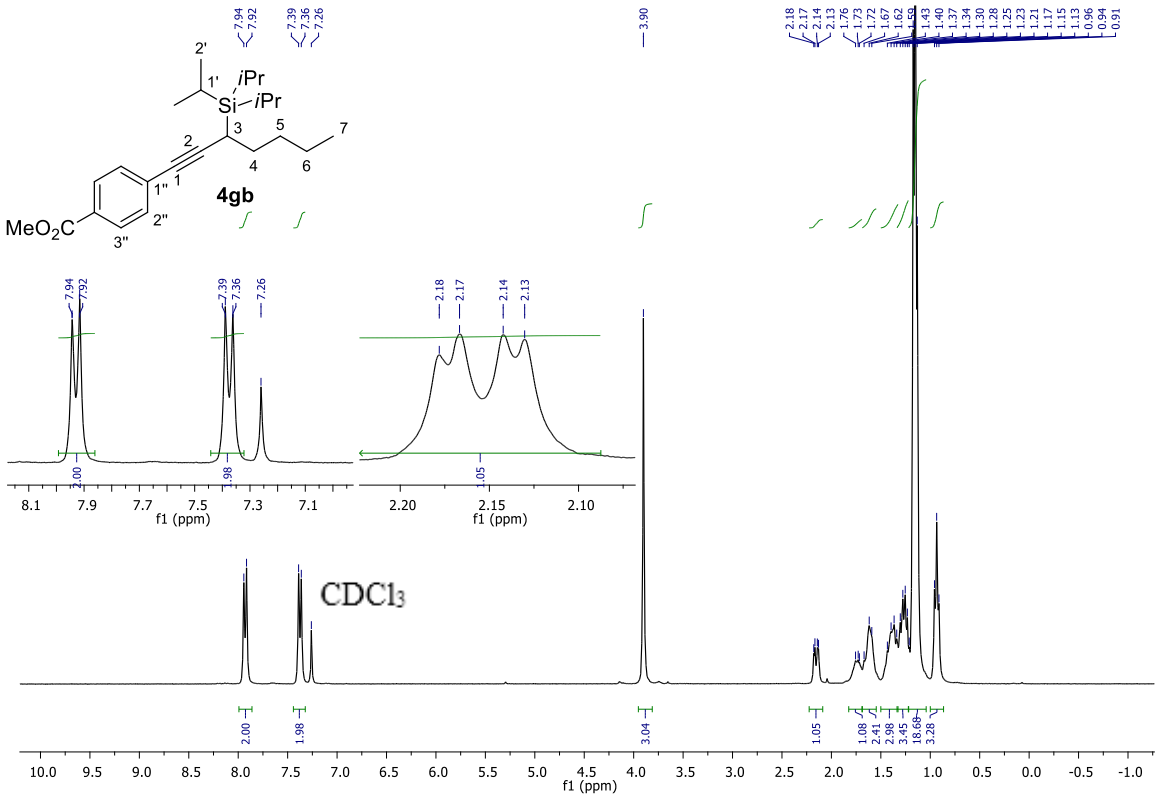


^{13}C NMR (75.5 MHz, $CDCl_3$)

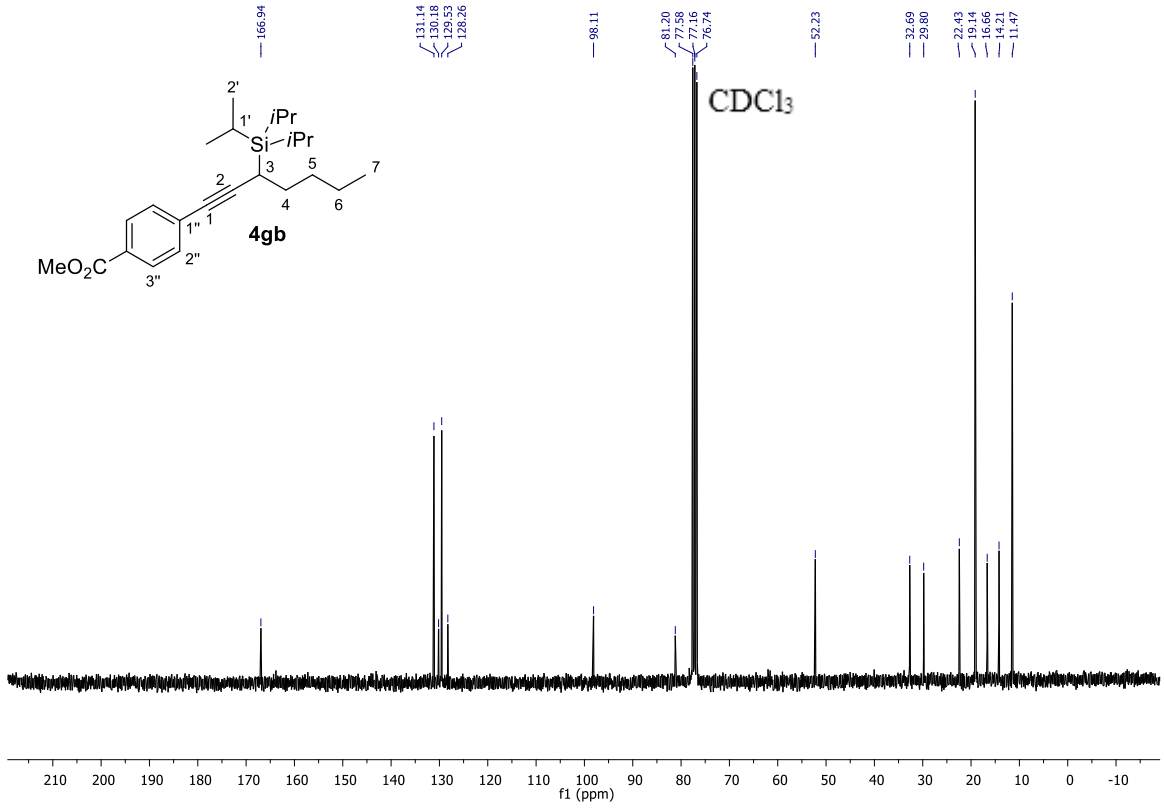


Methyl 4-(3-(triisopropylsilyl)hept-1-yn-1-yl)benzoate **4gb**

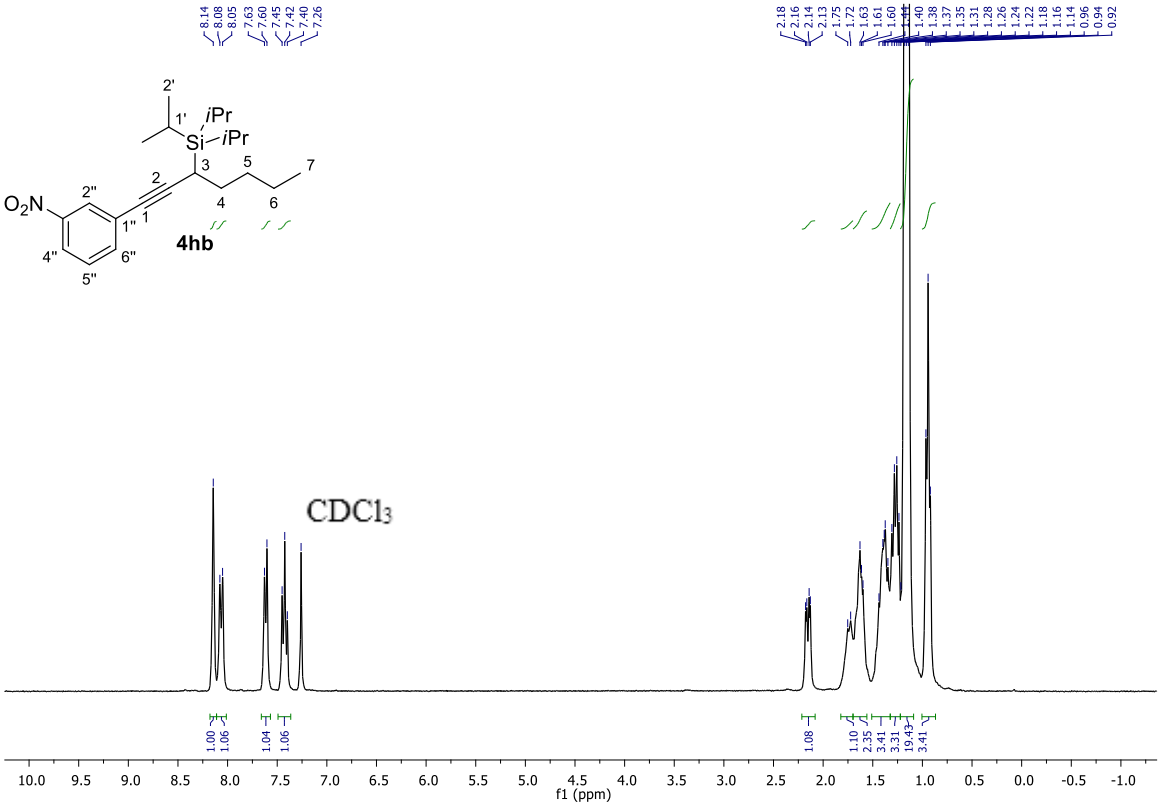
^{1}H NMR (300 MHz, $CDCl_3$)

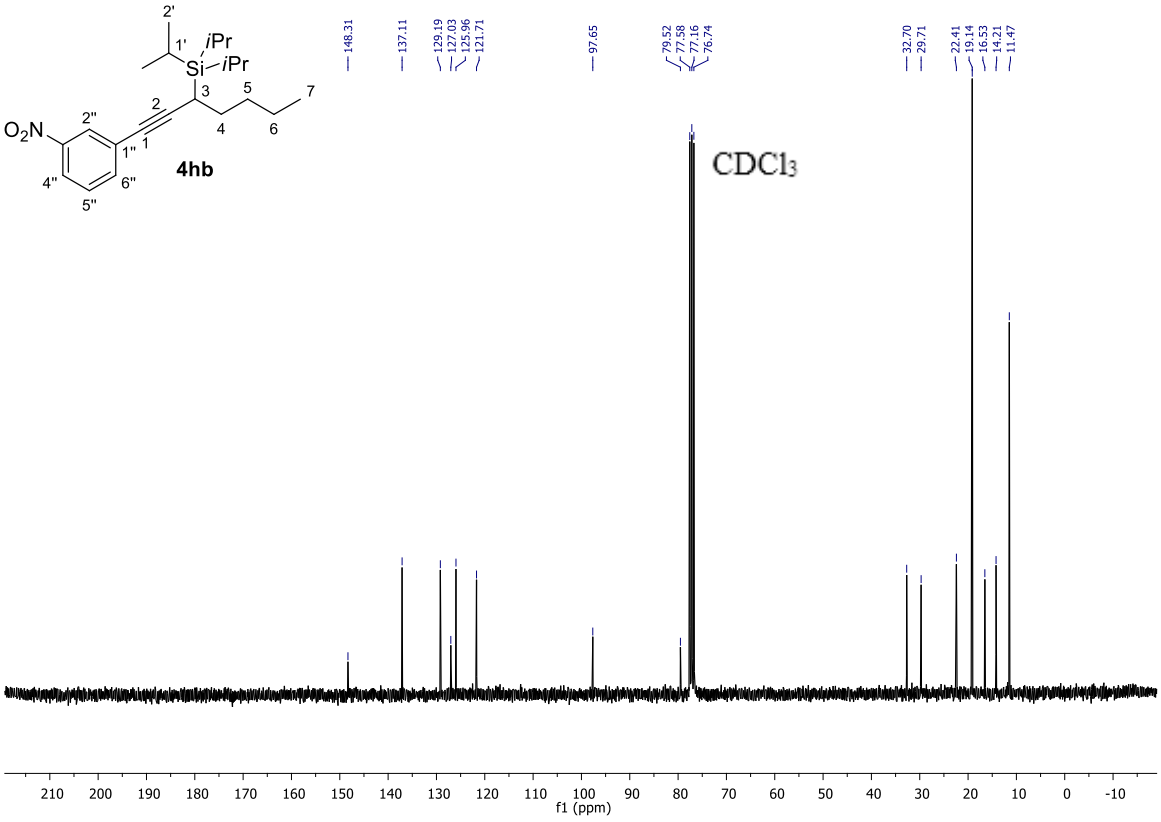


^{13}C NMR (75.5 MHz, $CDCl_3$)



Triisopropyl(1-(3-nitrophenyl)hept-1-yn-3-yl)silane **4hb**

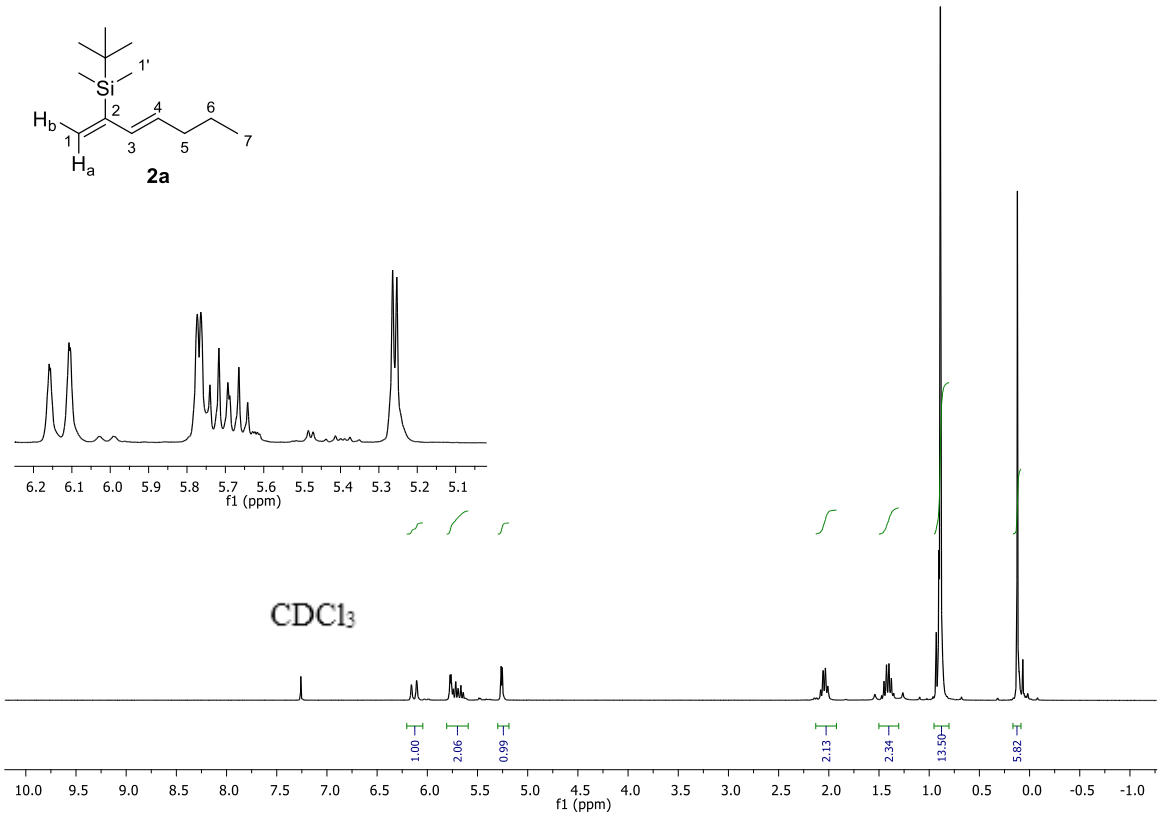




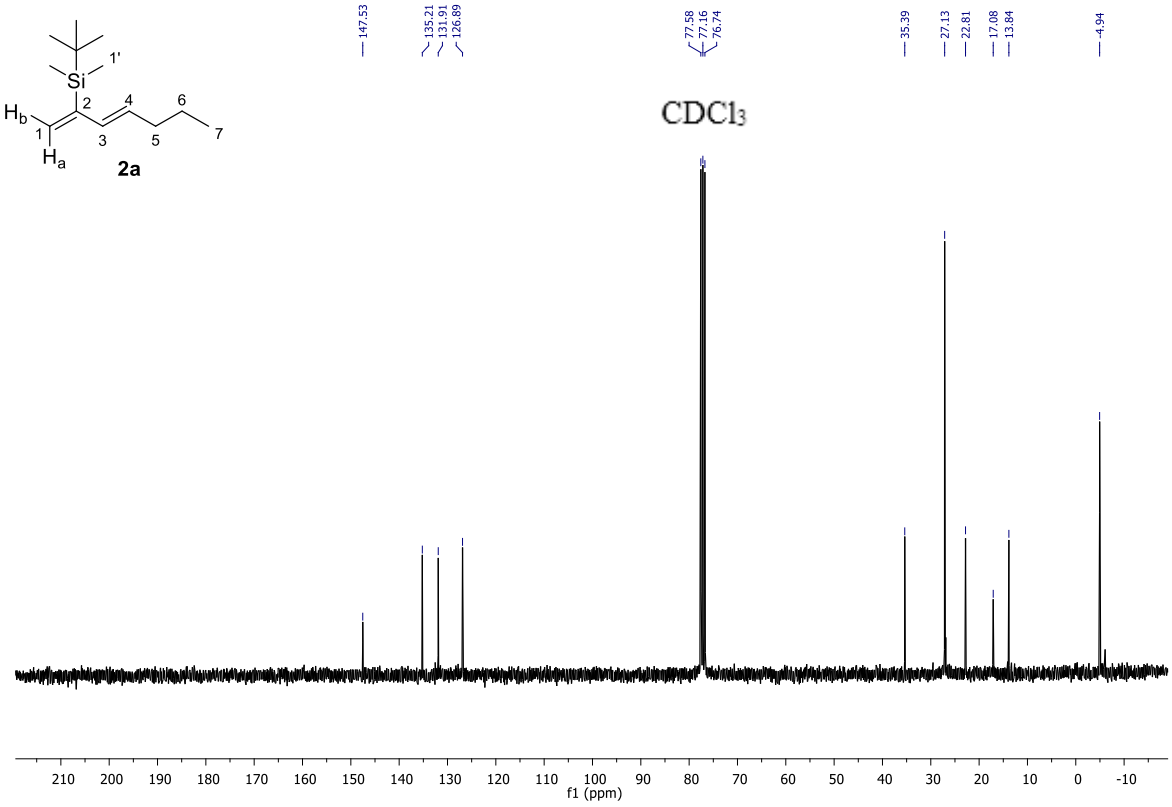
2. NMR spectra of rearranged products

2.1. Silyl dienes

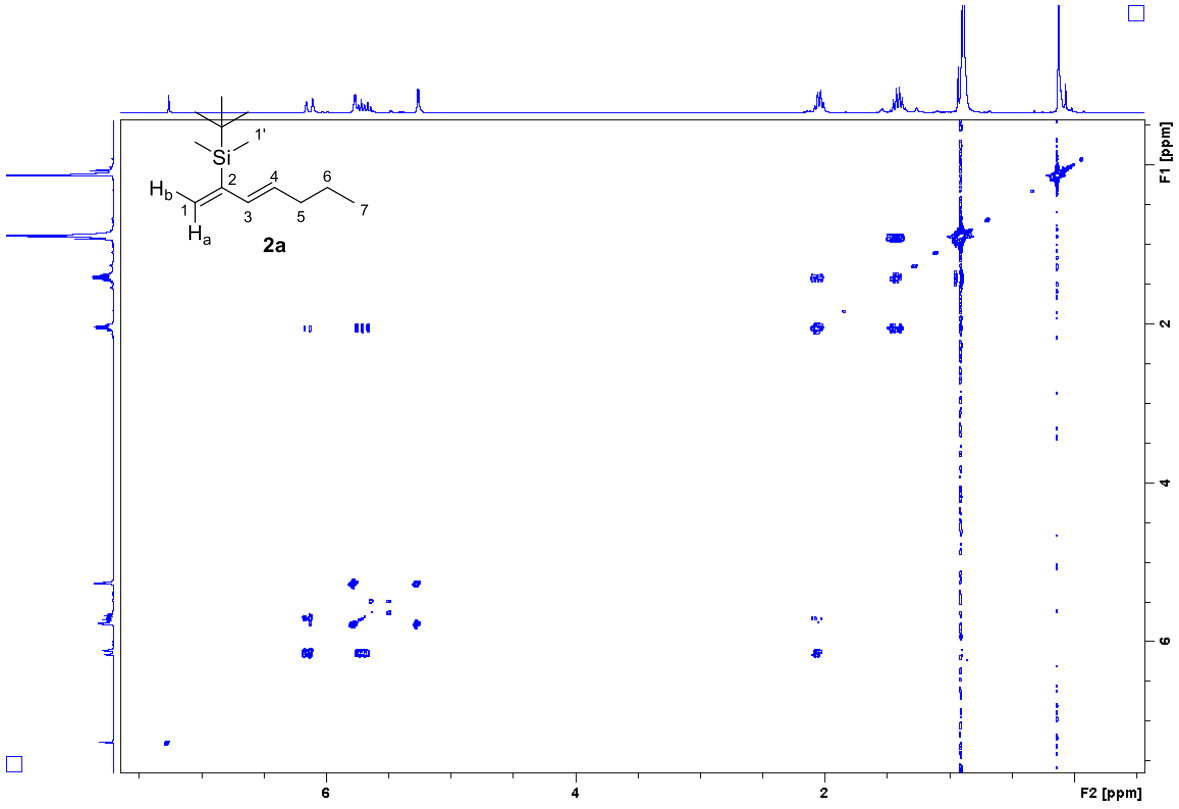
(*E*/*Z*)-tert-butyl(hepta-1,3-dien-2-yl)dimethylsilane **2a**



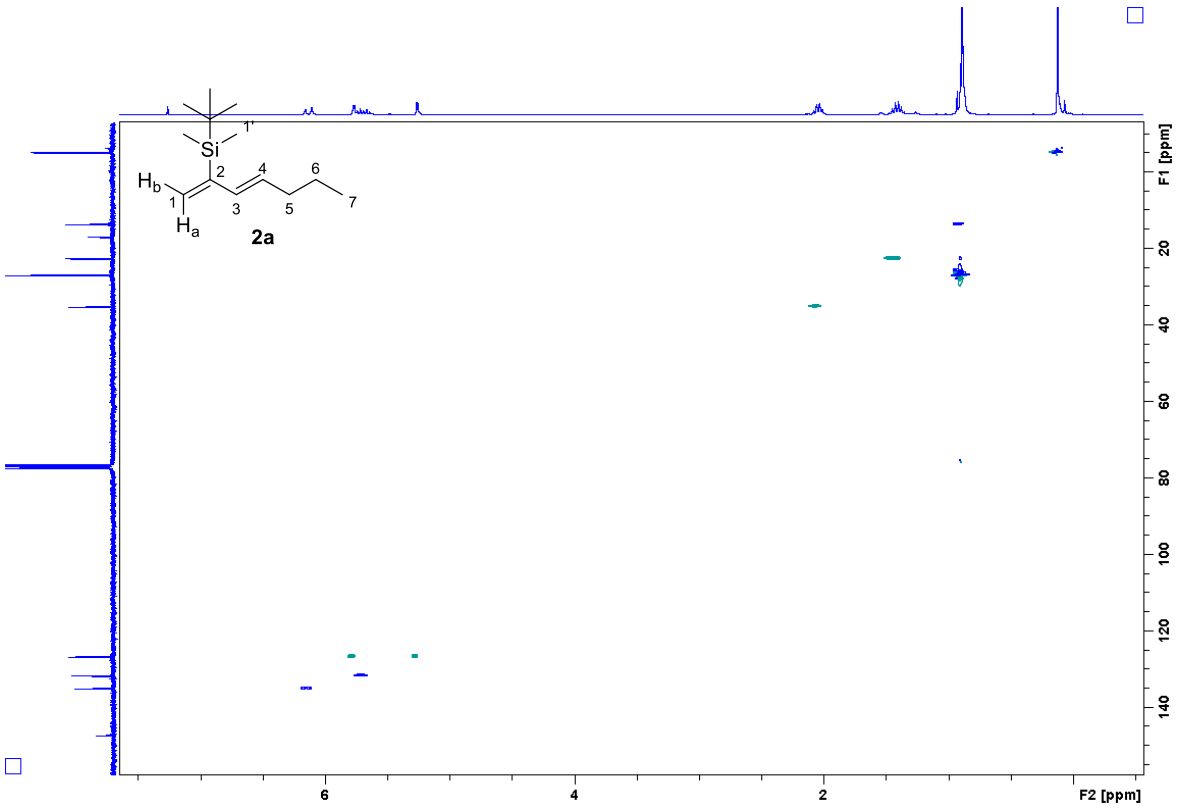
^{13}C NMR (75.5 MHz, $CDCl_3$)



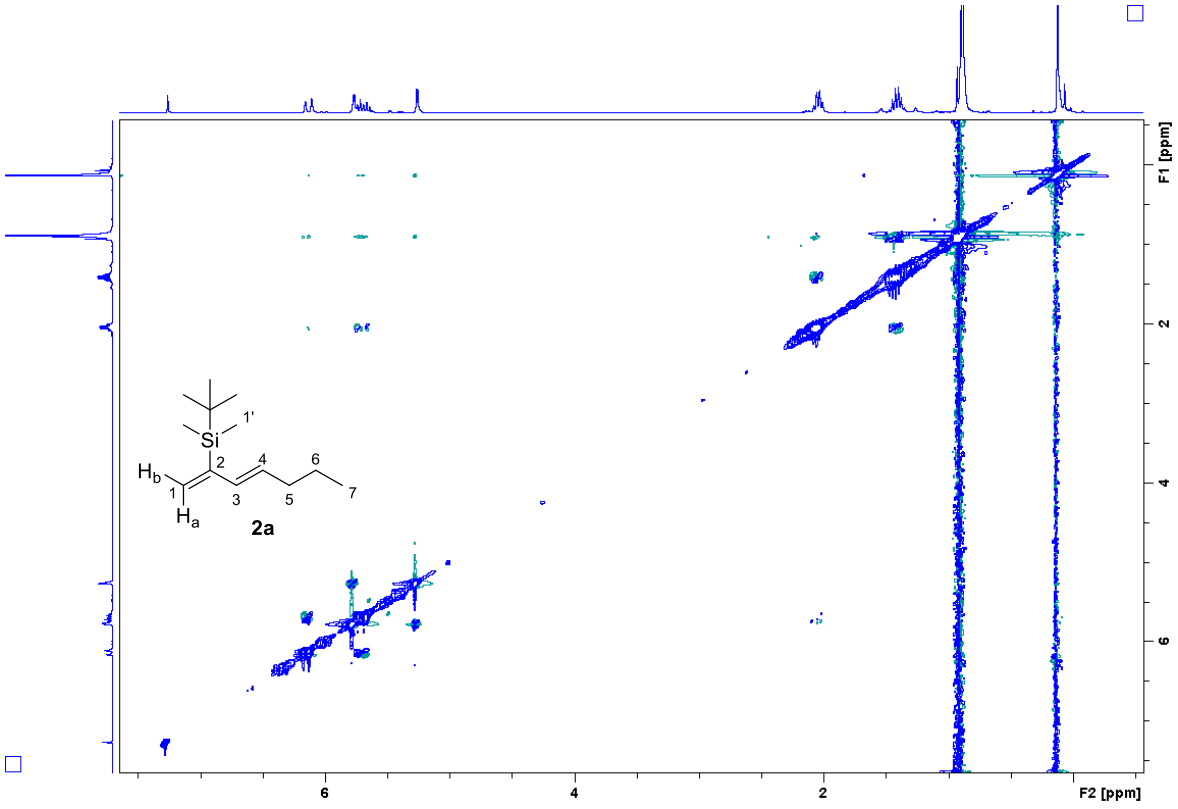
2D ^{1}H-^{1}H COSY NMR ($CDCl_3$)



2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

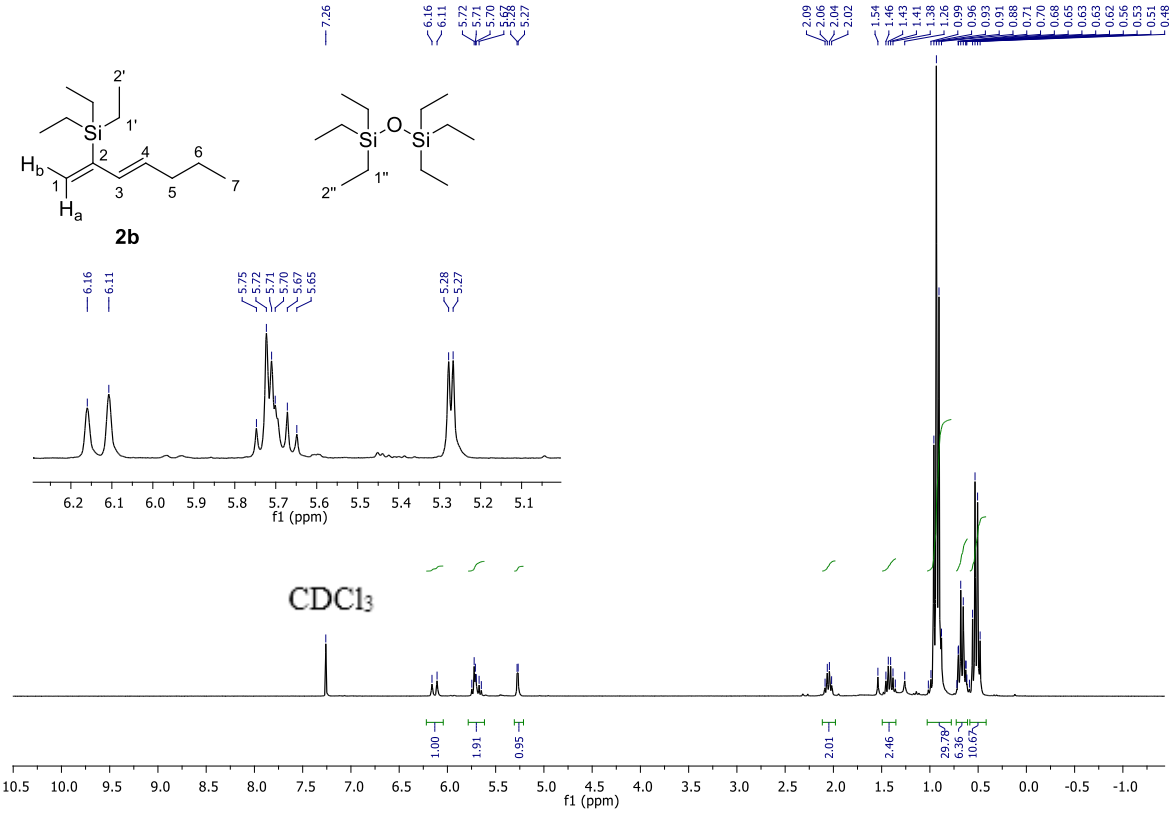


2D ^{1}H-^{1}H NOESY NMR ($CDCl_3$)

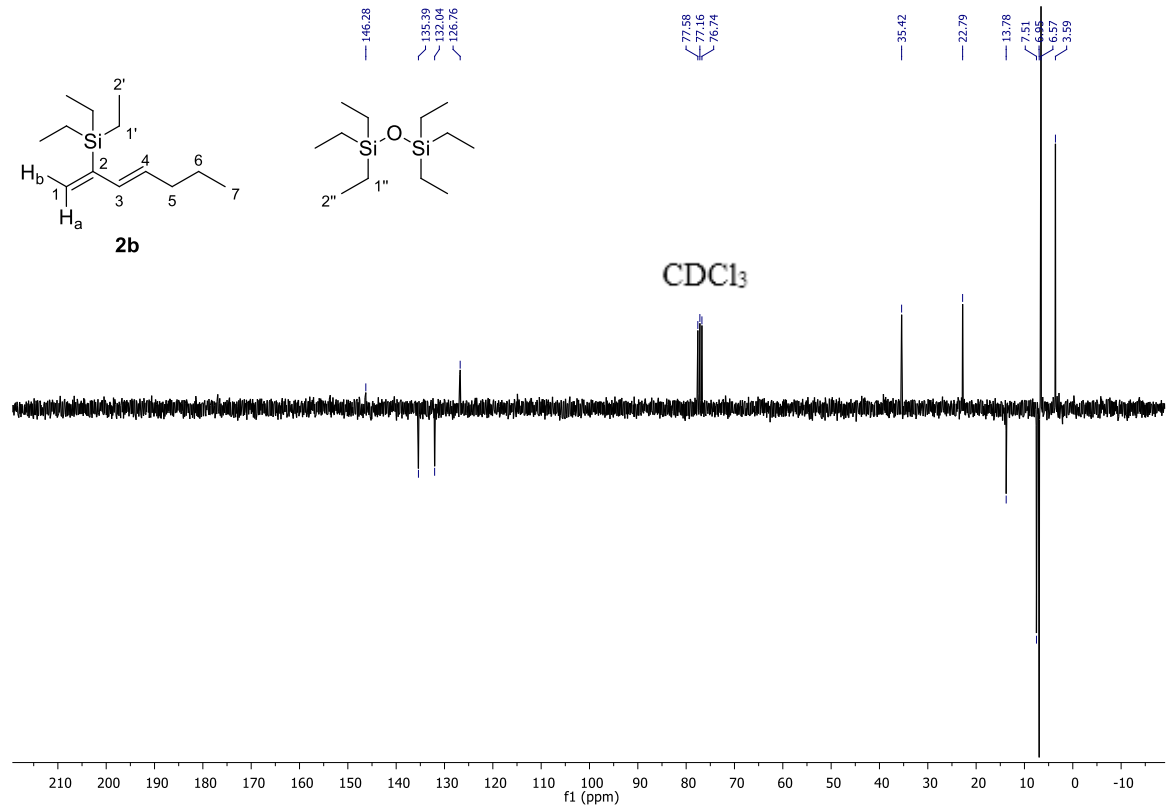


(*E*/*Z*)-triethyl(hepta-1,3-dien-2-yl)silane **2b**

^{1}H NMR (300 MHz, $CDCl_3$)

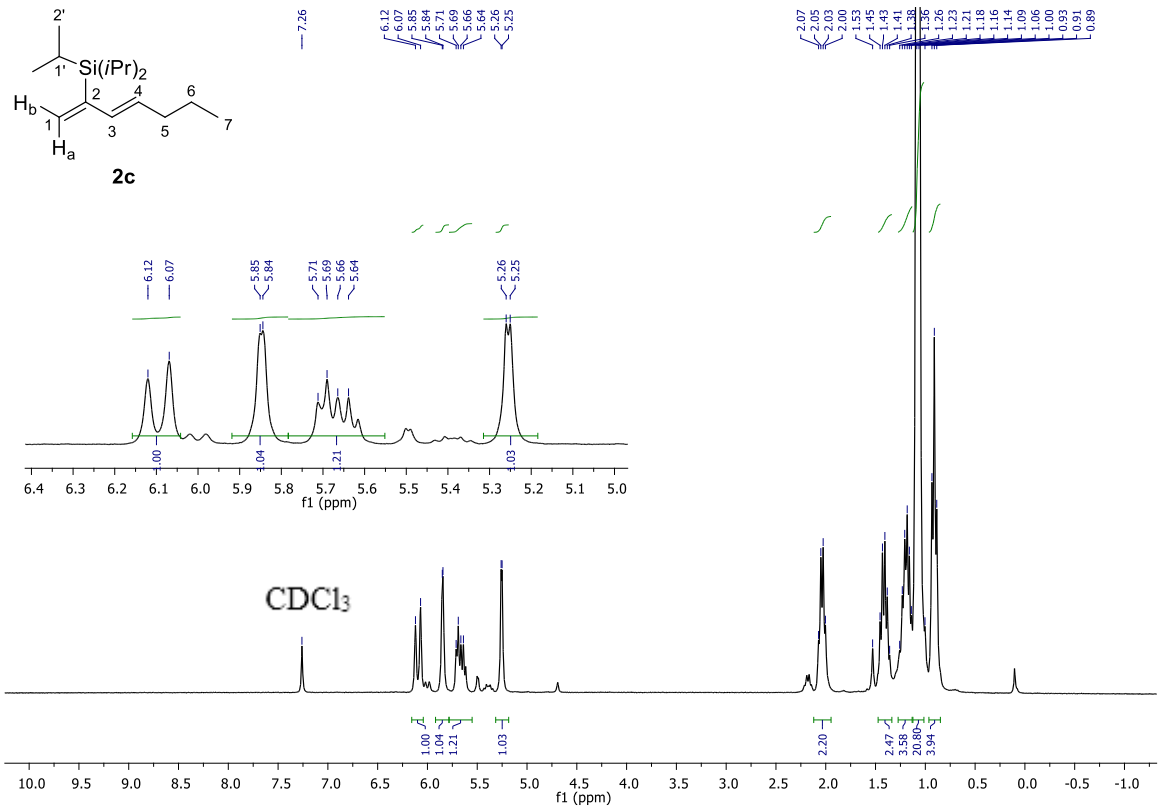


^{13}C NMR (75.5 MHz, $CDCl_3$)

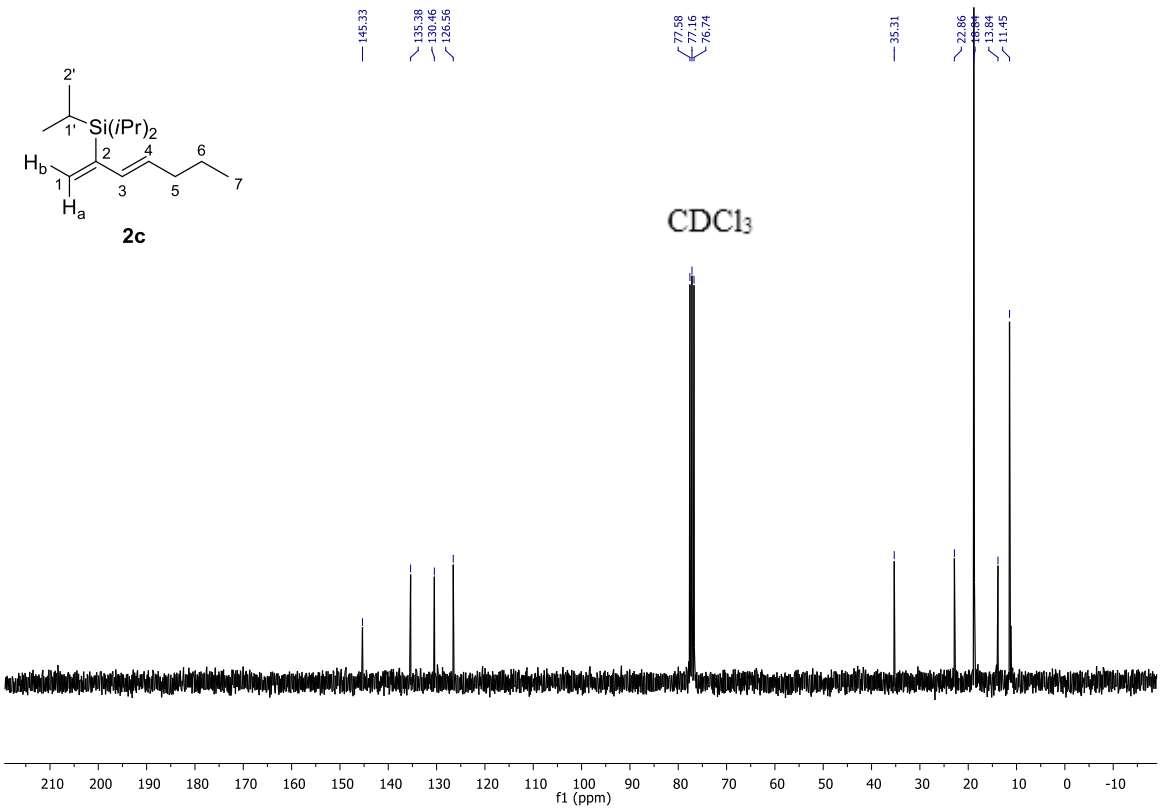


(*E*/*Z*)-hepta-1,3-dien-2-yltriisopropylsilane **2c**

^{1}H NMR (300 MHz, $CDCl_3$)

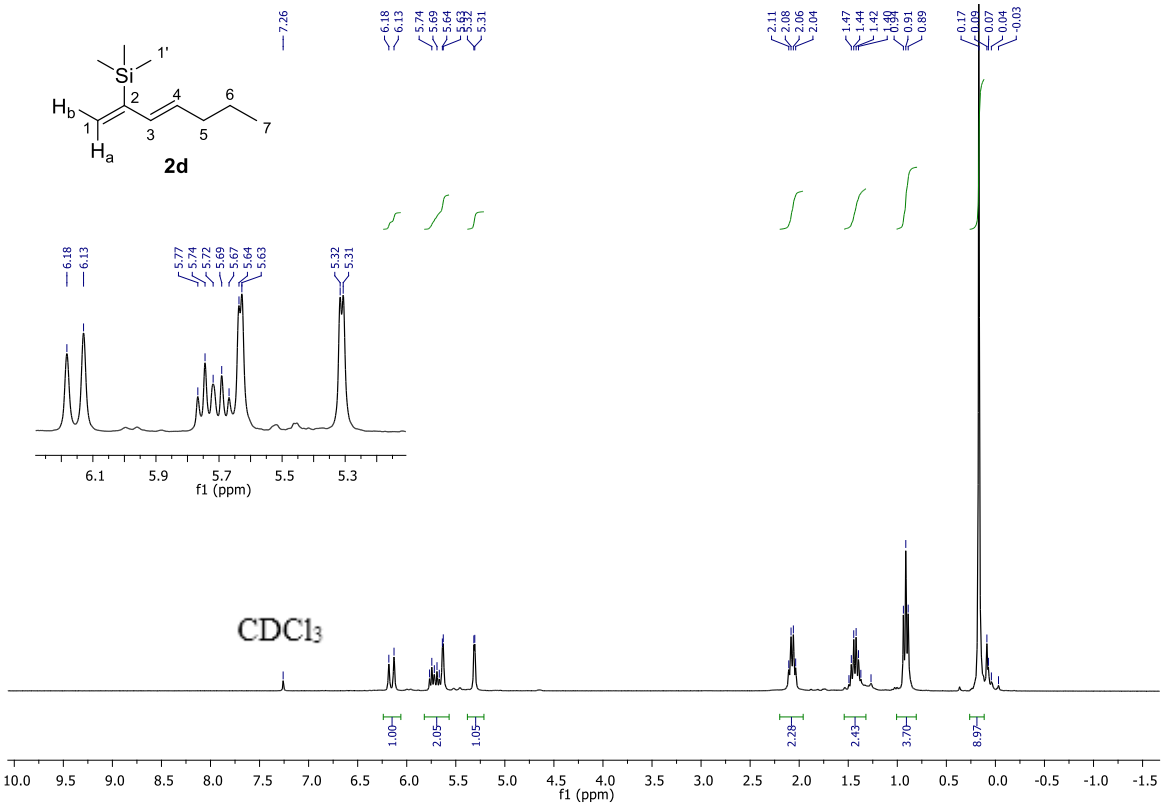


^{13}C NMR (75.5 MHz, $CDCl_3$)

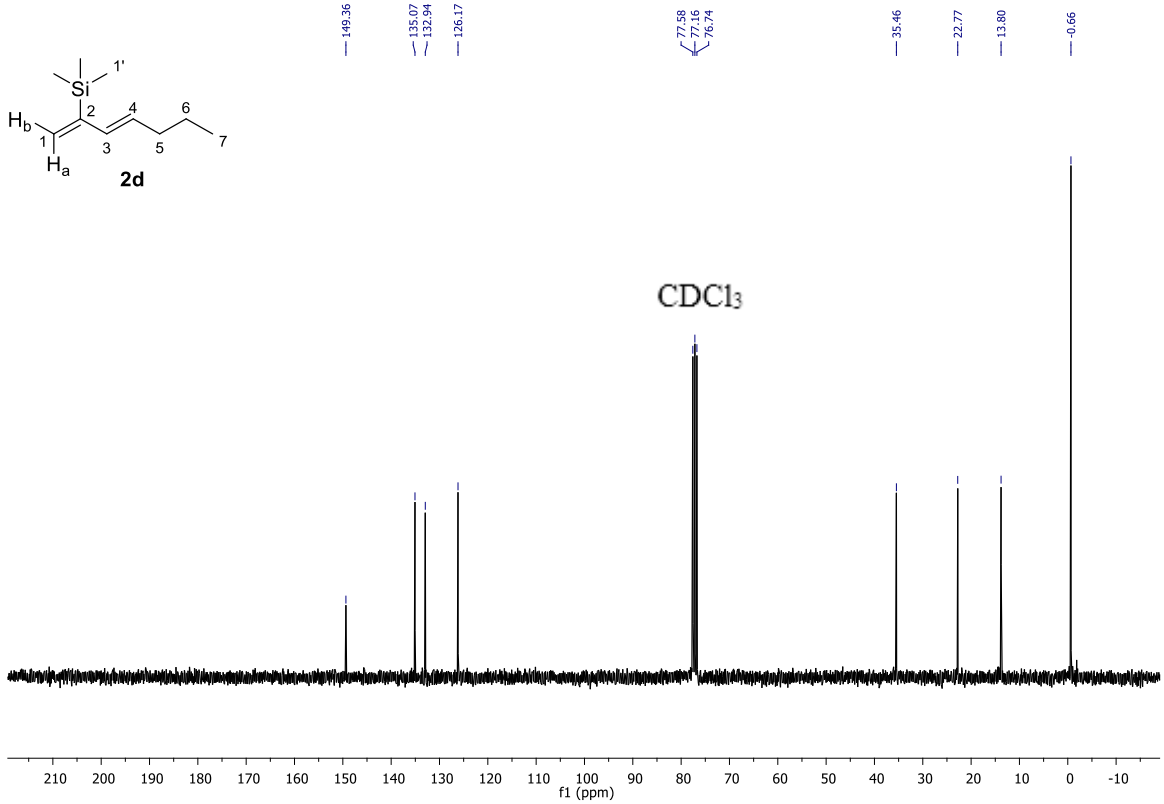


(*E*/*Z*)-hepta-1,3-dien-2-yltrimethylsilane **2d**

^{1}H NMR (300 MHz, $CDCl_3$)

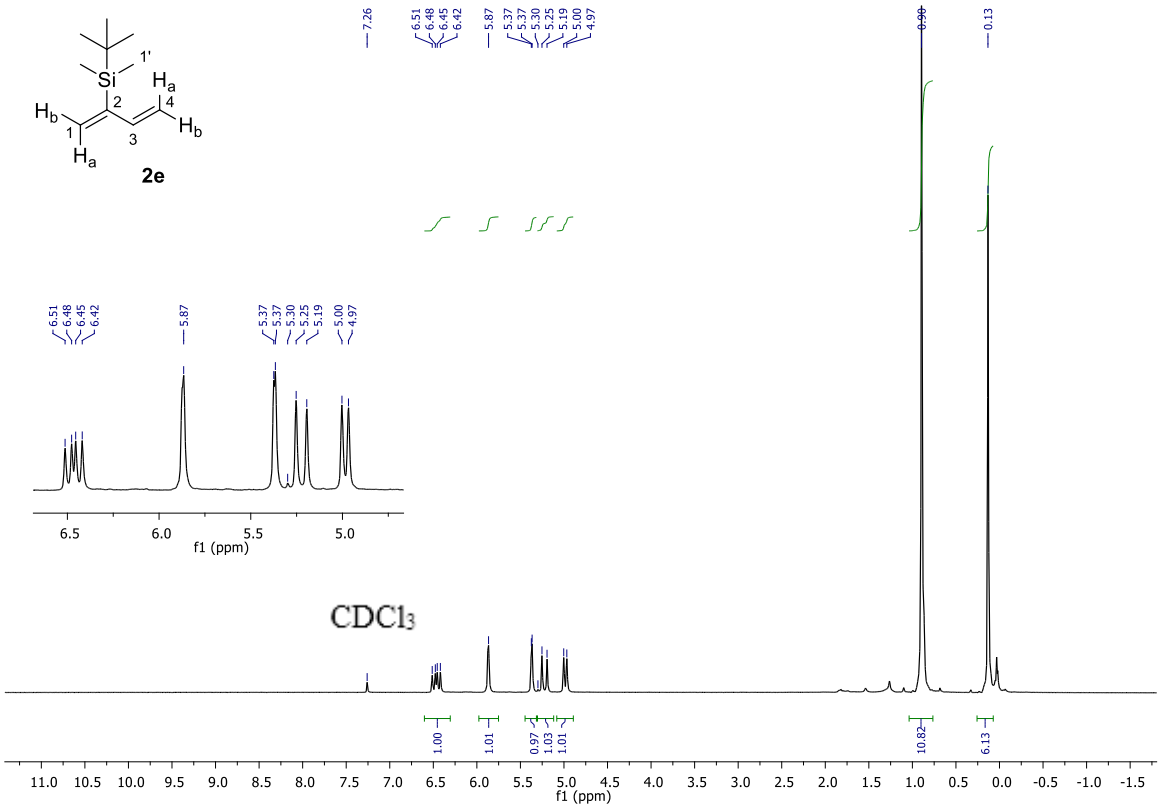


^{13}C NMR (75.5 MHz, $CDCl_3$)

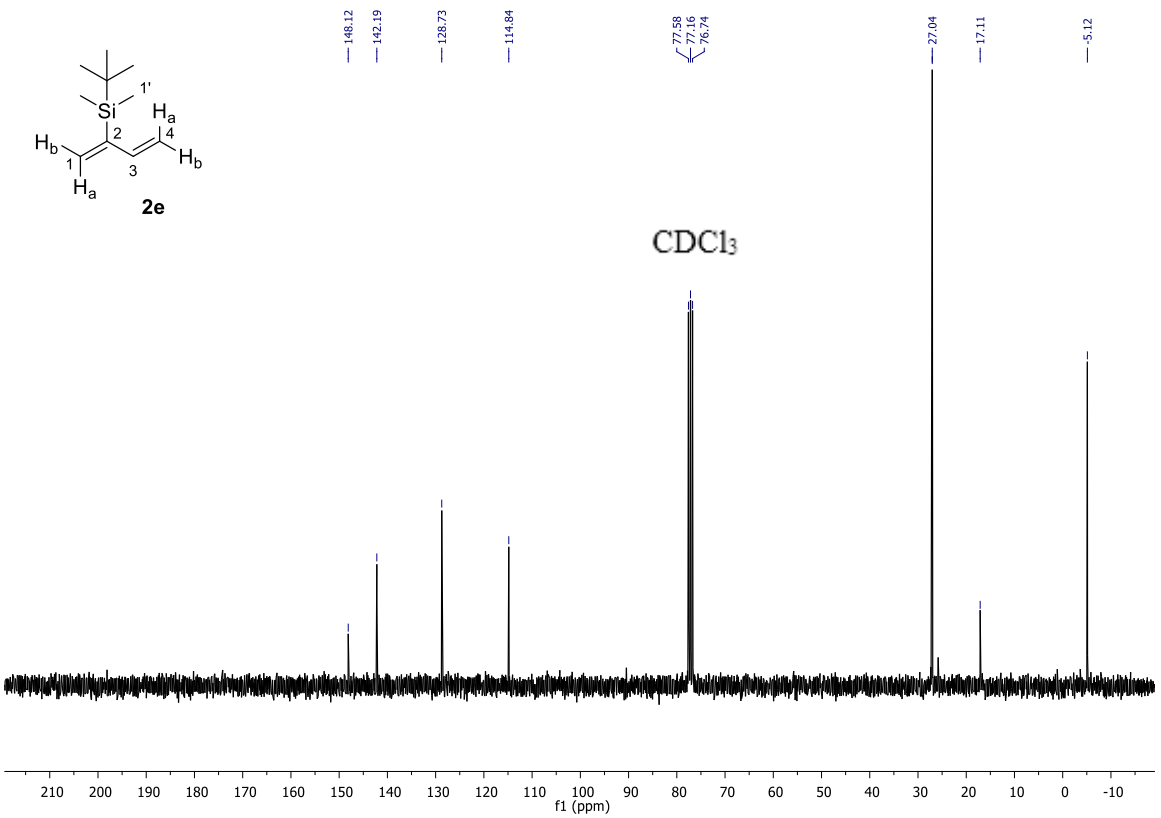


Buta-1,3-dien-2-yl(tert-butyl)dimethylsilane **2e**

^{1}H NMR (300 MHz, $CDCl_3$)

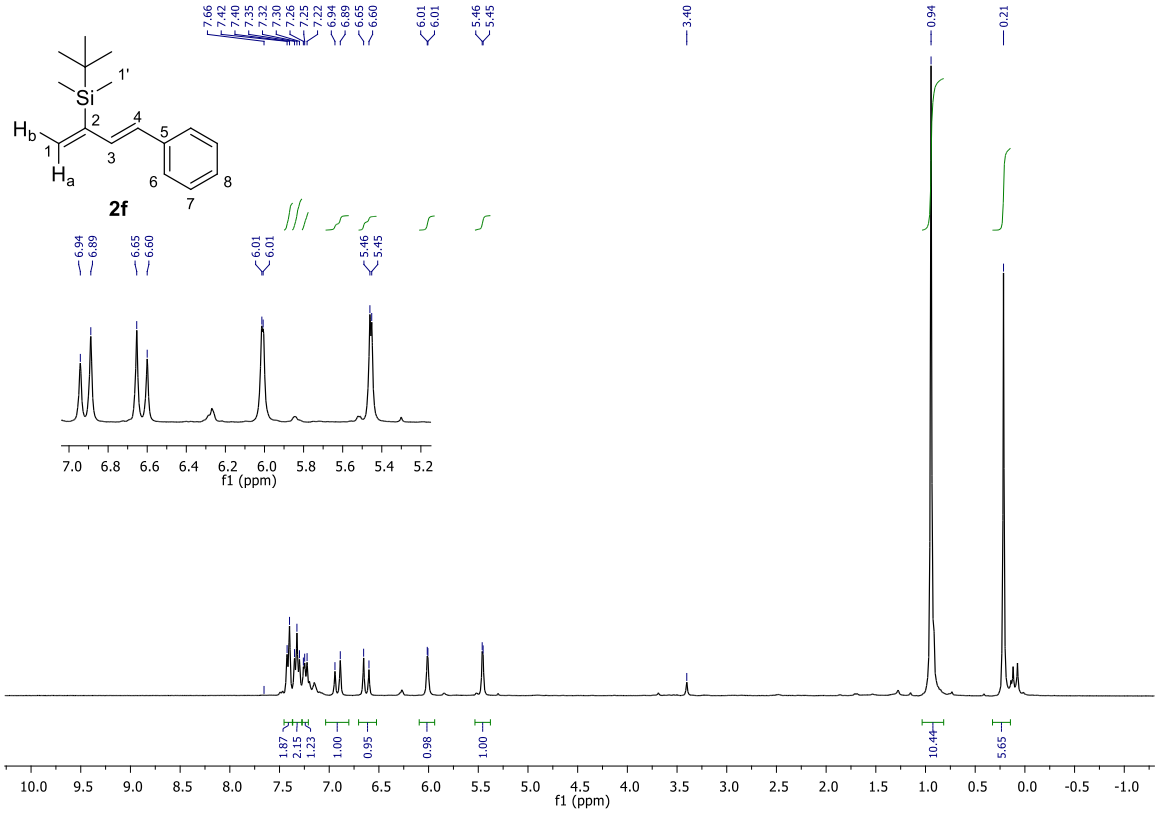


^{13}C NMR (75.5 MHz, $CDCl_3$)

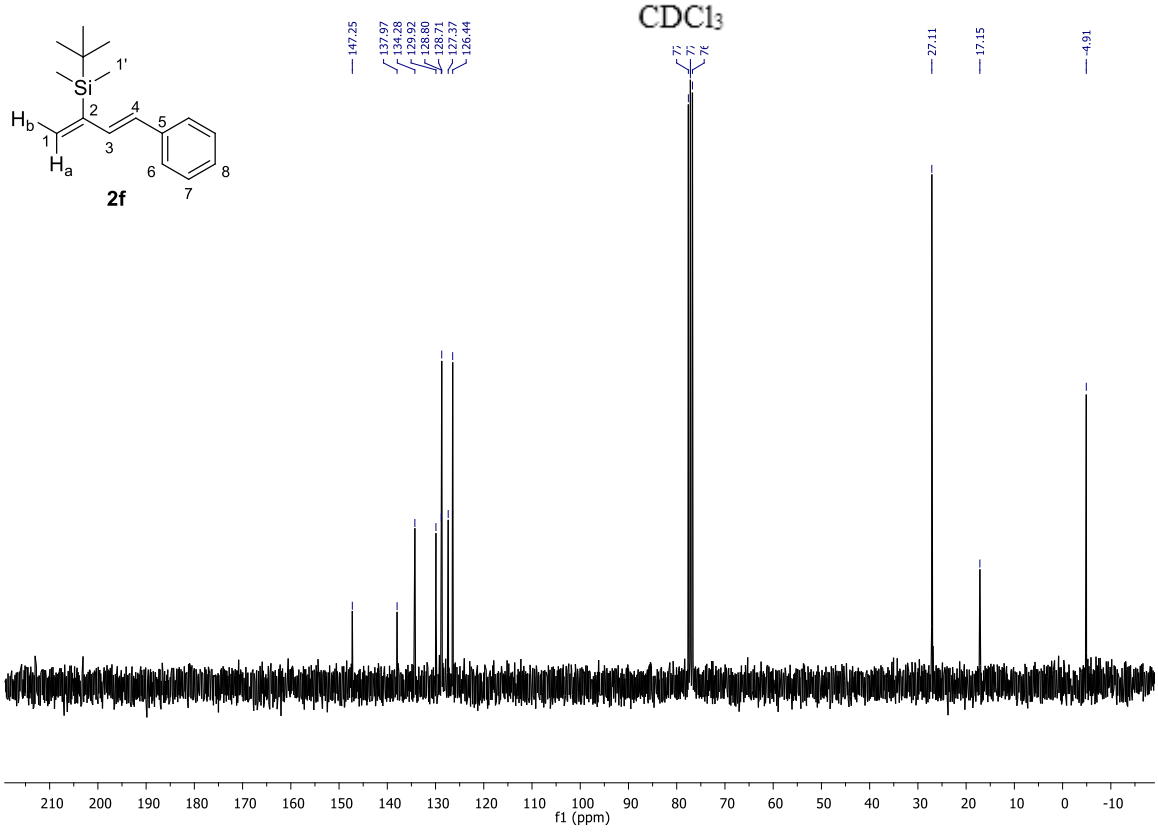


(*E*/*Z*)-tert-butyldimethyl(4-phenylbuta-1,3-dien-2-yl)silane **2f**

^{1}H NMR (300 MHz, $CDCl_3$)

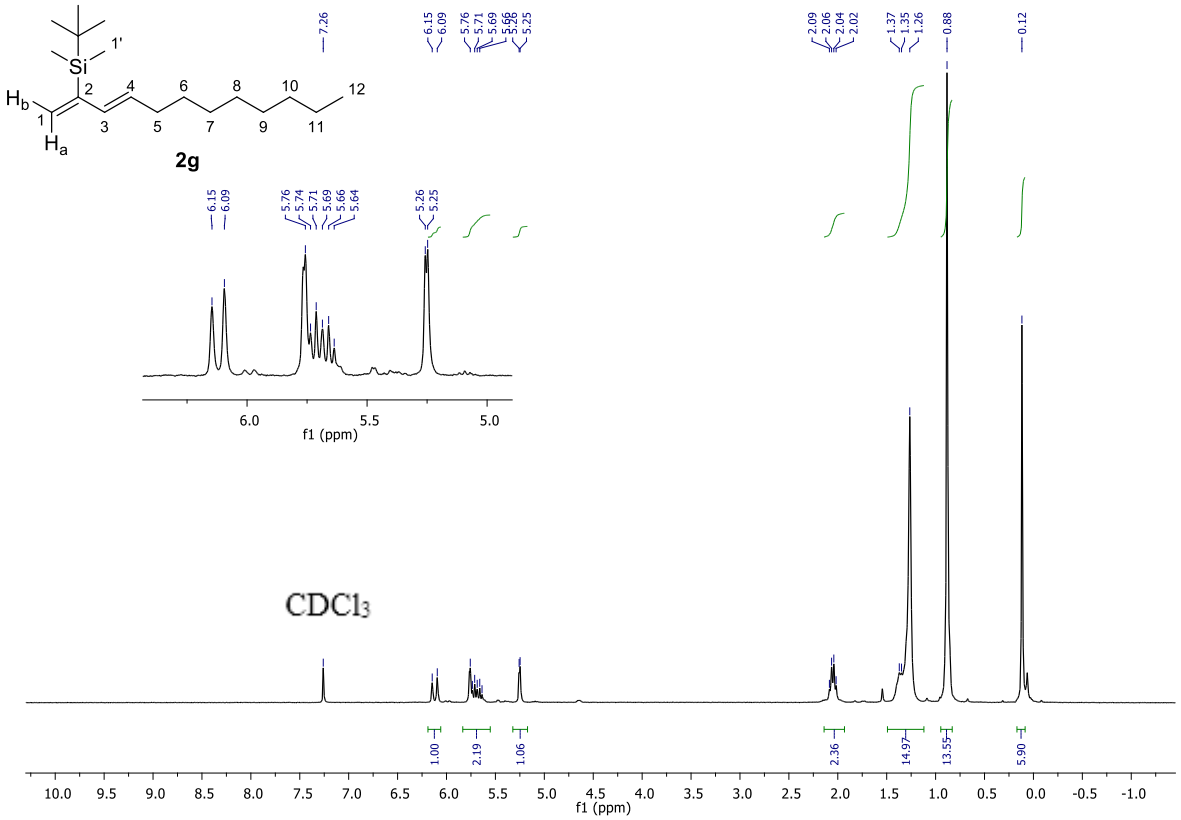


^{13}C NMR (75.5 MHz, $CDCl_3$)

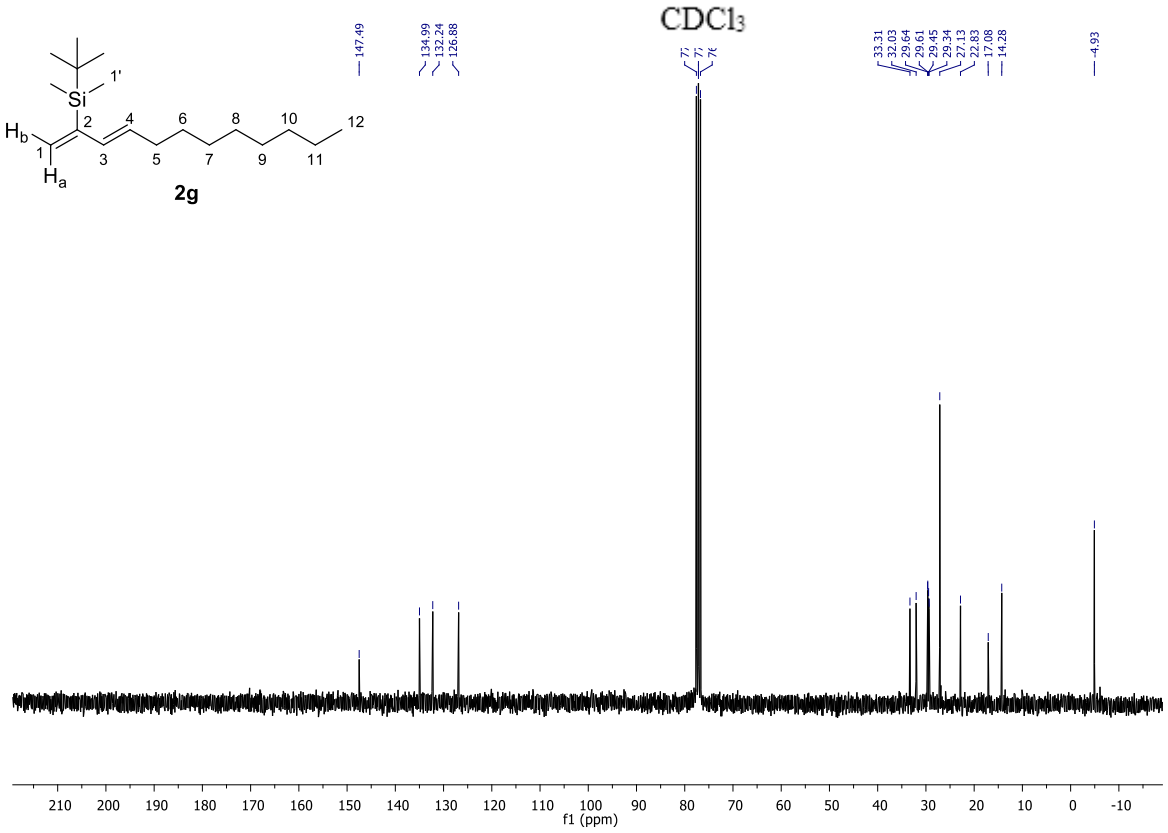


(*E*/*Z*)-tert-butyl(dodeca-1,3-dien-2-yl)dimethylsilane **2g**

^{1}H NMR (300 MHz, $CDCl_3$)

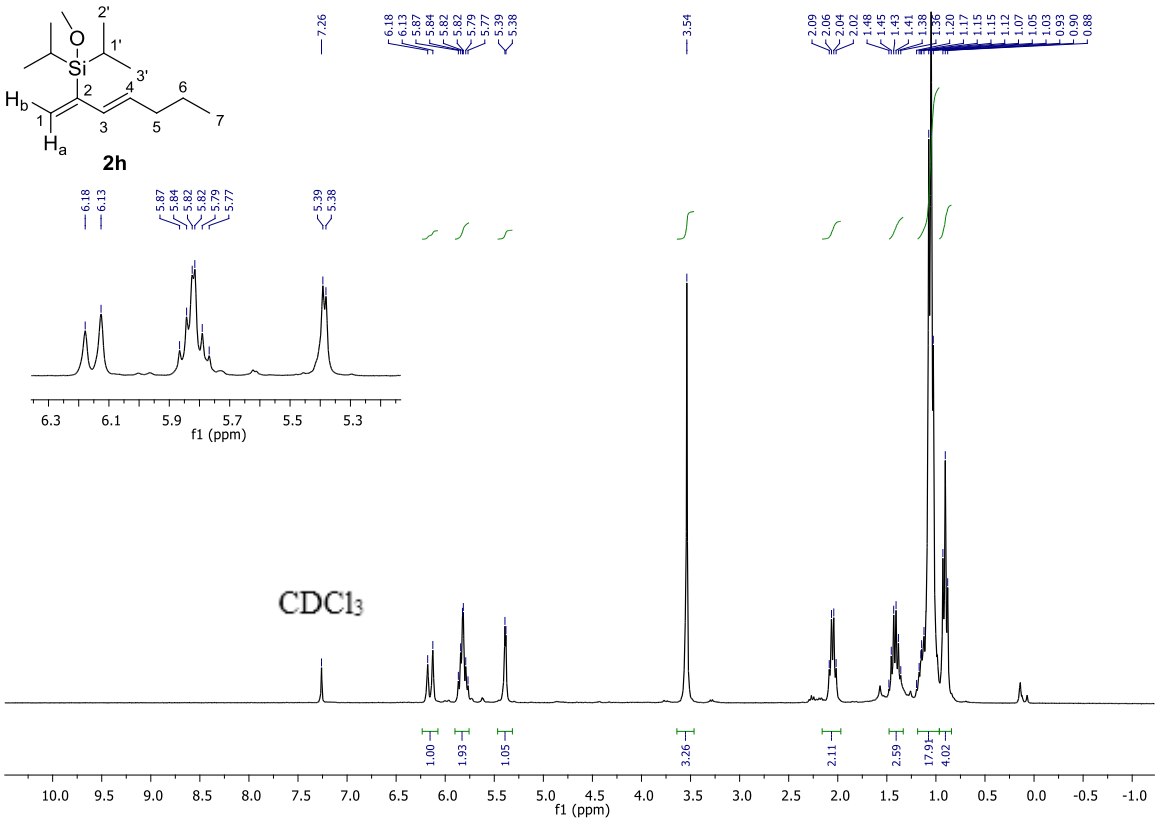


^{13}C NMR (75.5 MHz, $CDCl_3$)

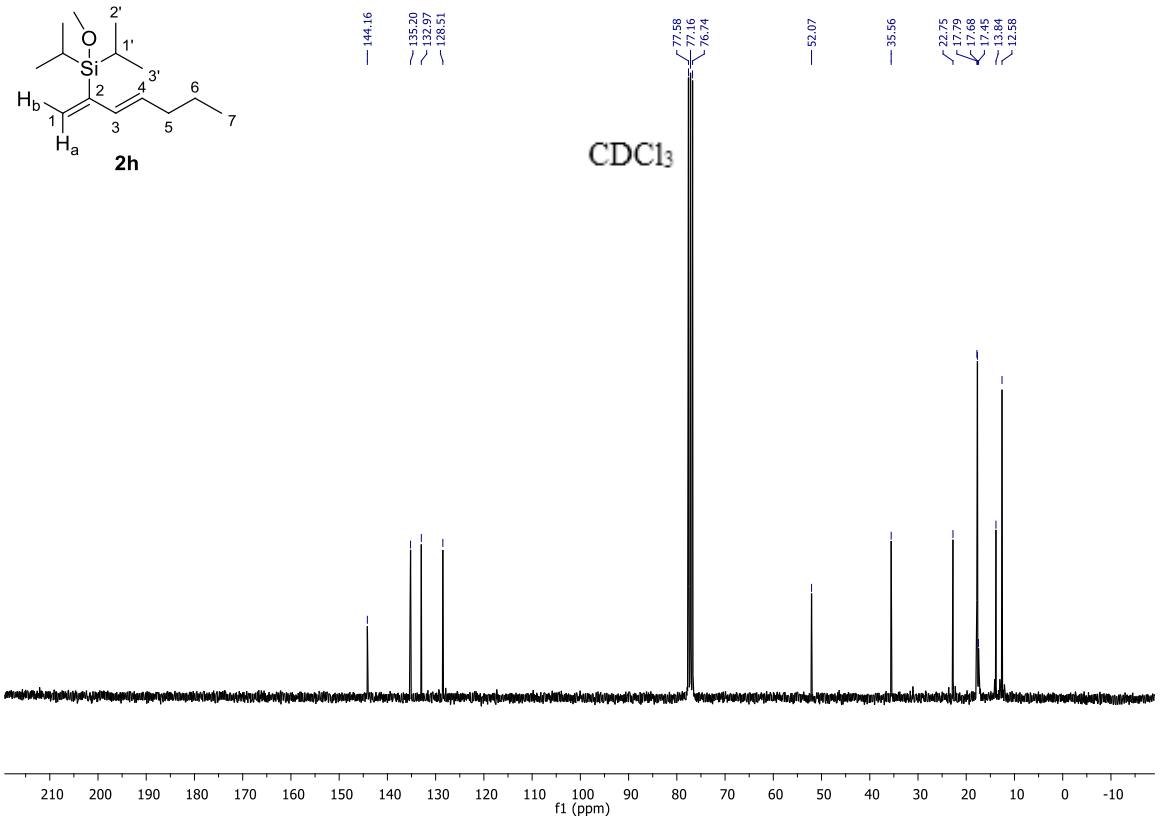


(*E*/*Z*)-hepta-1,3-dien-2-yldiisopropyl(methoxy)silane **2h**

^{1}H NMR (300 MHz, $CDCl_3$)

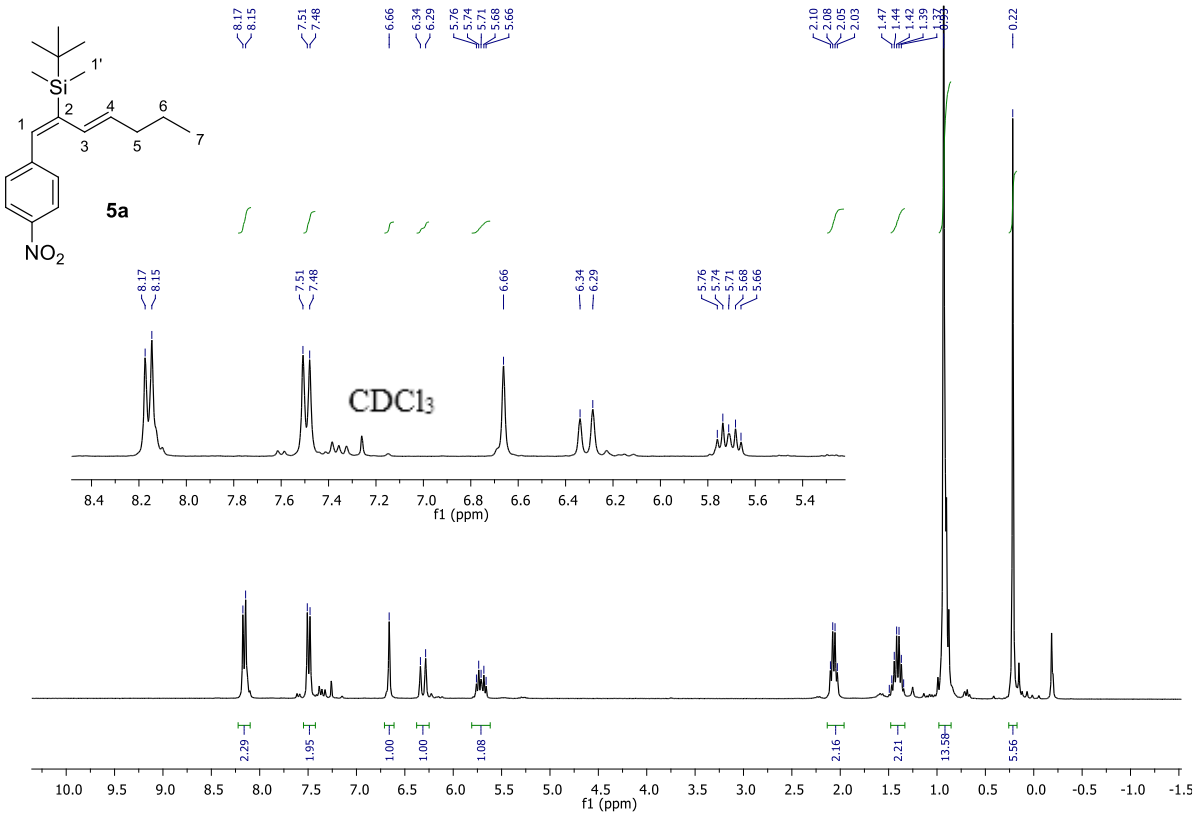


^{13}C NMR (75.5 MHz, $CDCl_3$)

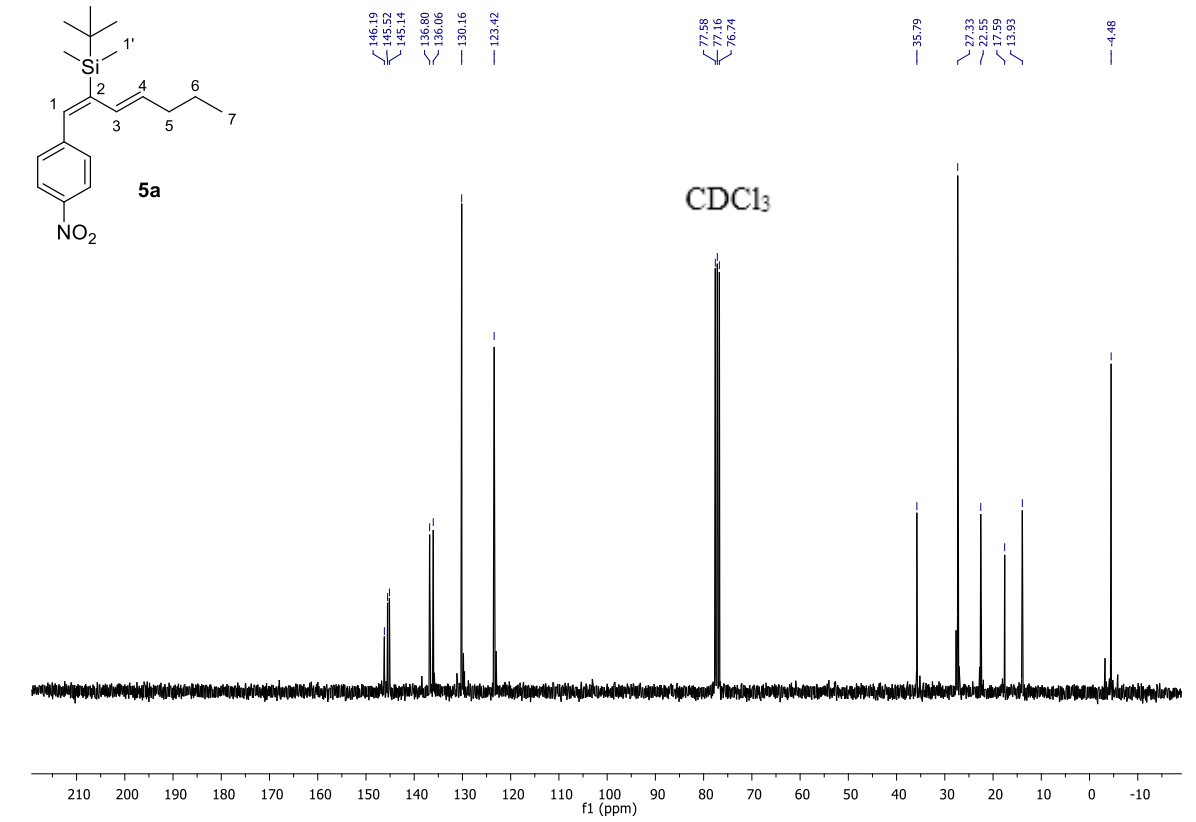


Tert-butyldimethyl((1*E*/*Z*,3*E*)-1-(4-nitrophenyl)hepta-1,3-dien-2-yl)silane **5a**

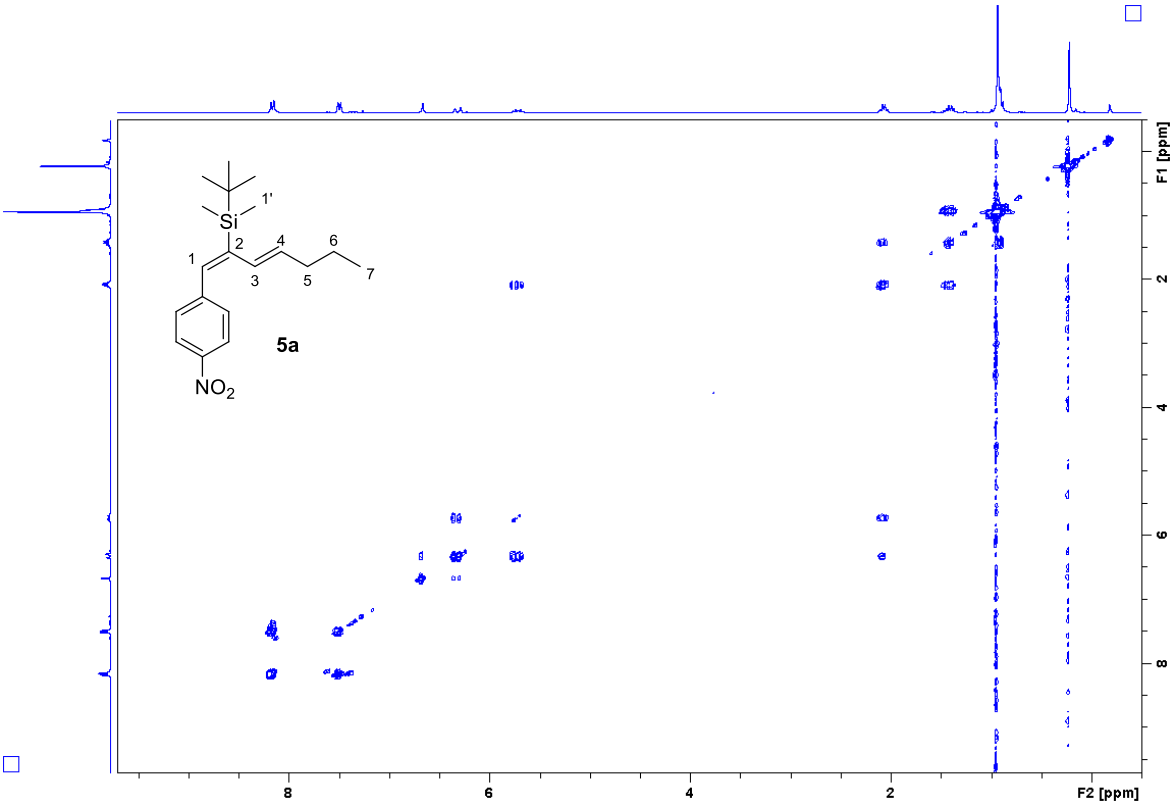
^{1}H NMR (300 MHz, $CDCl_3$)



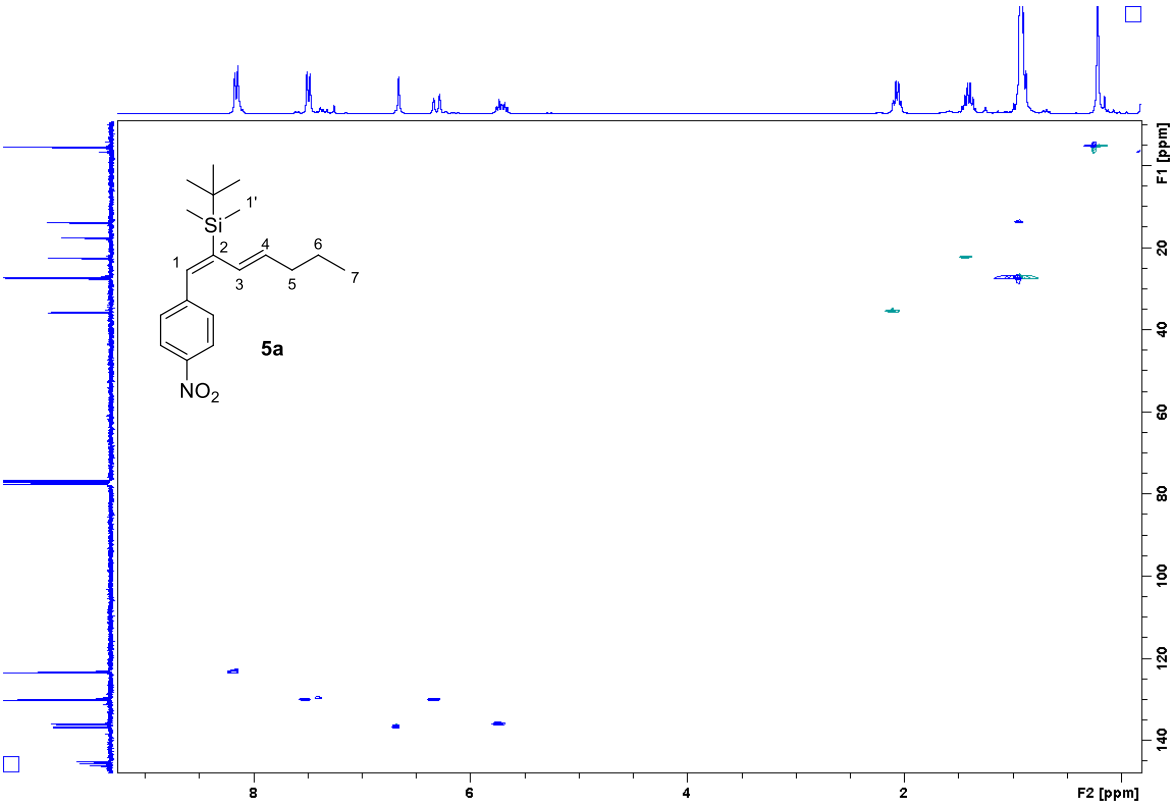
^{13}C NMR (75.5 MHz, $CDCl_3$)



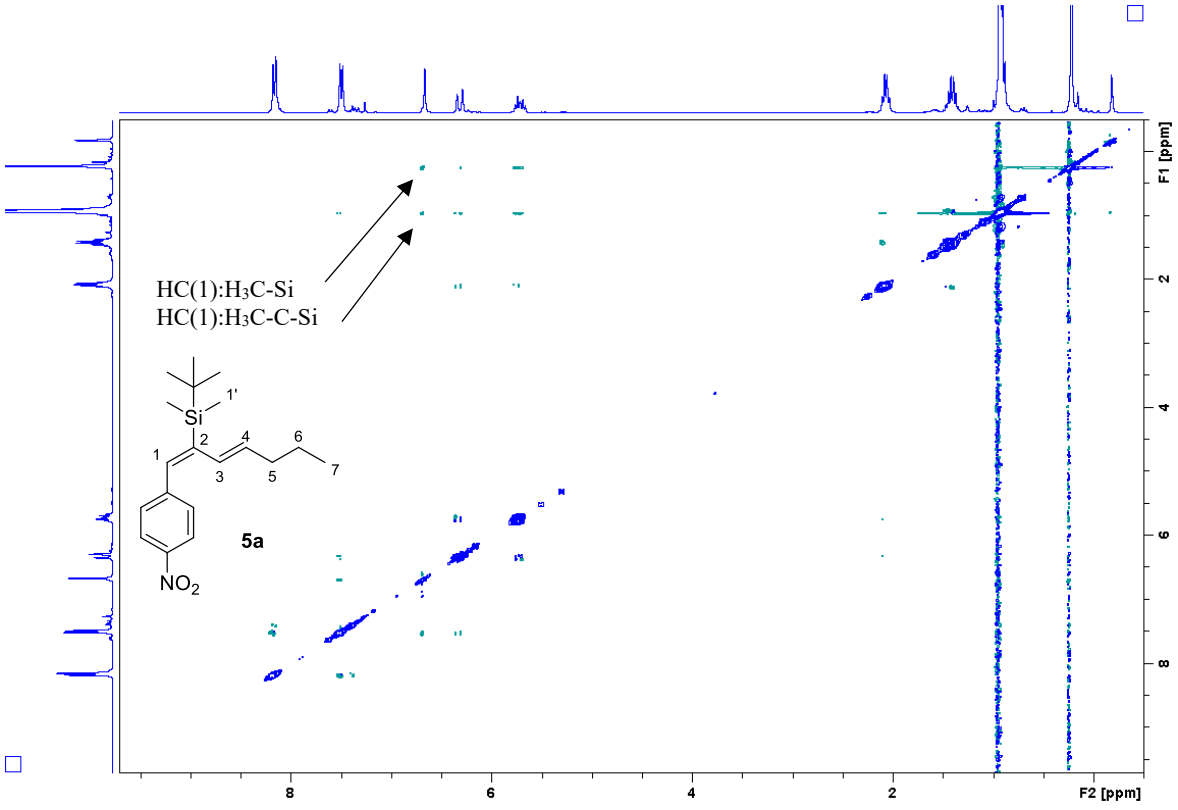
2D ^{1}H-^{1}H COSY NMR ($CDCl_3$)



2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

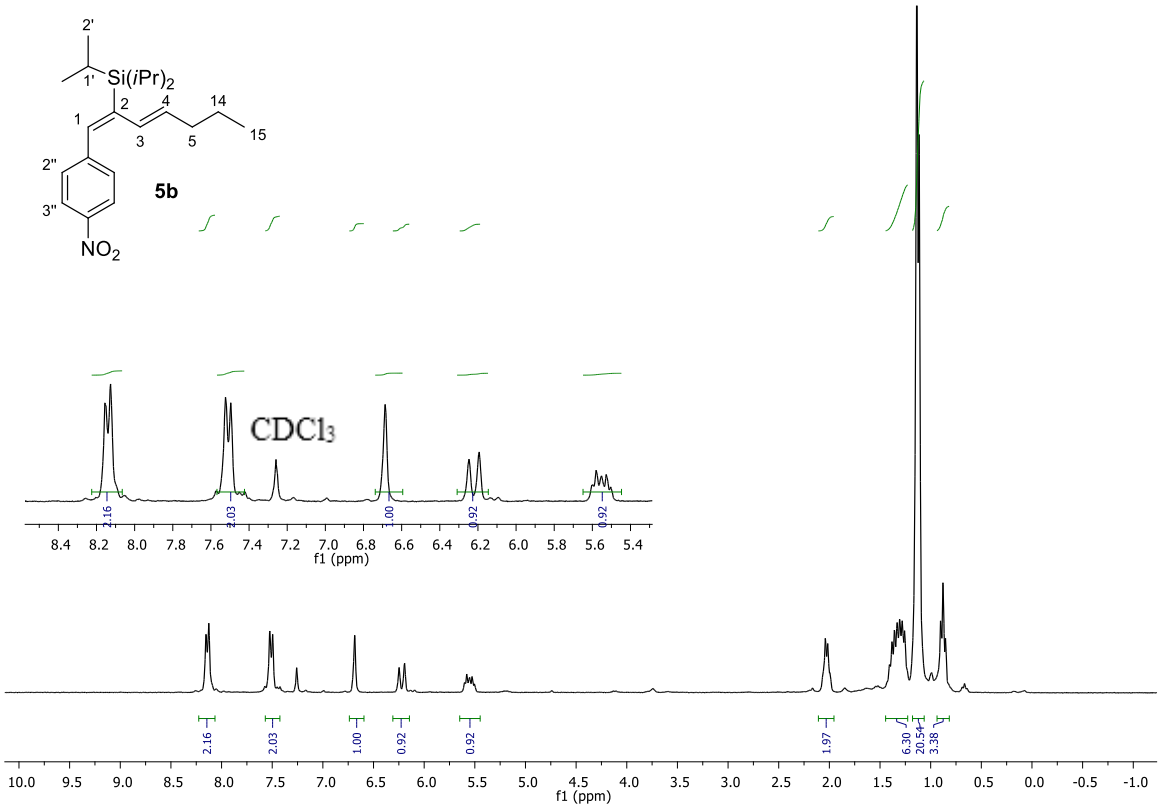


2D ^{1}H-^{1}H NOESY NMR ($CDCl_3$)

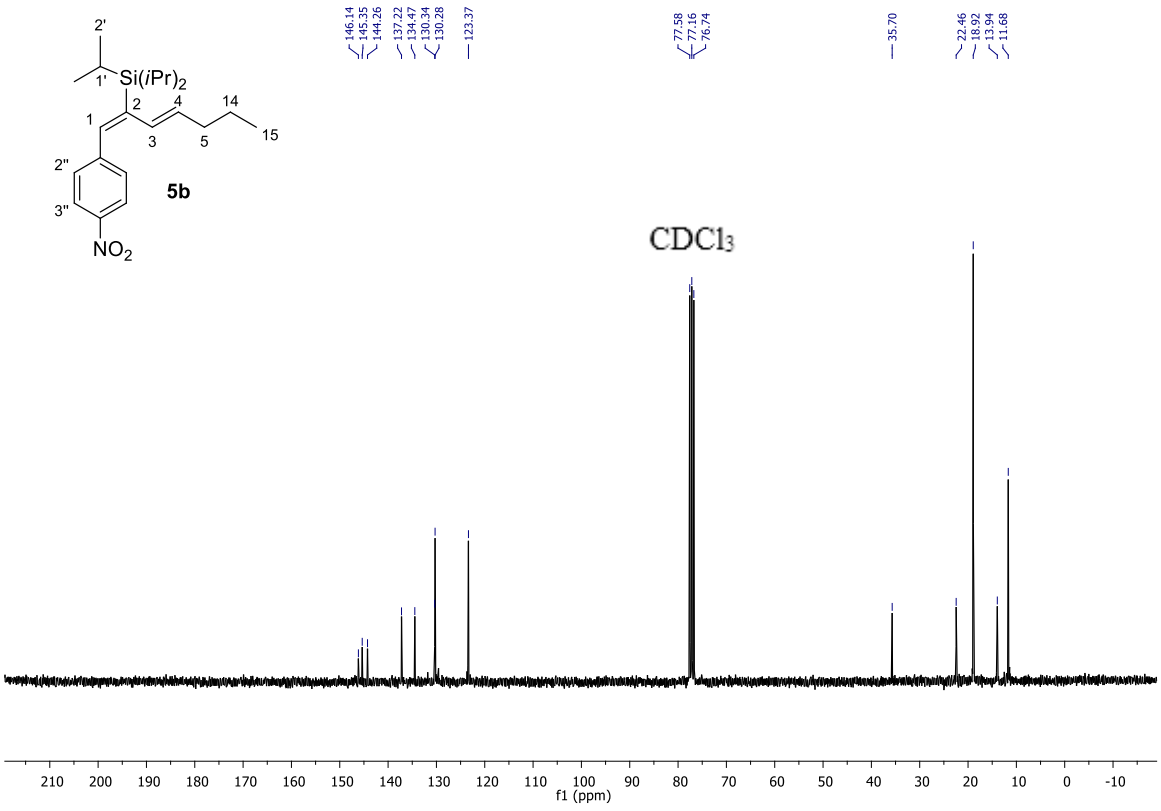


Triisopropyl((1*E*,3*E*)-1-(4-nitrophenyl)hepta-1,3-dien-2-yl)silane **5b**

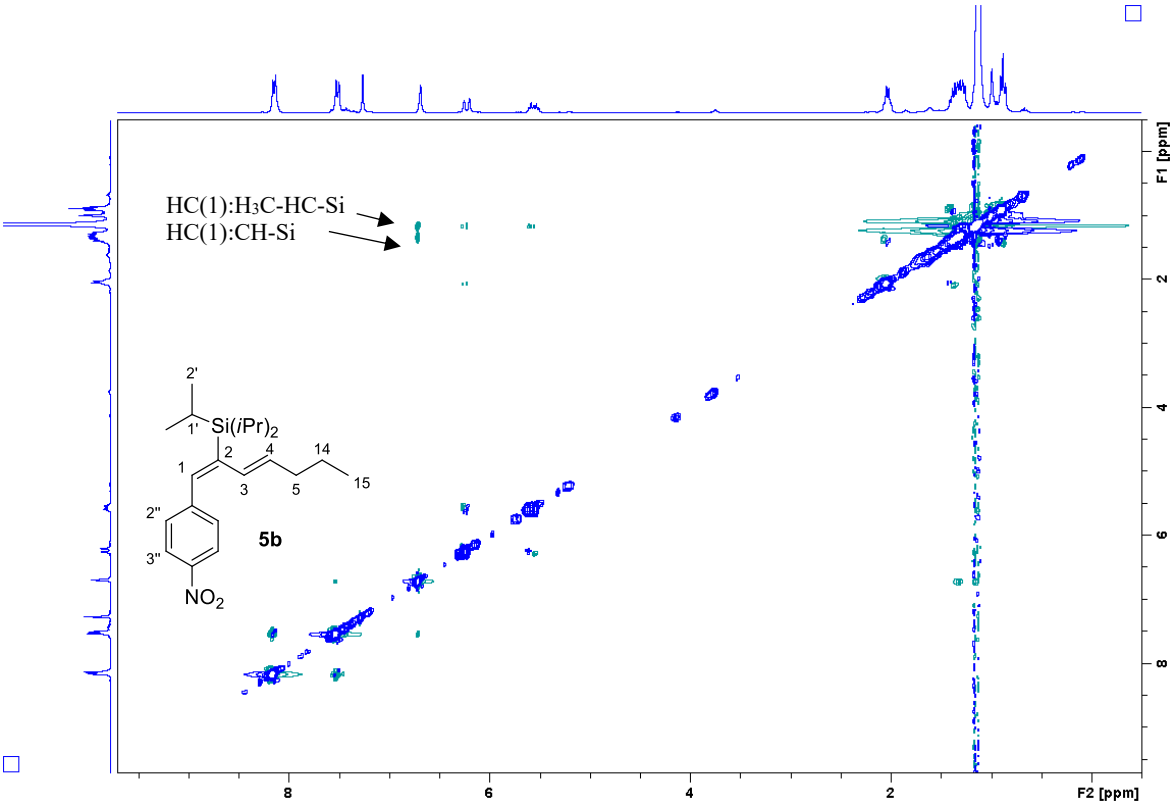
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

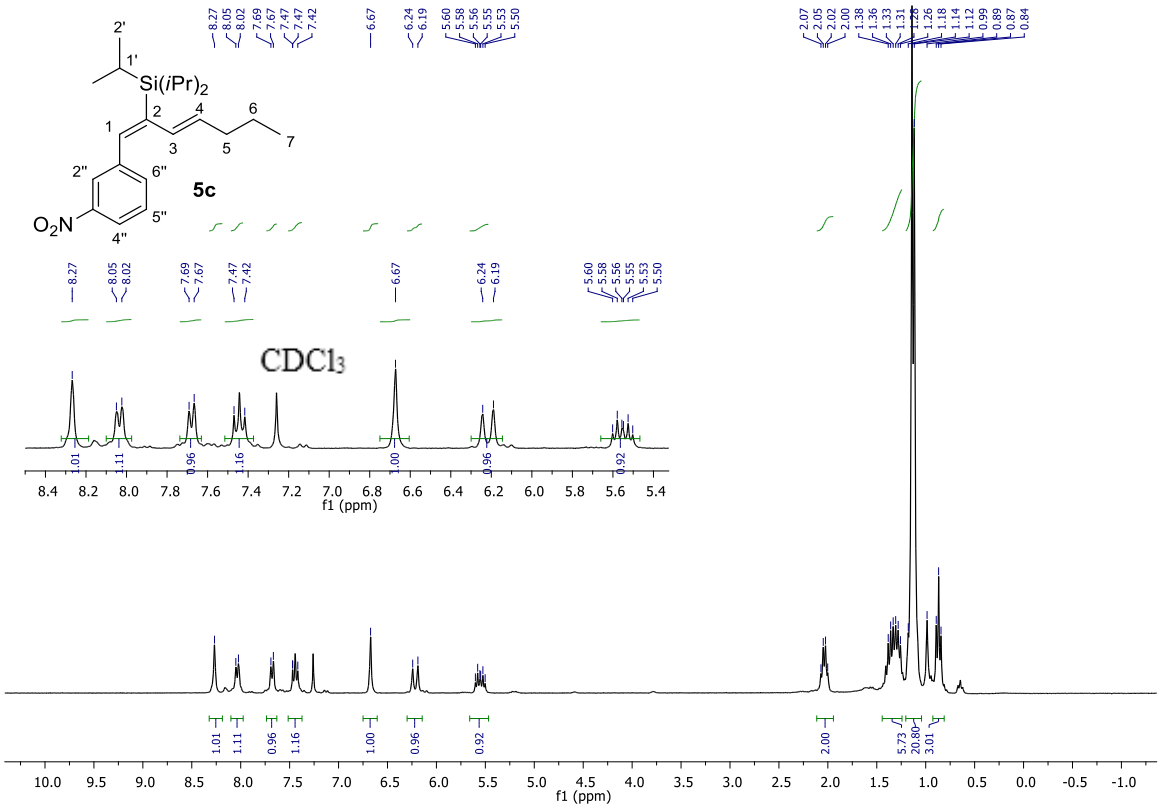


2D ^{1}H-^{1}H NOESY NMR ($CDCl_3$)

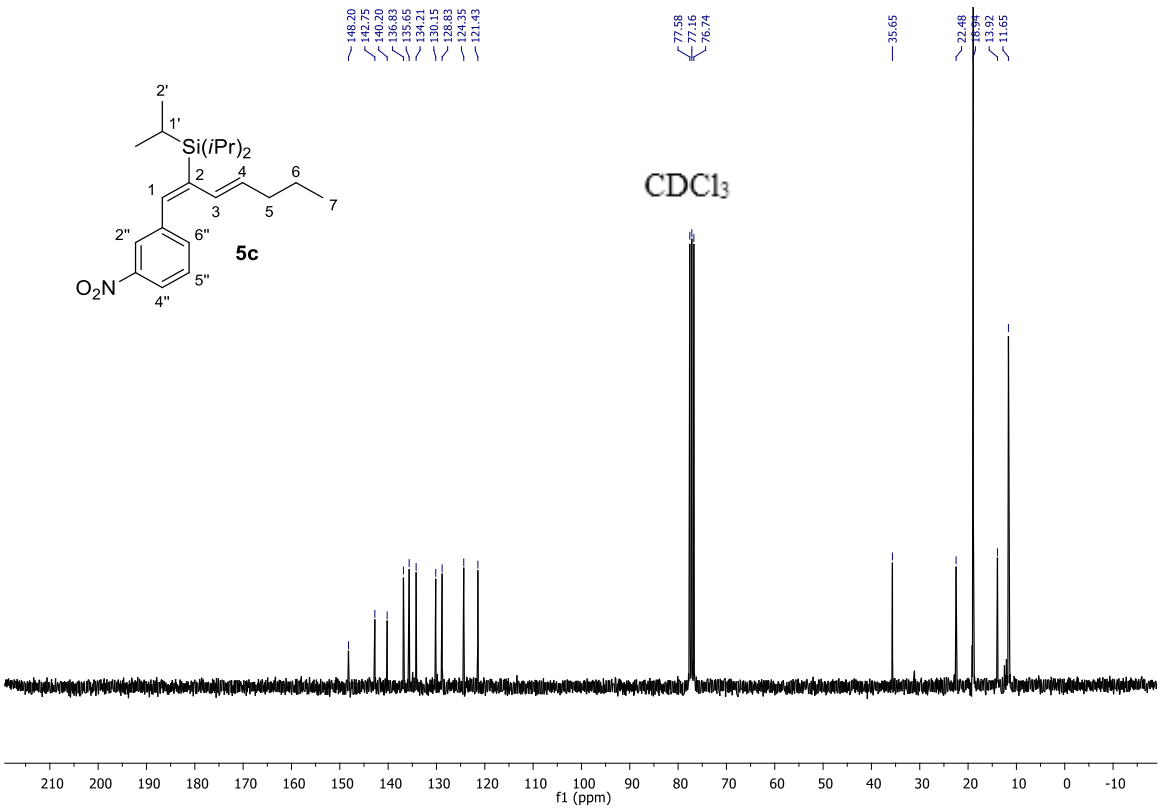


Triisopropyl((1*E*,3*E*)-1-(3-nitrophenyl)hepta-1,3-dien-2-yl)silane **5c**

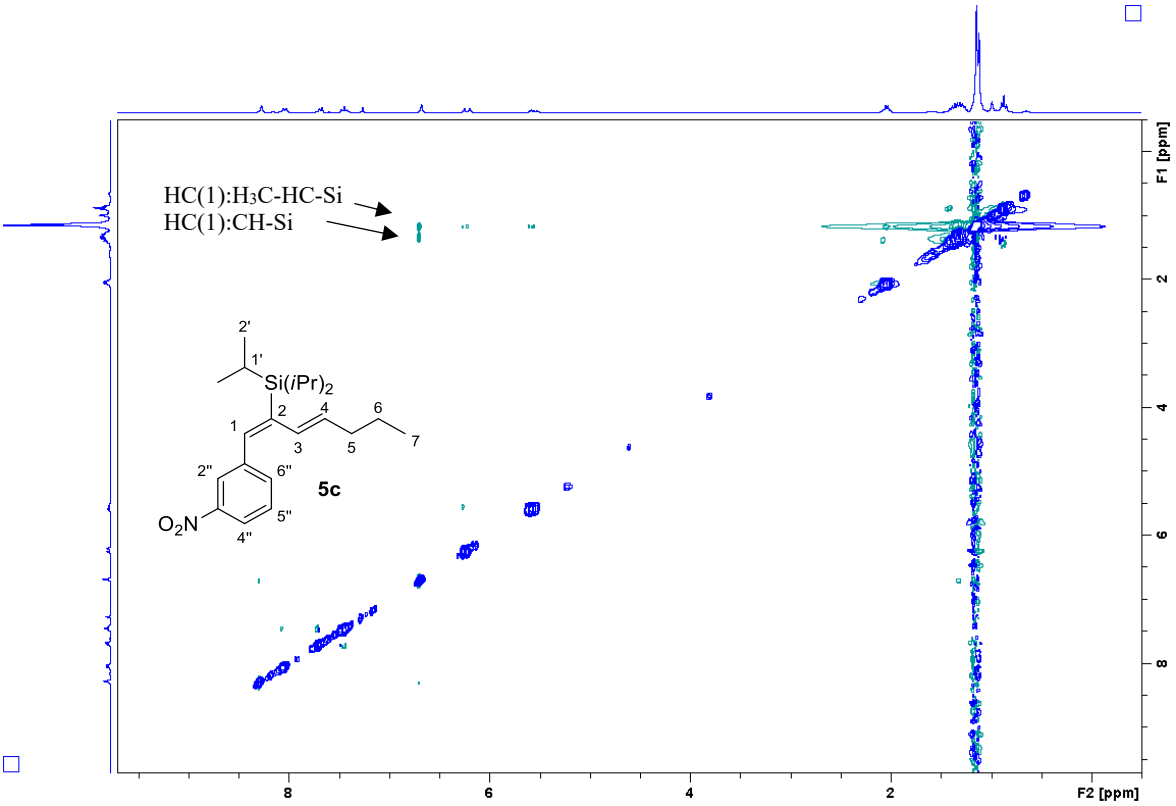
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)



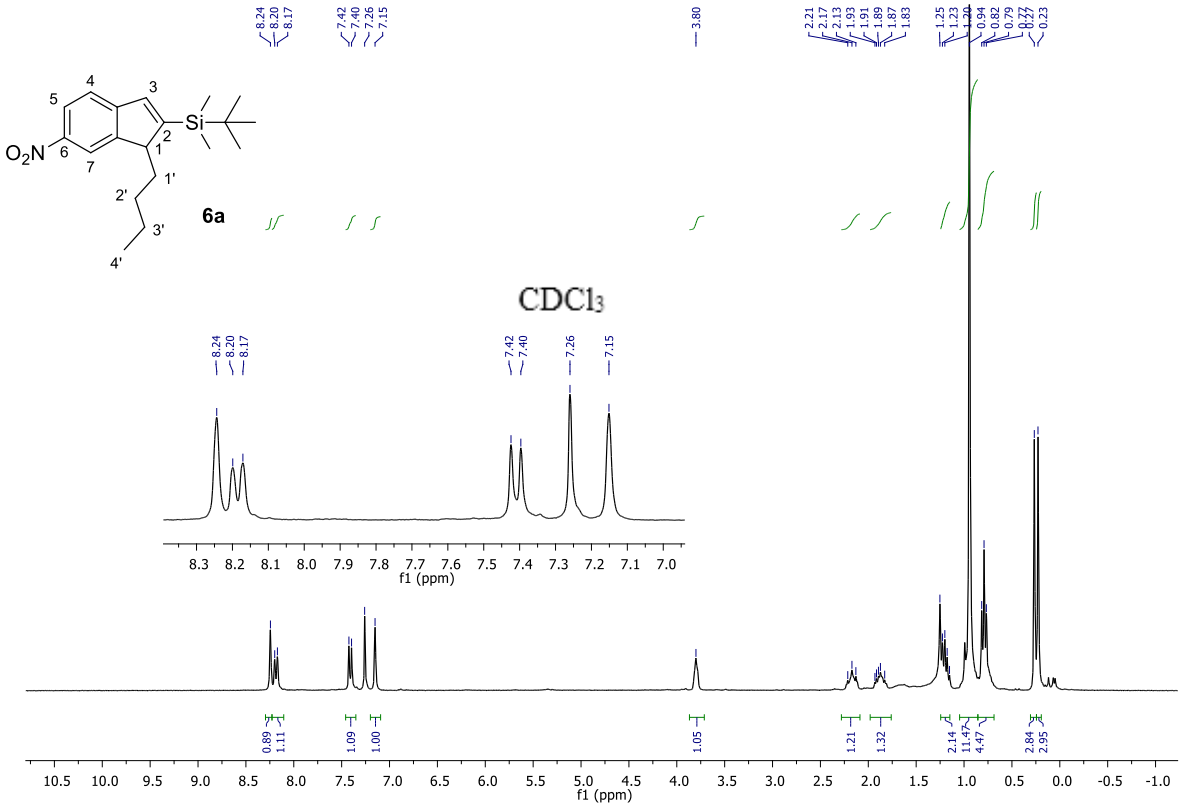
2D-NOESY ^{1}H NMR (300 MHz, $CDCl_3$)



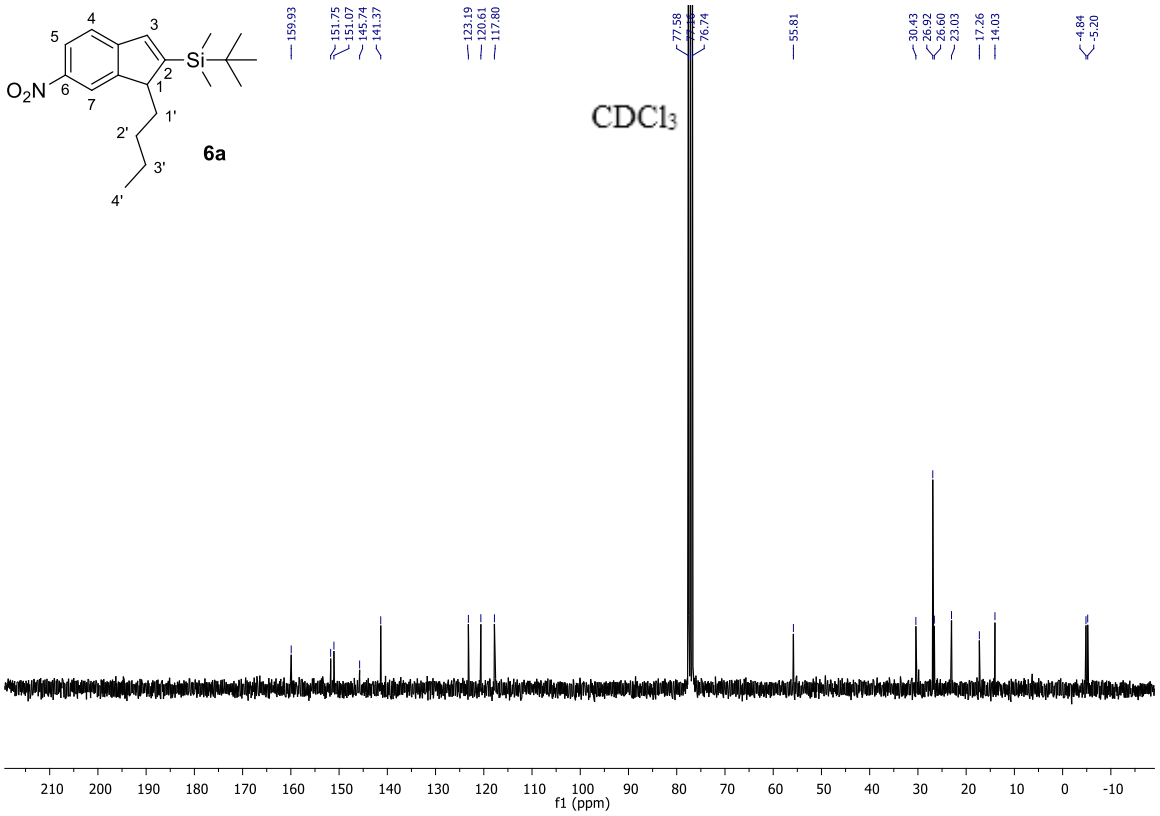
2.2. Silyl indenes

Tert-butyl(1-butyl-6-nitro-1H-inden-2-yl)dimethylsilane **6a**

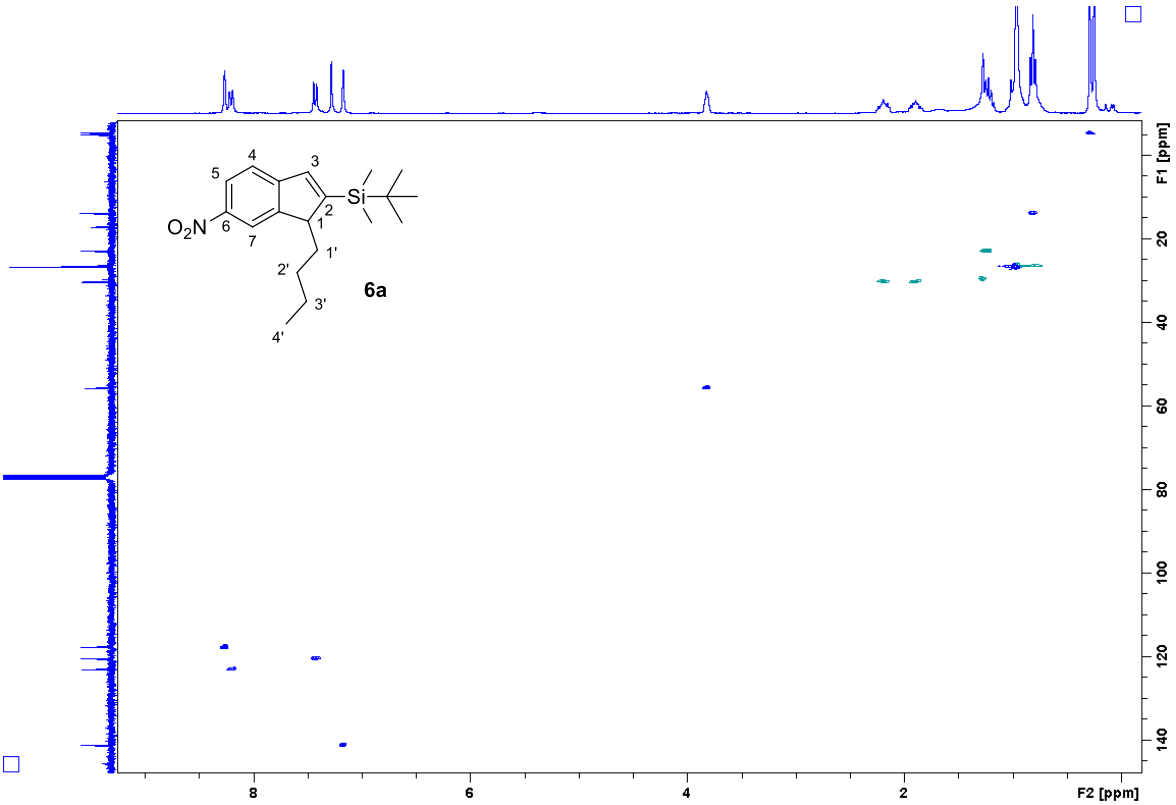
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

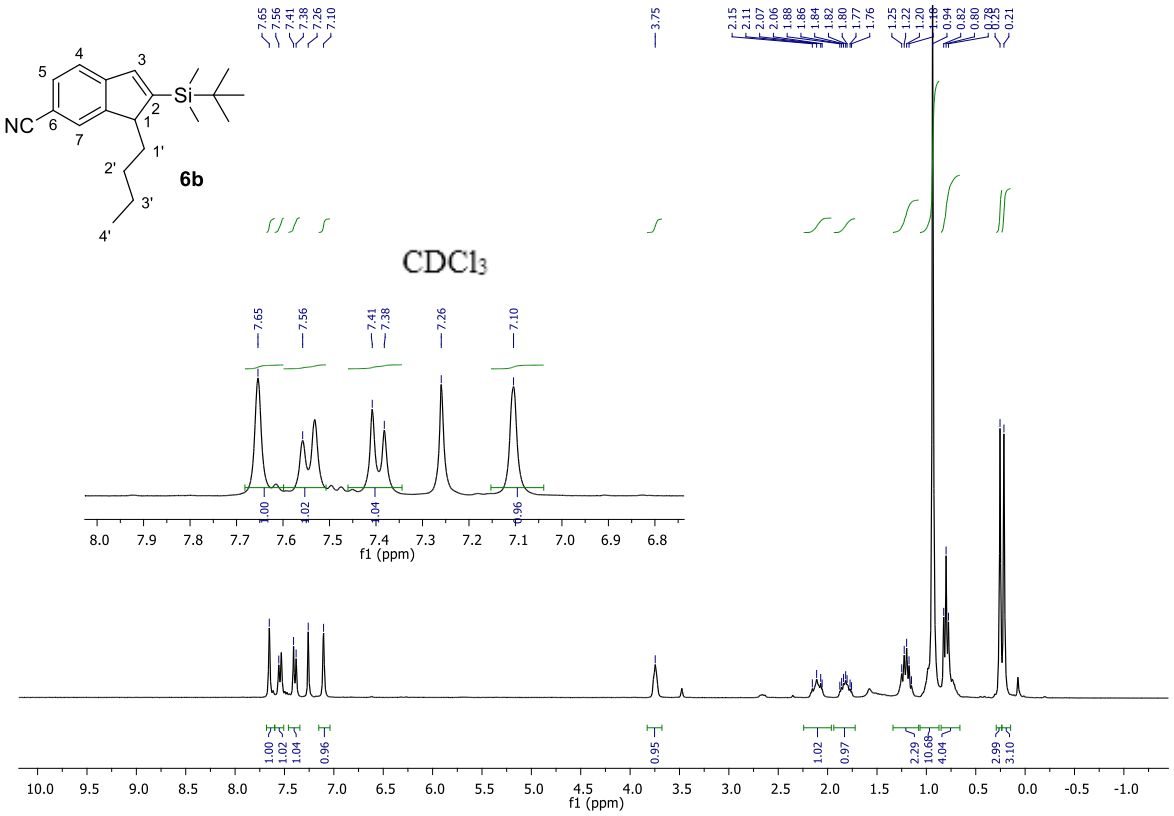


2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

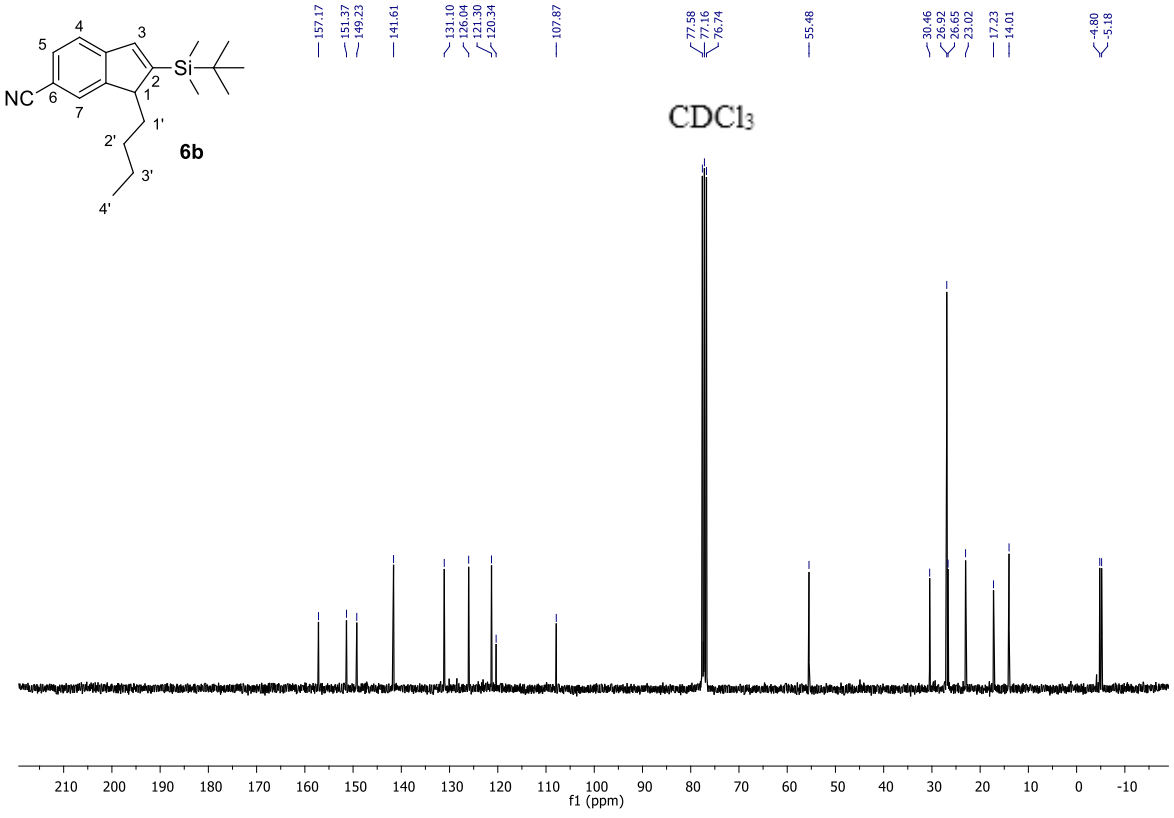


1-Butyl-2-(tert-butyldimethylsilyl)-1H-indene-6-carbonitrile **6b**

^{1}H NMR (300 MHz, $CDCl_3$)

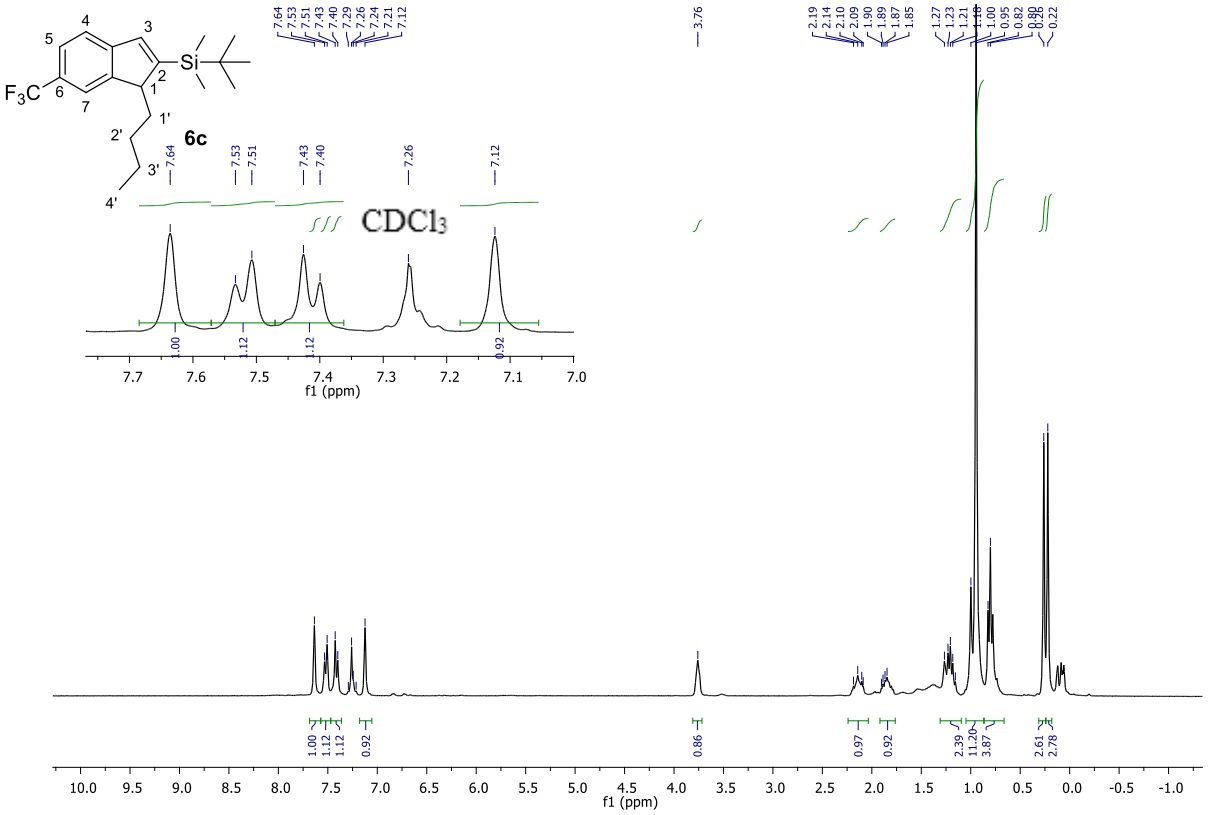


^{13}C NMR (75.5 MHz, $CDCl_3$)

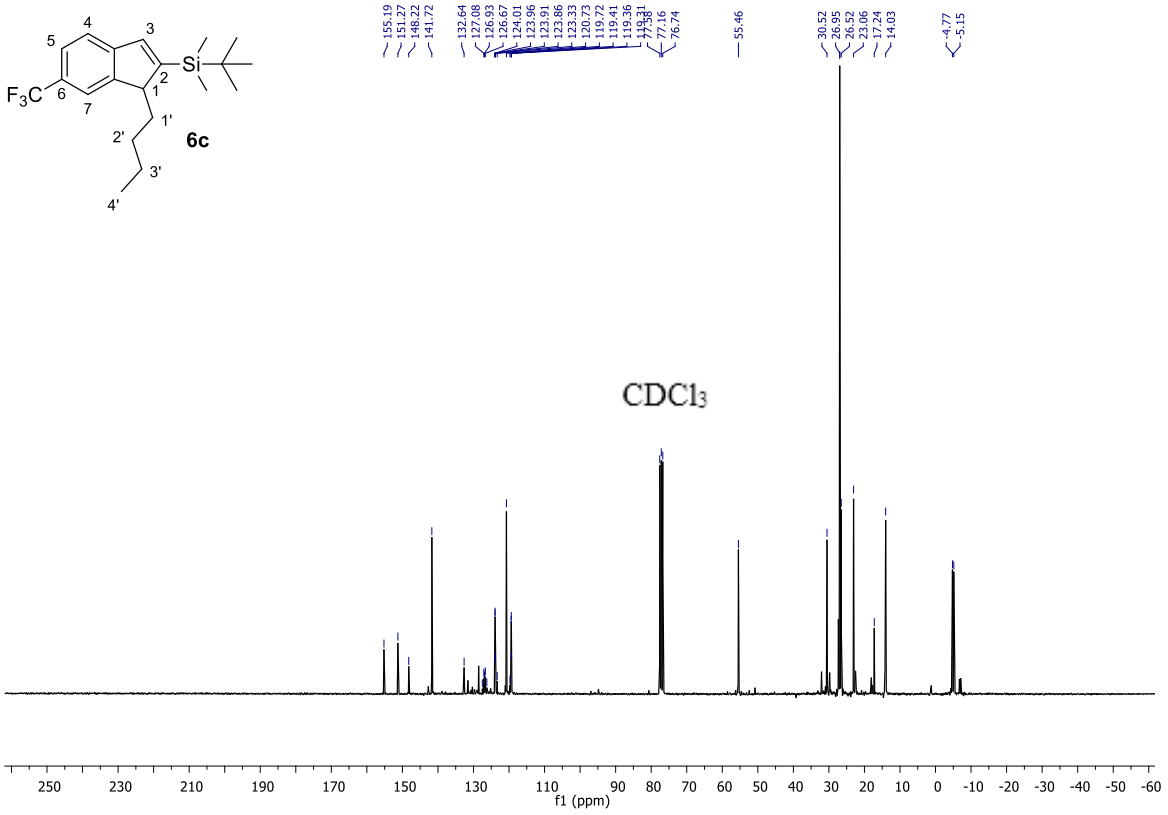


Tert-butyl(1-butyl-6-(trifluoromethyl)-1H-inden-2-yl)dimethylsilane **6c**

^{1}H NMR (300 MHz, $CDCl_3$)

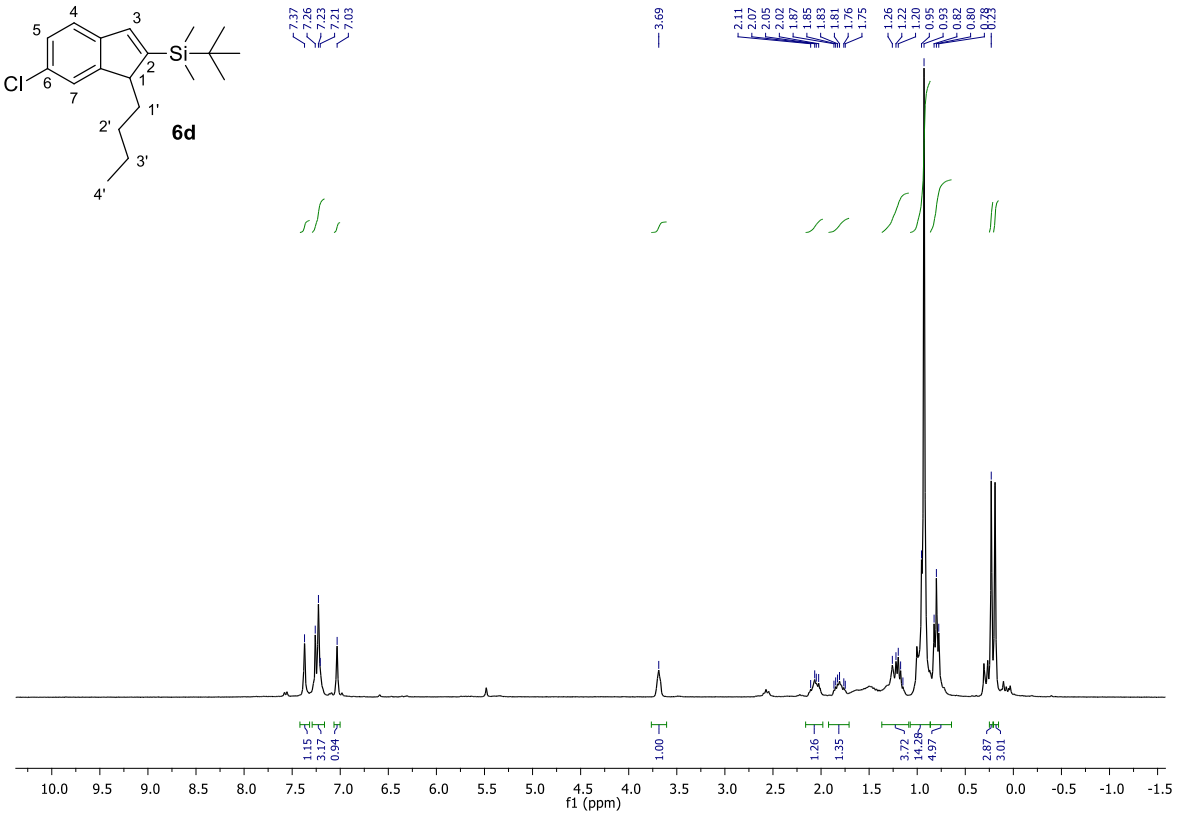


^{13}C NMR (75.5 MHz, $CDCl_3$)

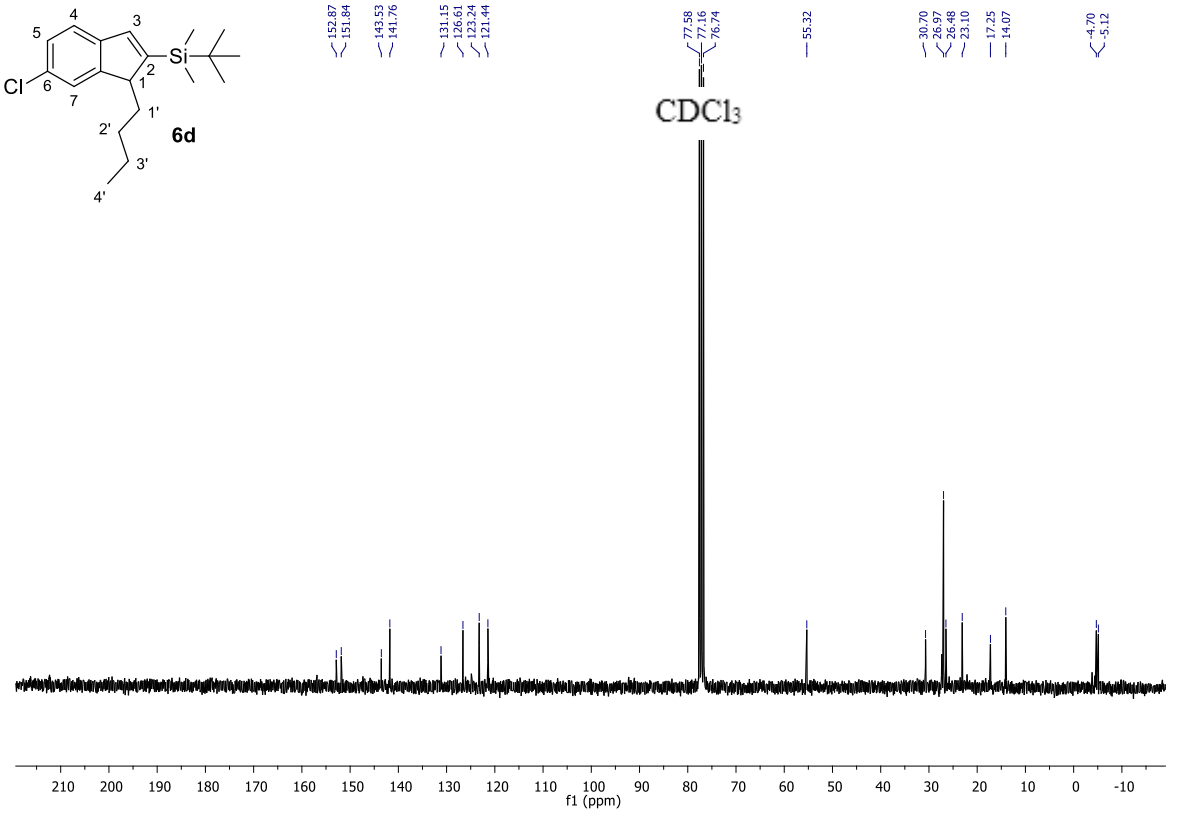


Tert-butyl(1-butyl-6-chloro-1H-inden-2-yl)dimethylsilane **6d**

^{1}H NMR (300 MHz, $CDCl_3$)

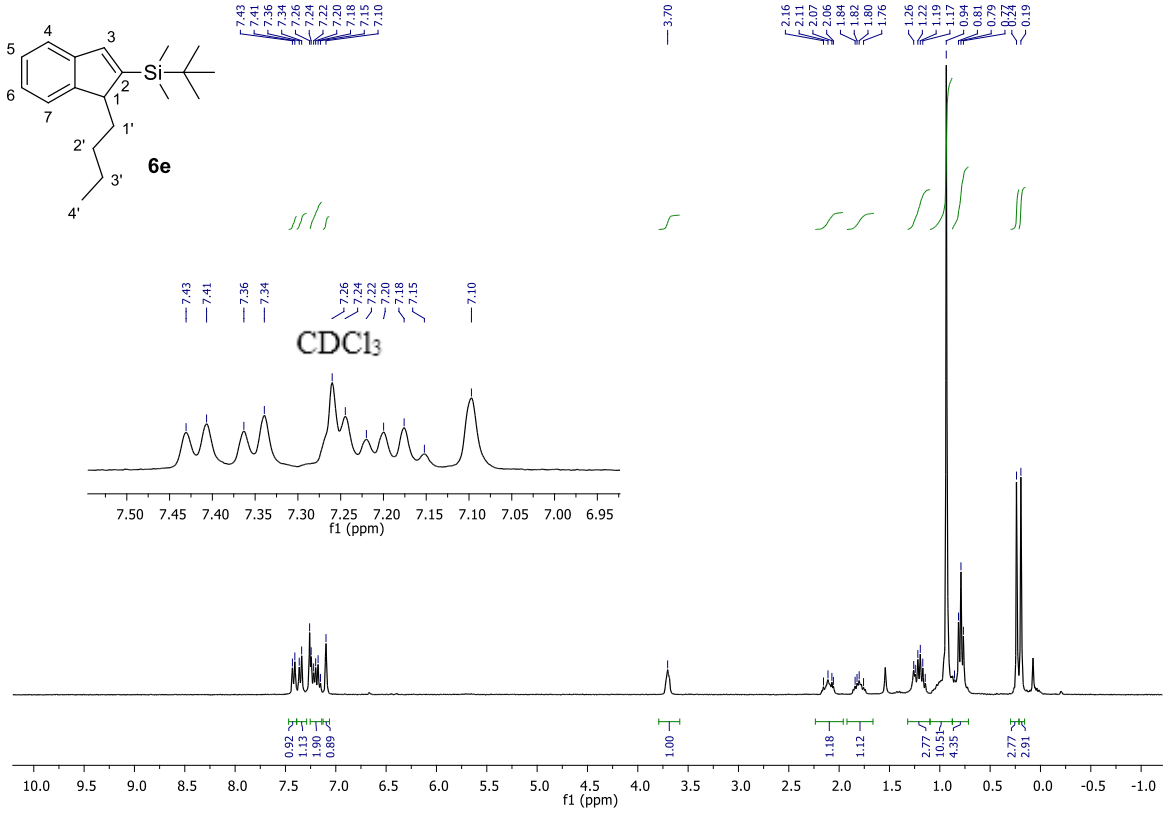


^{13}C NMR (75.5 MHz, $CDCl_3$)

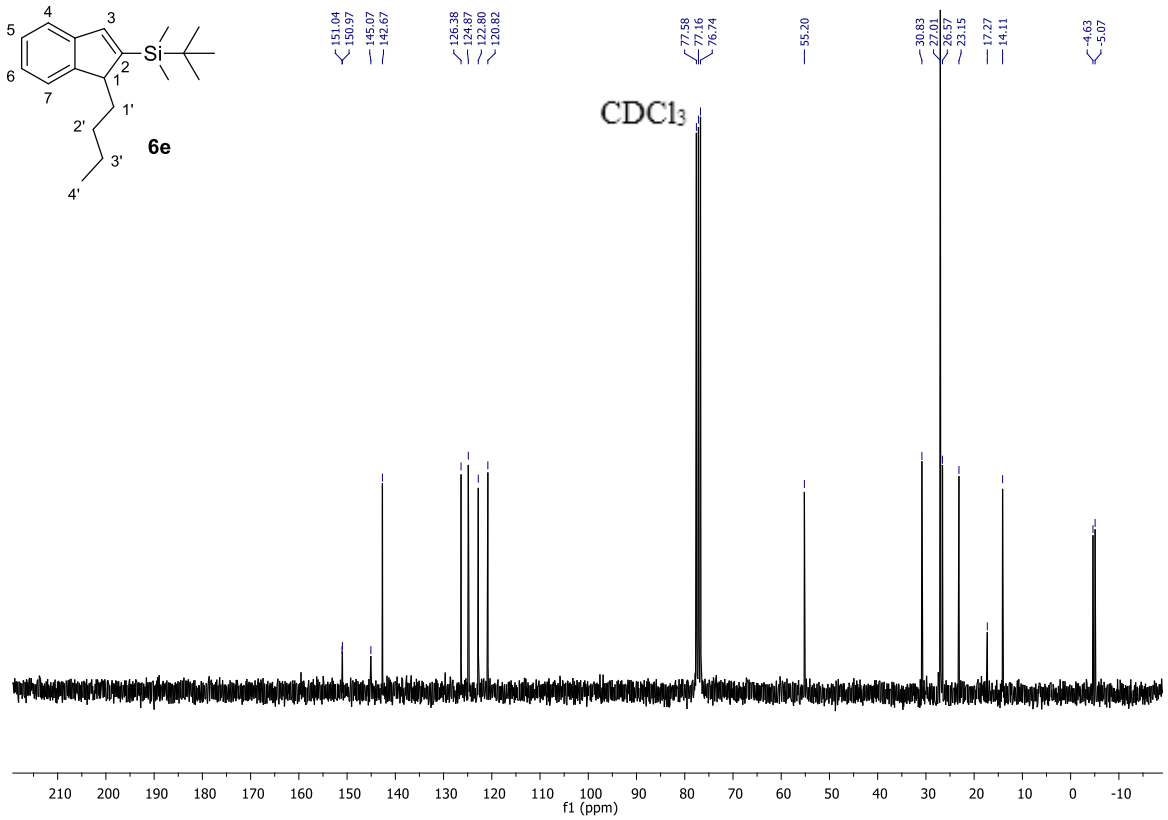


Tert-butyl(1-butyl-1H-inden-2-yl)dimethylsilane **6e**

^{1}H NMR (300 MHz, $CDCl_3$)

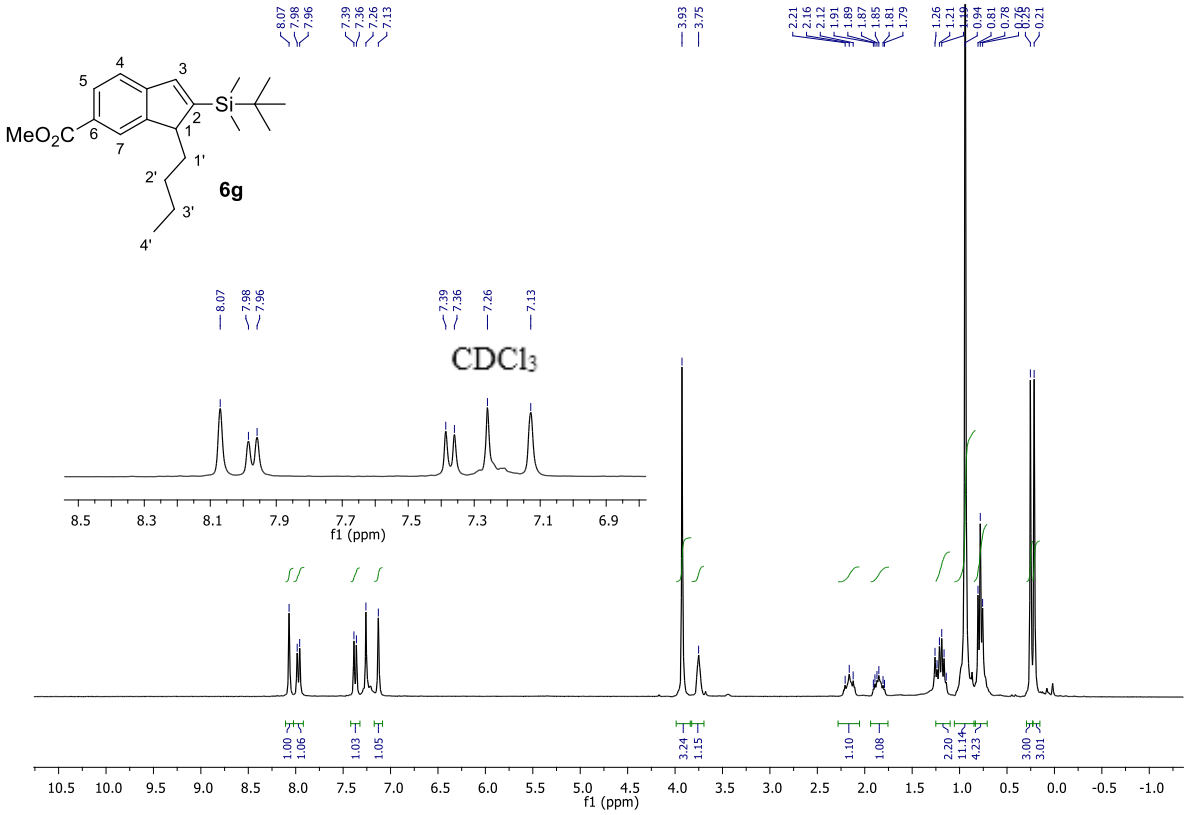


^{13}C NMR (75.5 MHz, $CDCl_3$)

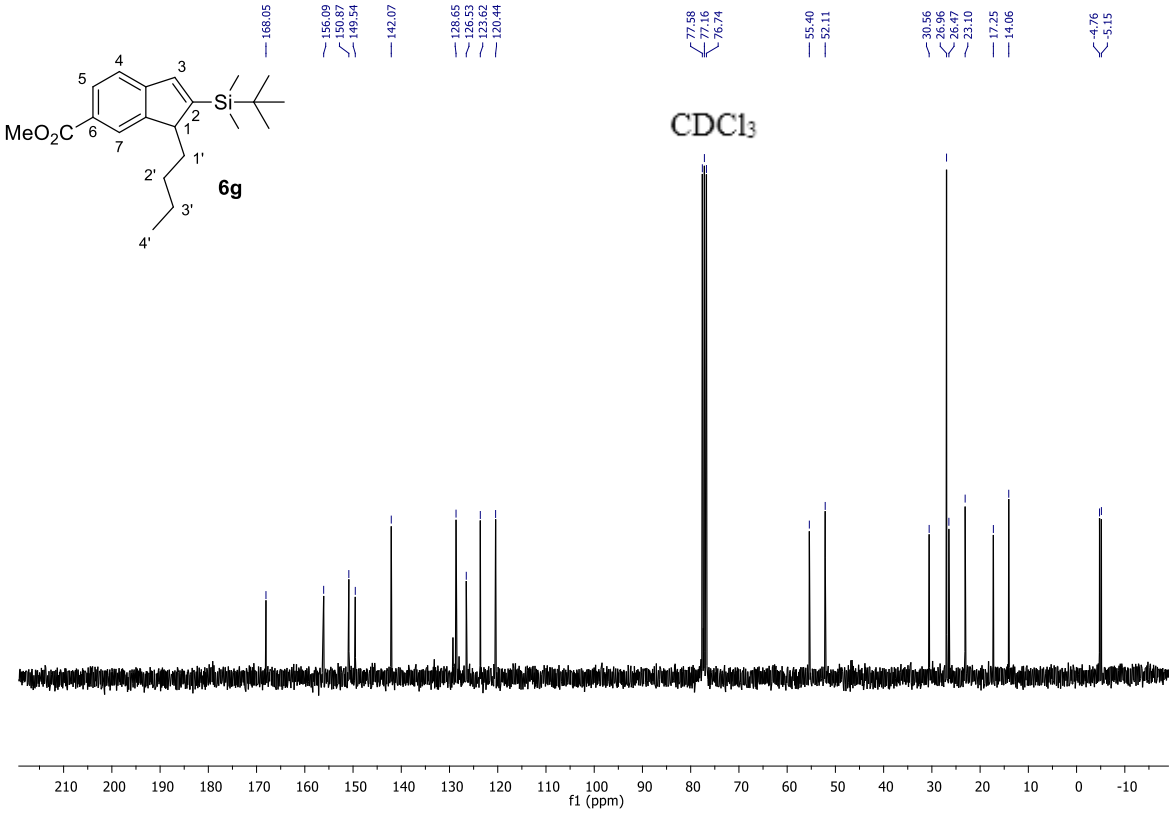


Methyl 1-butyl-2-(*tert*-butyldimethylsilyl)-1H-indene-6-carboxylate **6g**

^{1}H NMR (300 MHz, $CDCl_3$)

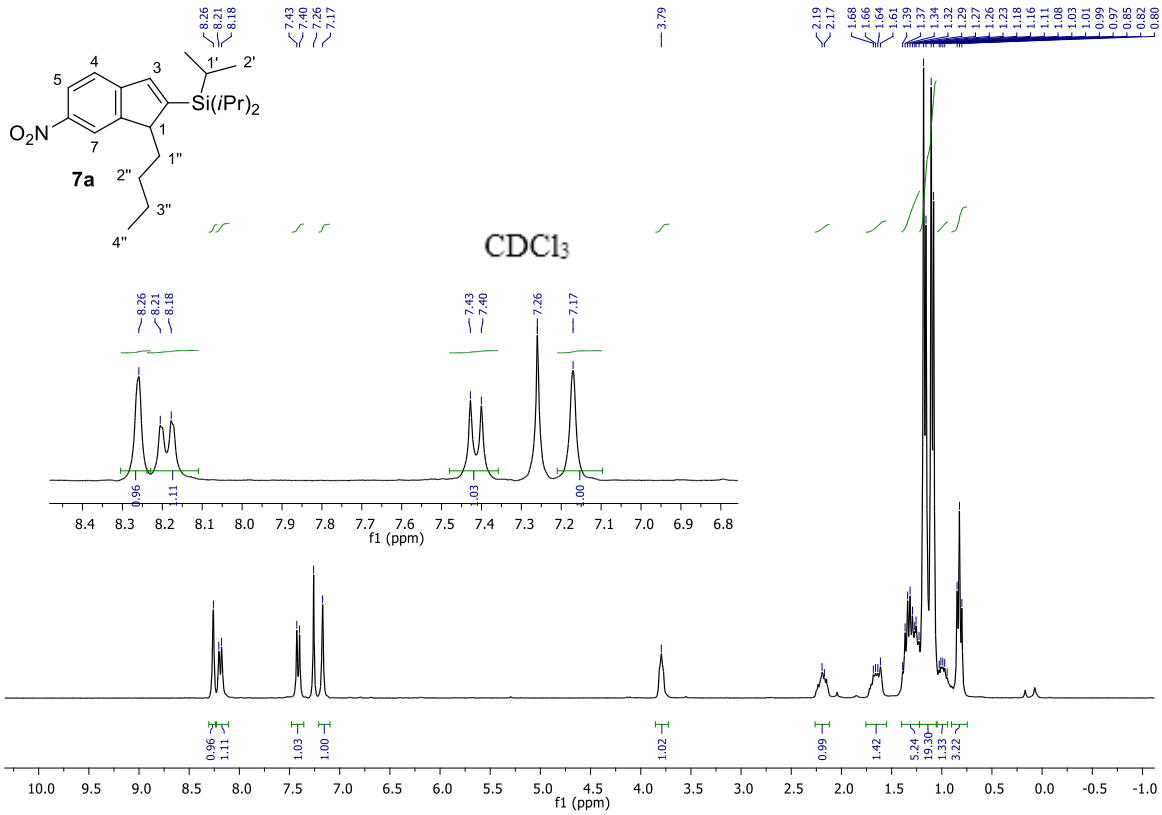


^{13}C NMR (75.5 MHz, $CDCl_3$)

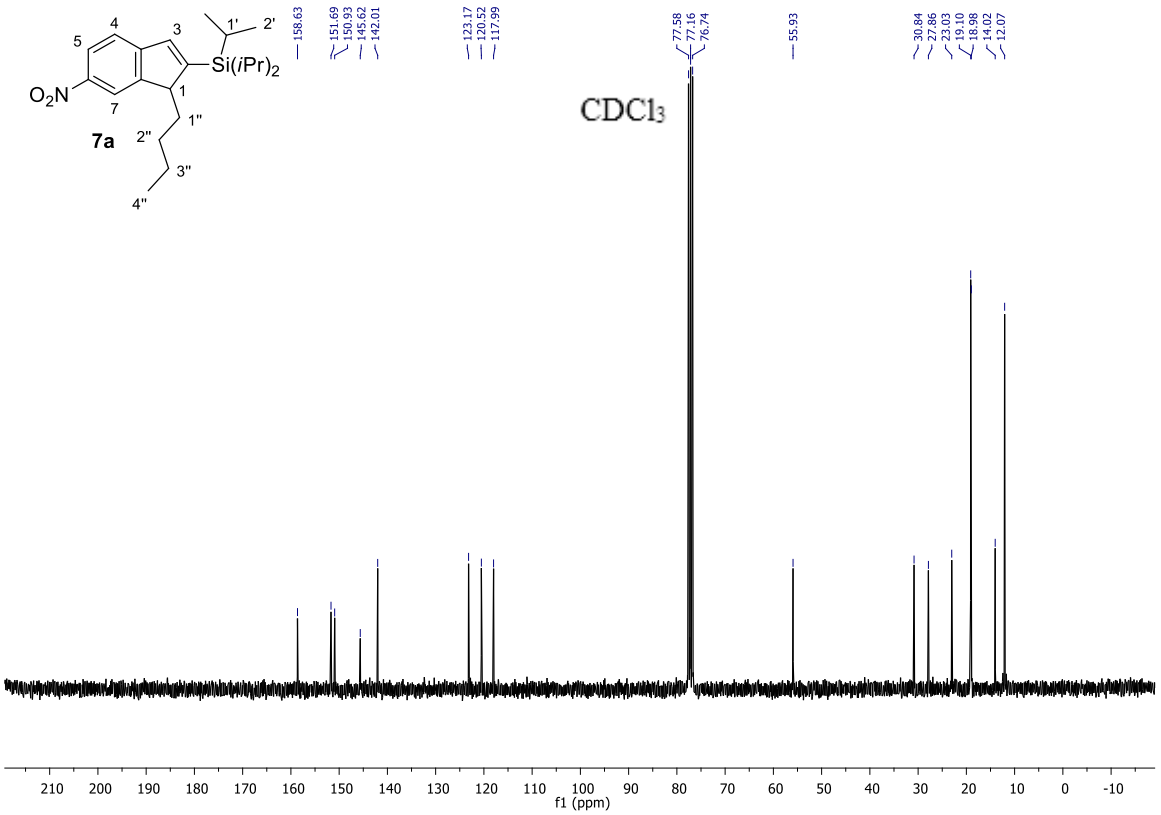


(1-Butyl-6-nitro-1H-inden-2-yl)triisopropylsilane **7a**

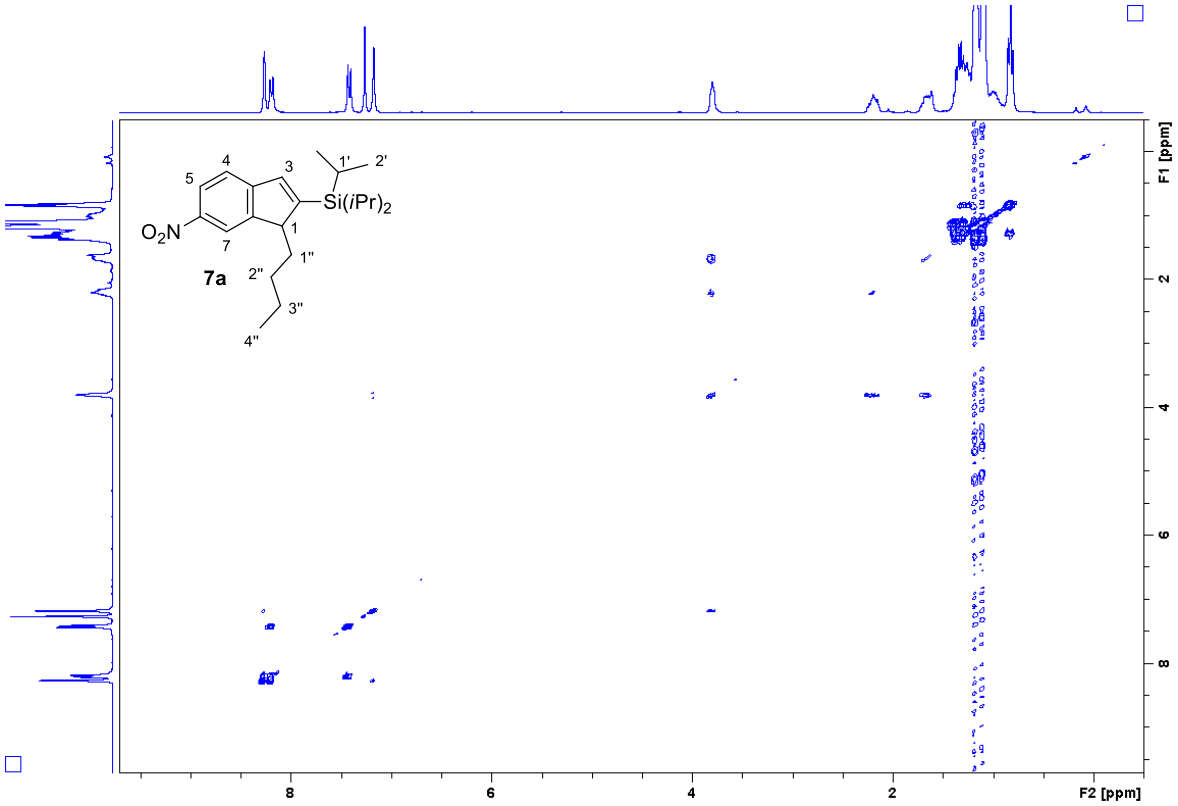
^{1}H NMR (300 MHz, $CDCl_3$)



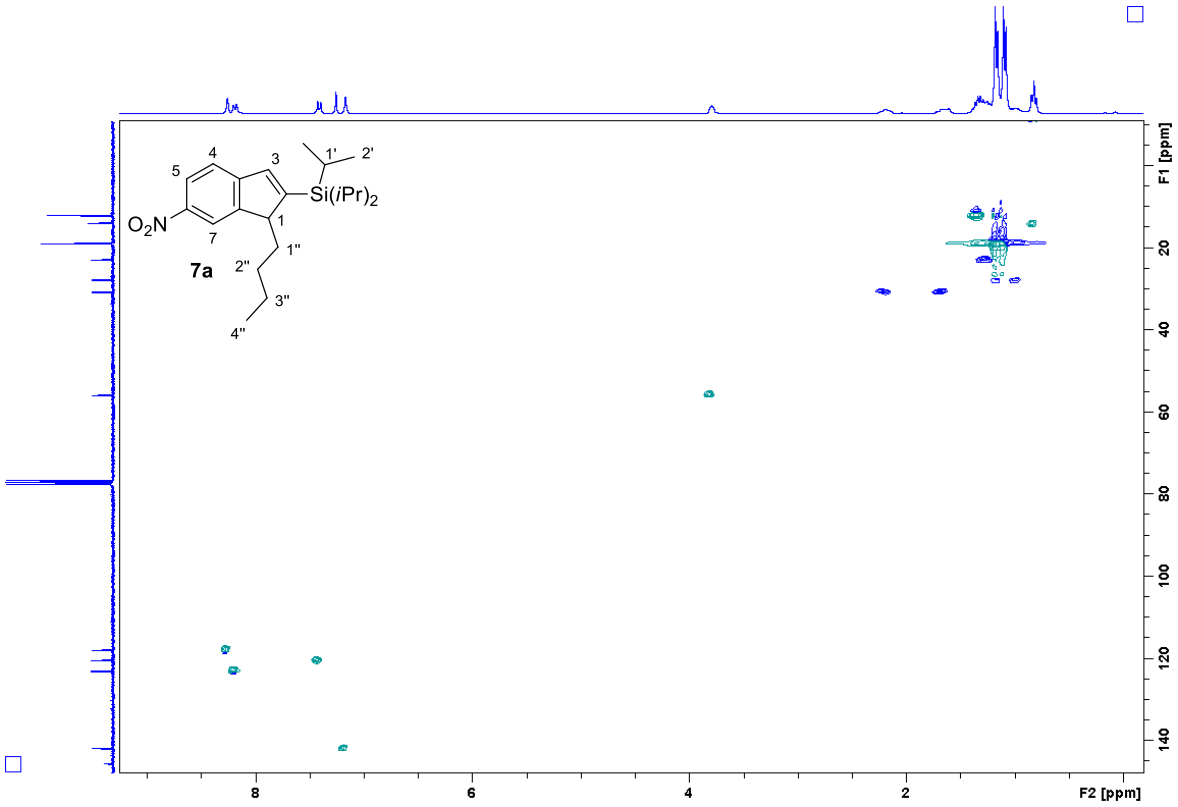
^{13}C NMR (75.5 MHz, $CDCl_3$)



2D ^{1}H-^{1}H COSY NMR ($CDCl_3$)

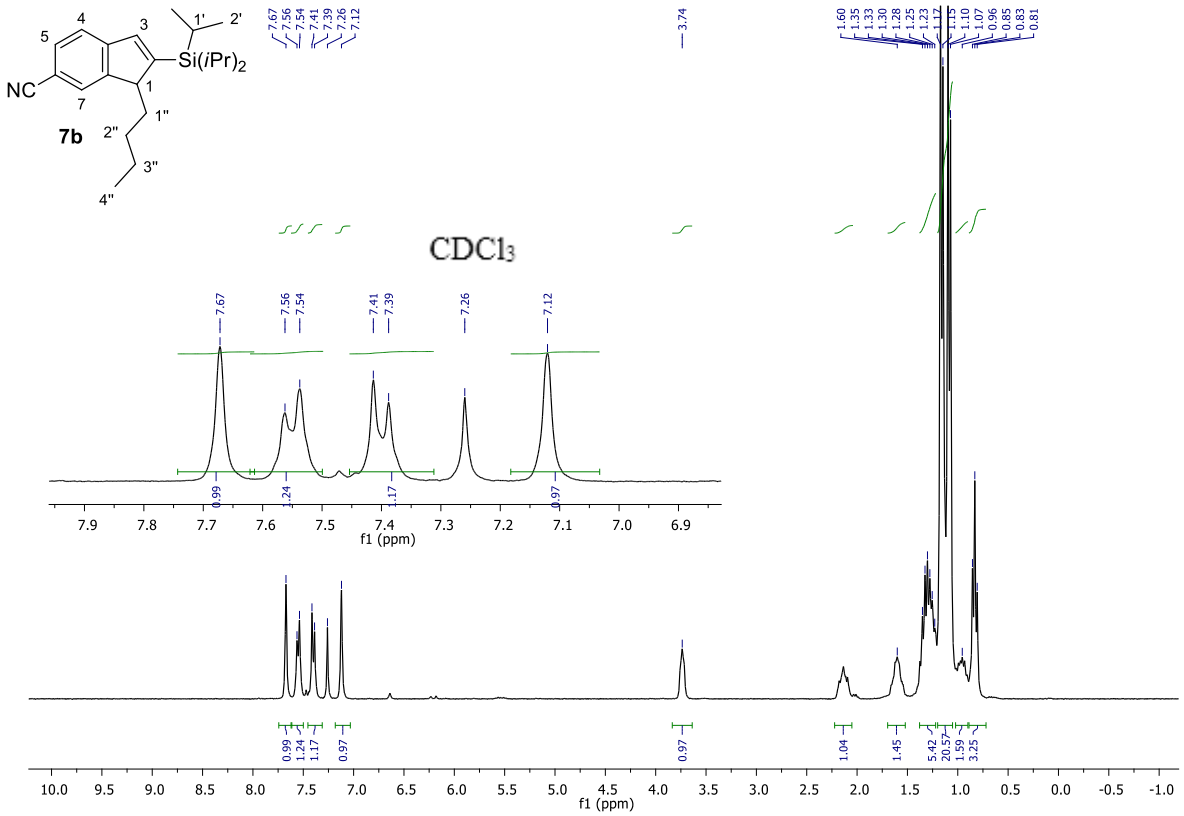


2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

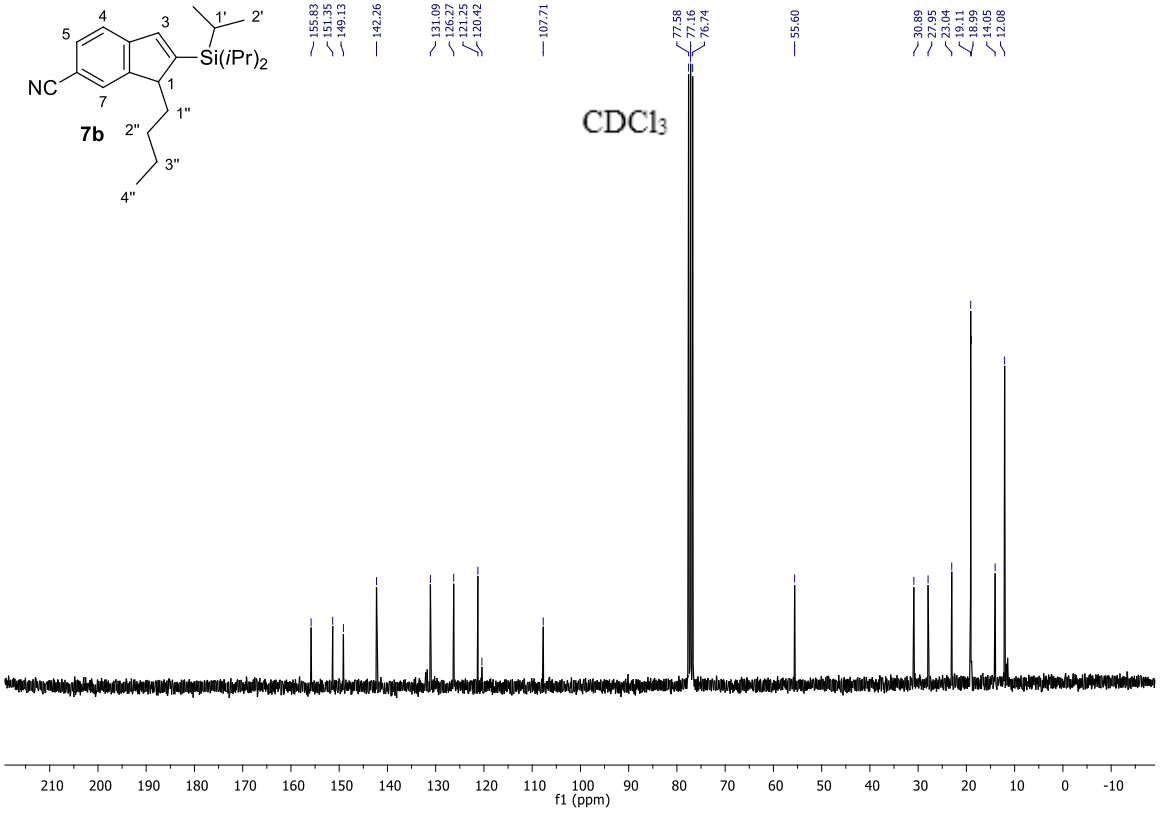


1-Butyl-2-(triisopropylsilyl)-1H-indene-6-carbonitrile **7b**

^{1}H NMR (300 MHz, $CDCl_3$)

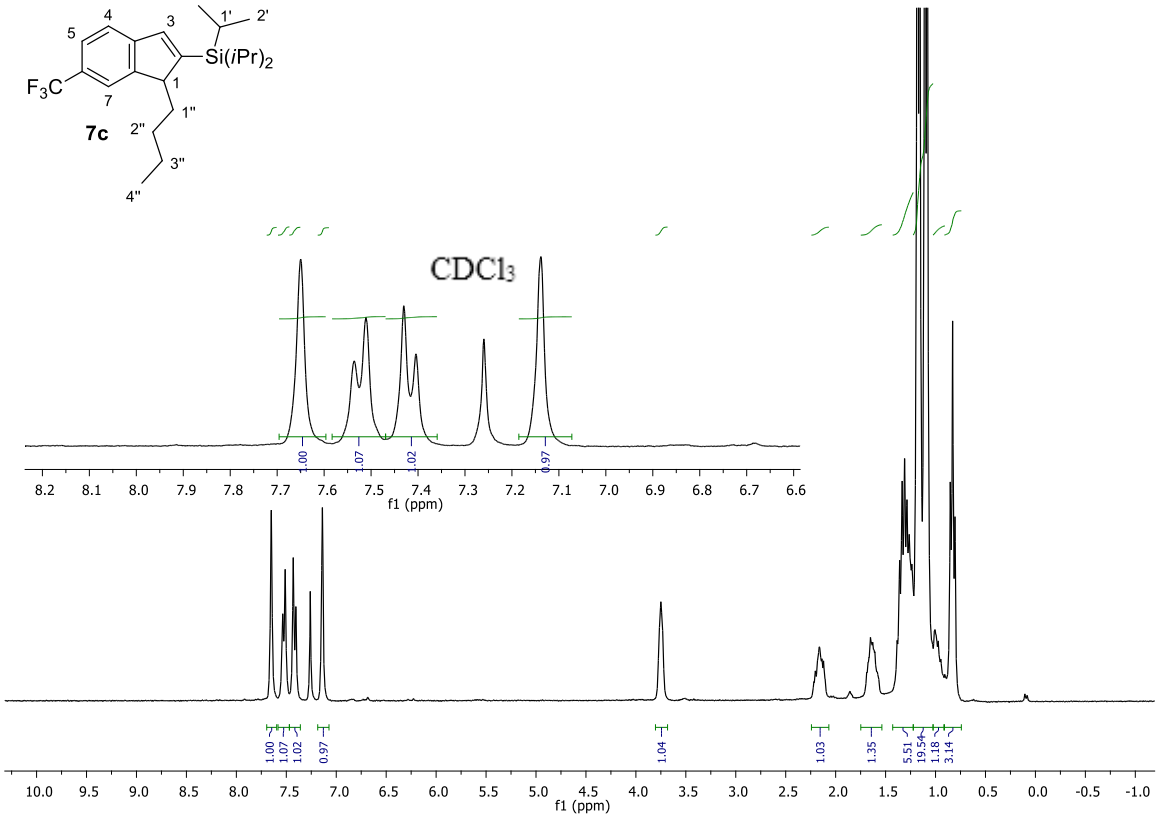


^{13}C NMR (75.5 MHz, $CDCl_3$)

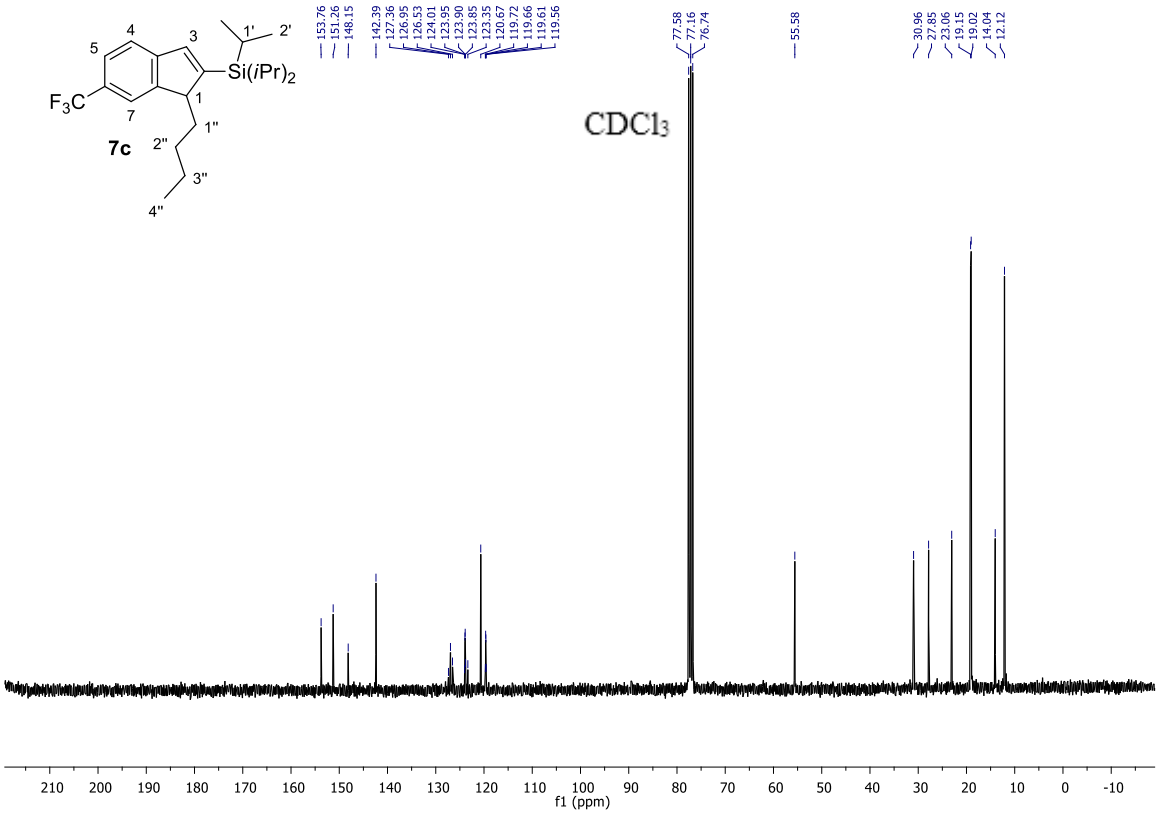


(1-Butyl-6-(trifluoromethyl)-1H-inden-2-yl)triisopropylsilane **7c**

^{1}H NMR (300 MHz, $CDCl_3$)

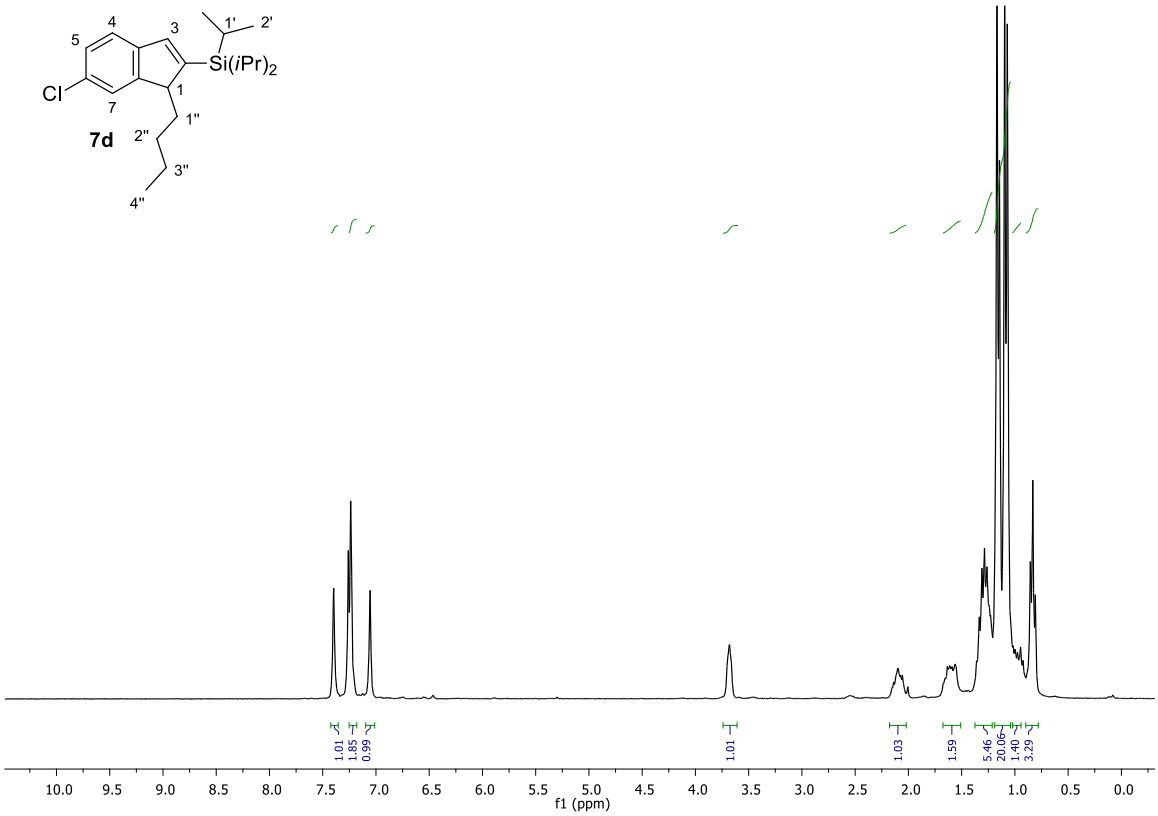


^{13}C NMR (75.5 MHz, $CDCl_3$)

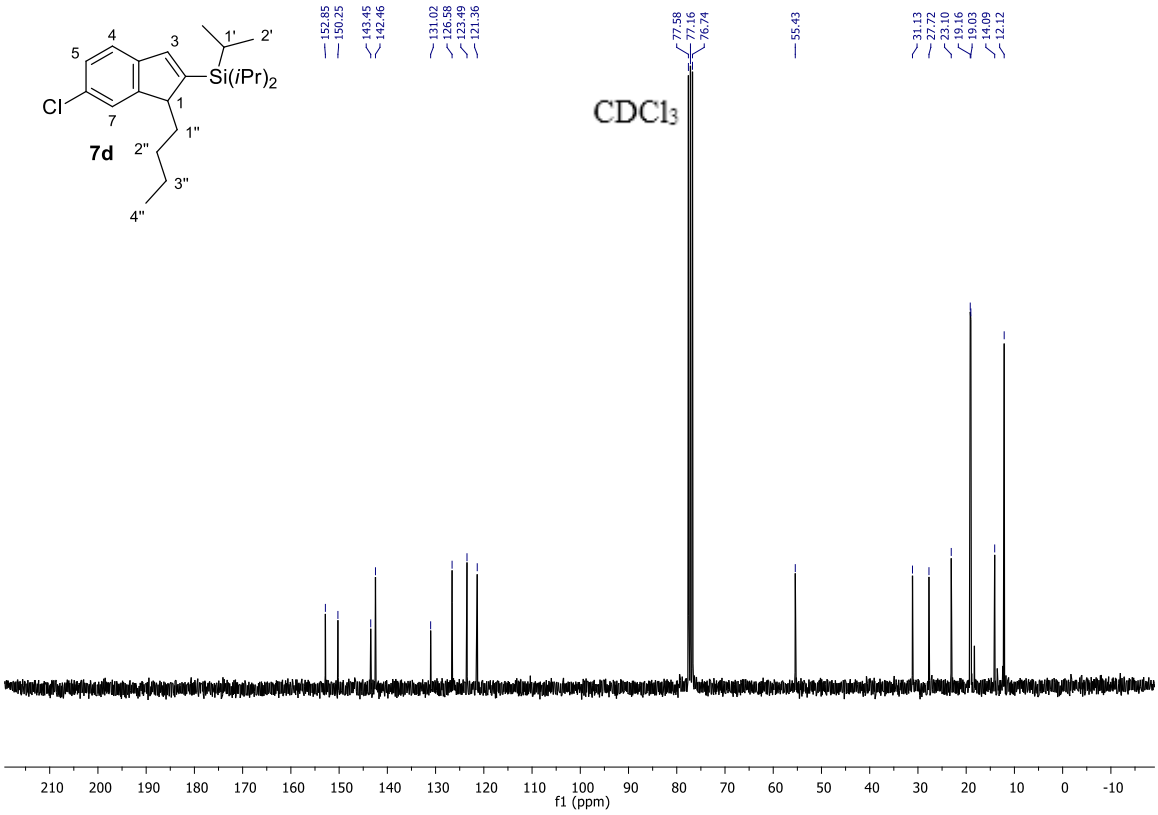


(1-Butyl-6-chloro-1H-inden-2-yl)triisopropylsilane **7d**

^{1}H NMR (300 MHz, $CDCl_3$)

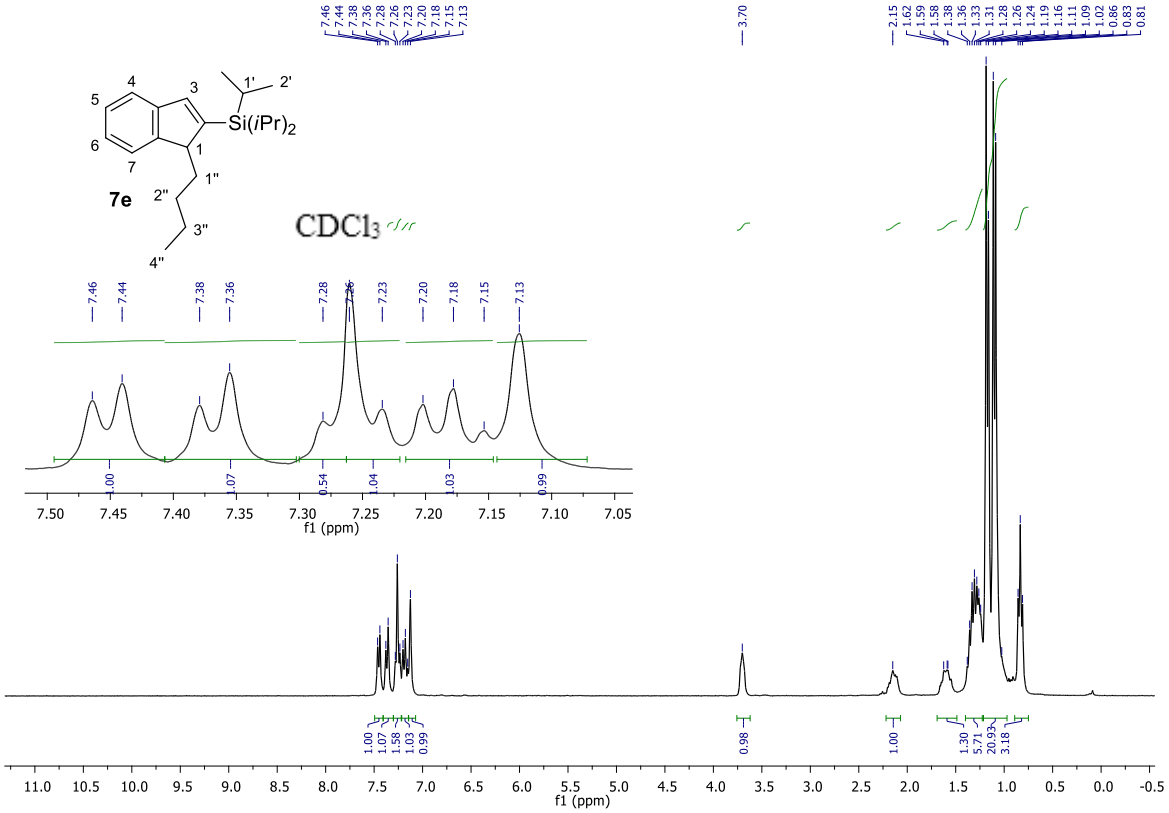


^{13}C NMR (75.5 MHz, $CDCl_3$)

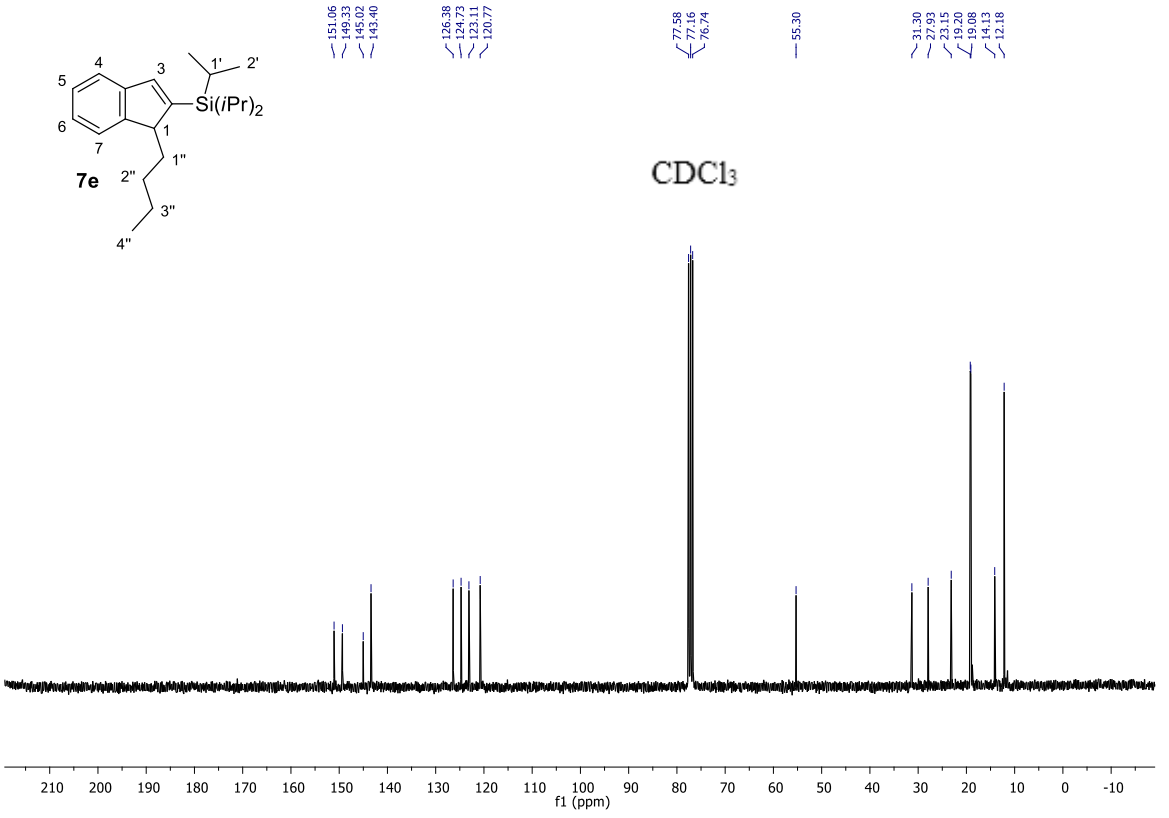


(1-Butyl-1H-inden-2-yl)triisopropylsilane **7e**

^{1}H NMR (300 MHz, $CDCl_3$)

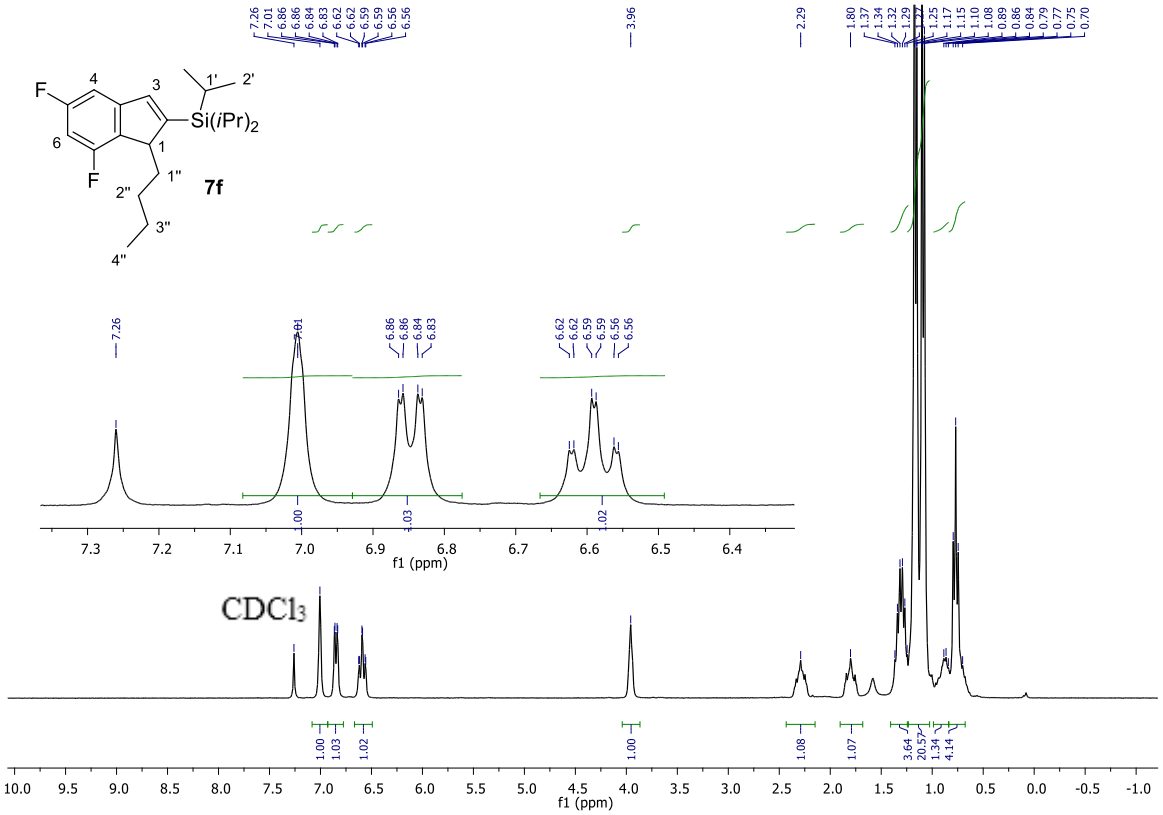


^{13}C NMR (75.5 MHz, $CDCl_3$)

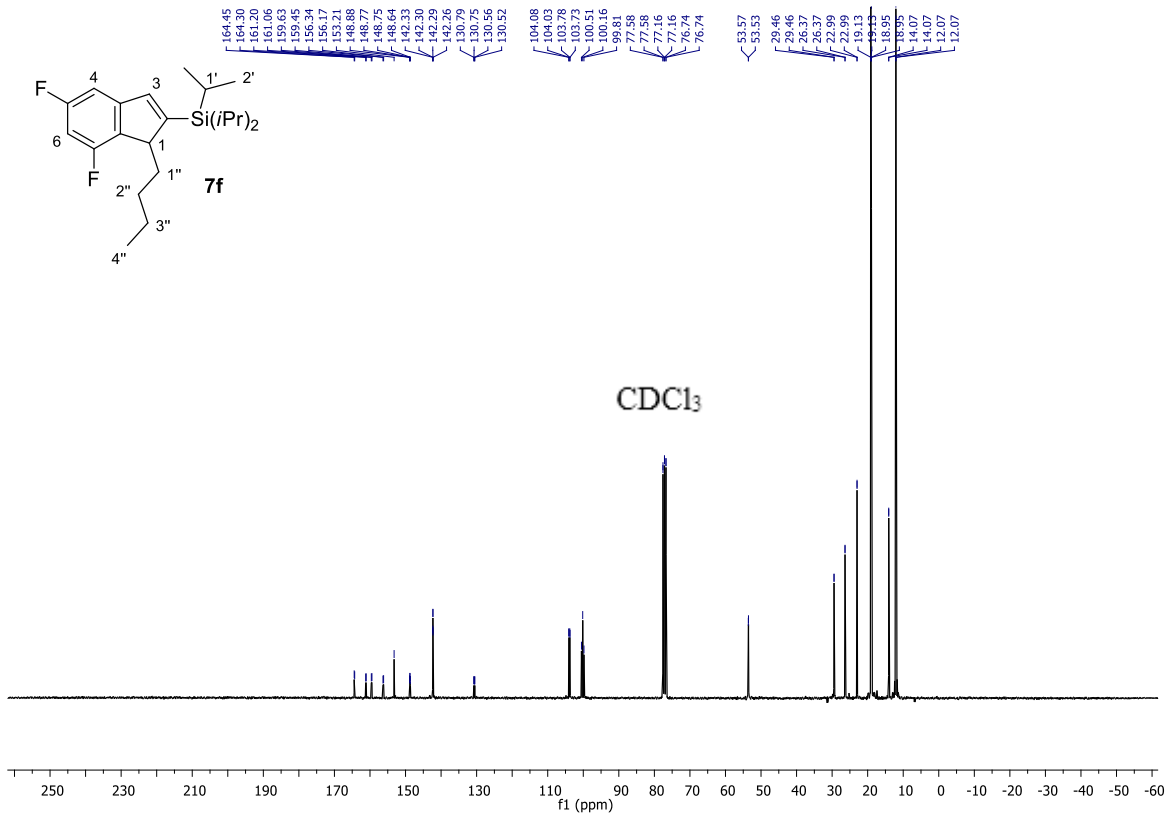


(1-Butyl-5,7-difluoro-1H-inden-2-yl)triisopropylsilane **7f**

^{1}H NMR (300 MHz, $CDCl_3$)

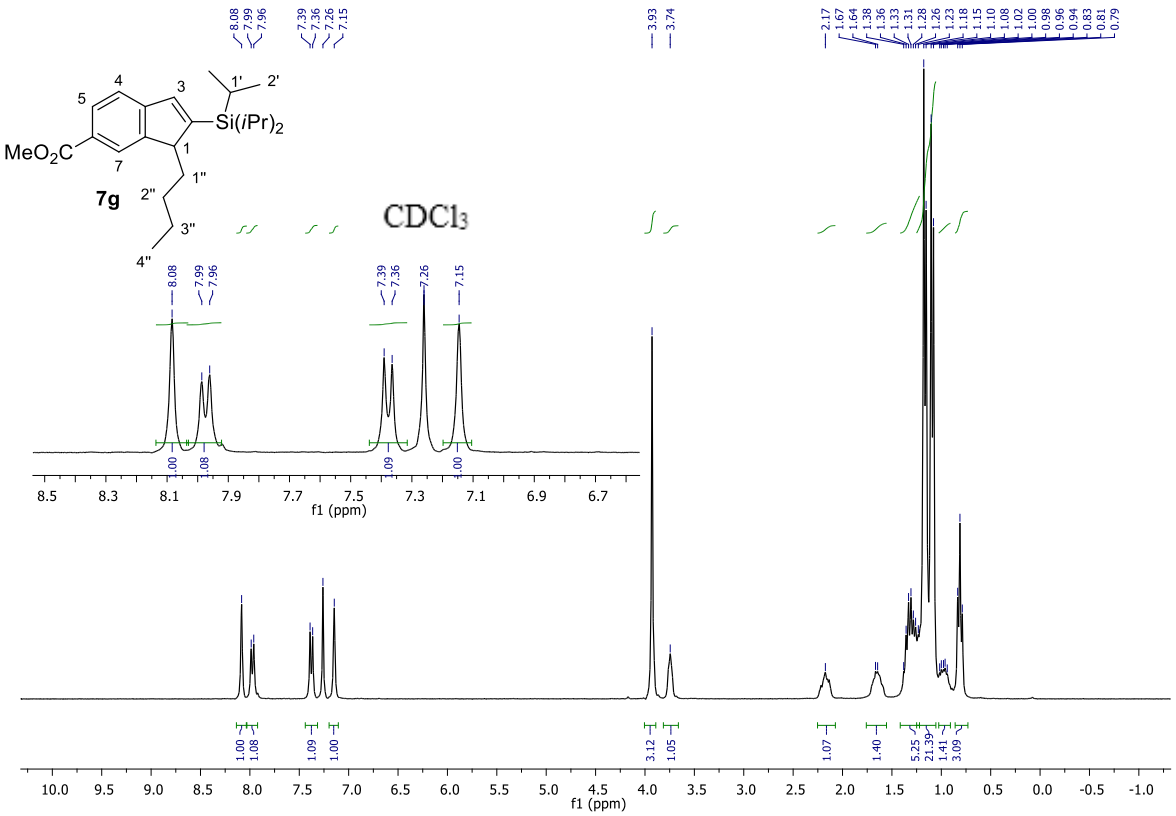


^{13}C NMR (75.5 MHz, $CDCl_3$)

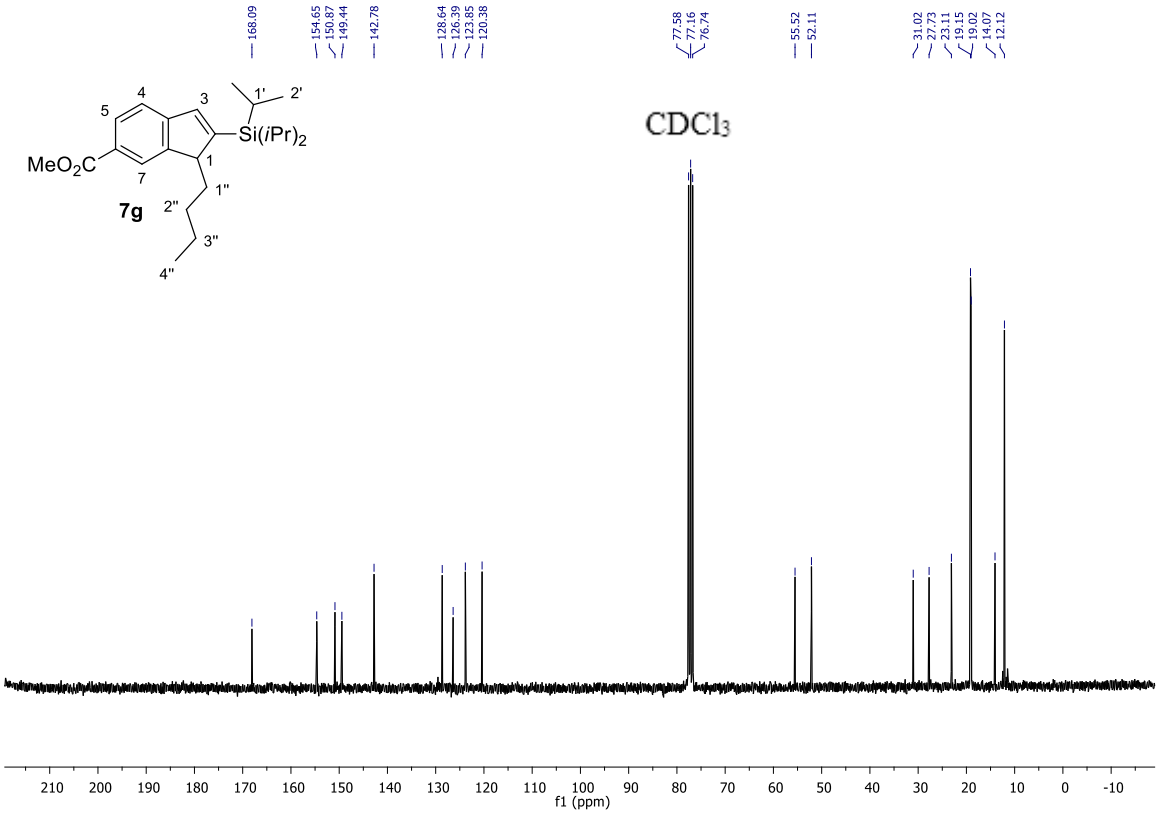


Methyl 1-butyl-2-(triisopropylsilyl)-1H-indene-6-carboxylate **7g**

^{1}H NMR (300 MHz, $CDCl_3$)



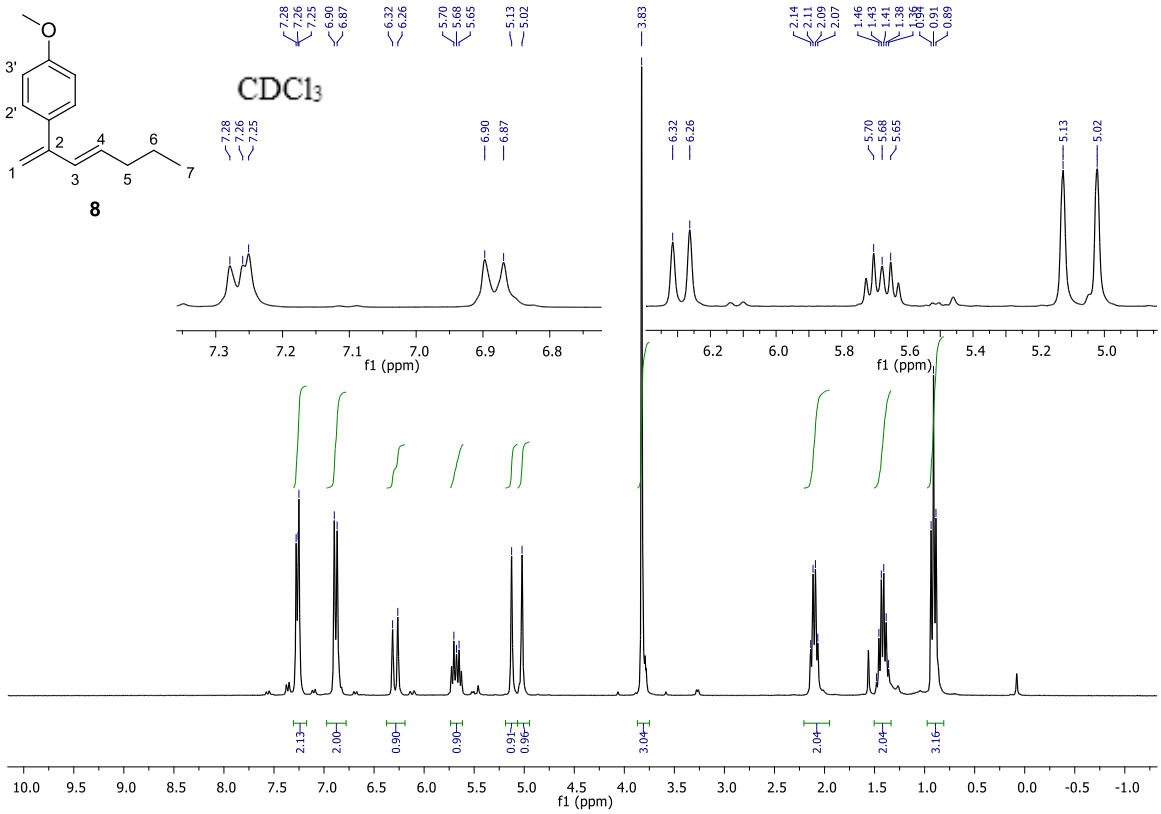
^{13}C NMR (75.5 MHz, $CDCl_3$)



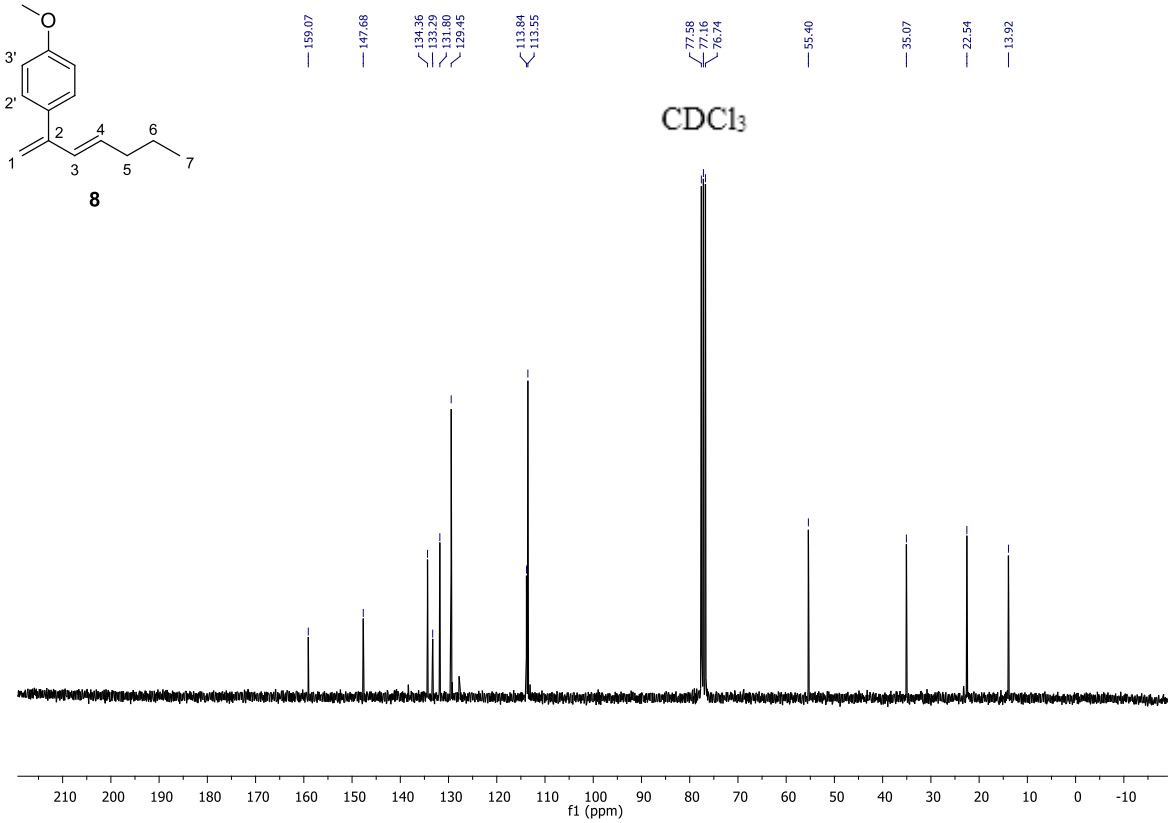
3. NMR spectra of Hiyama, Diels-Alder and bromodesilylation products

(*E*)-1-(hepta-1,3-dien-2-yl)-4-methoxybenzene **8**

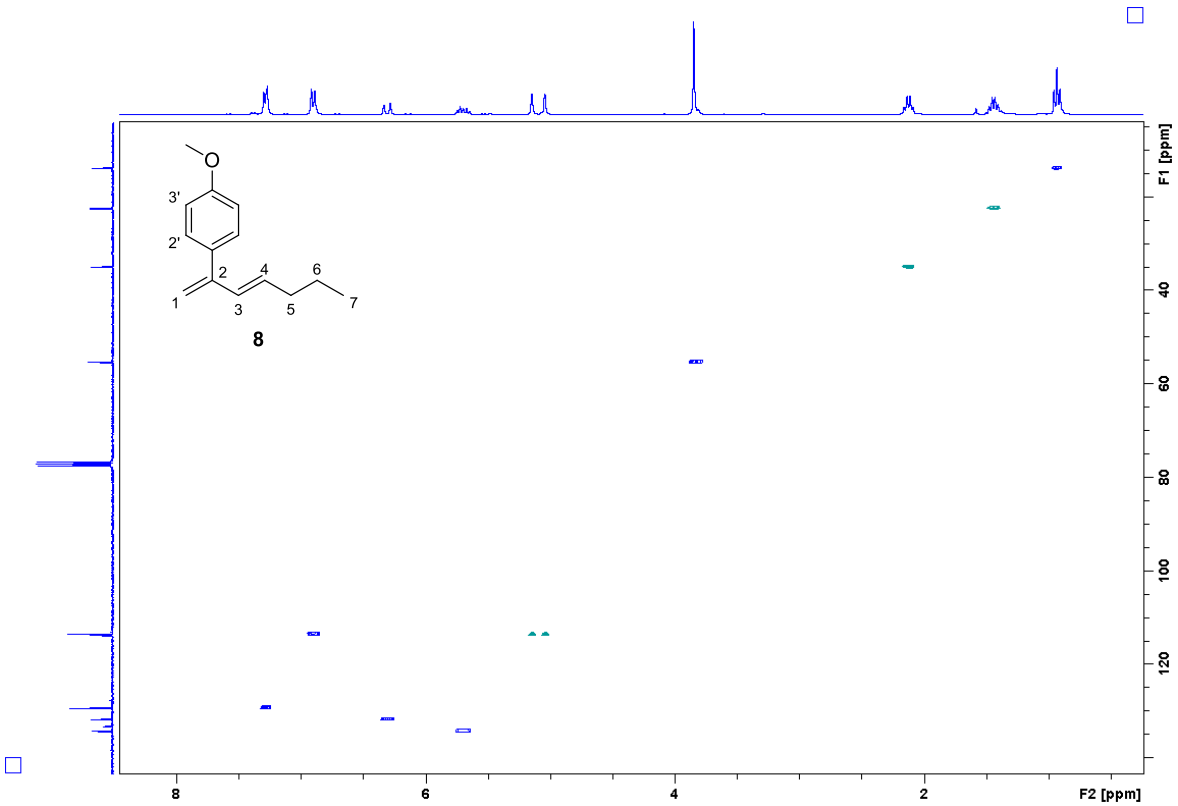
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

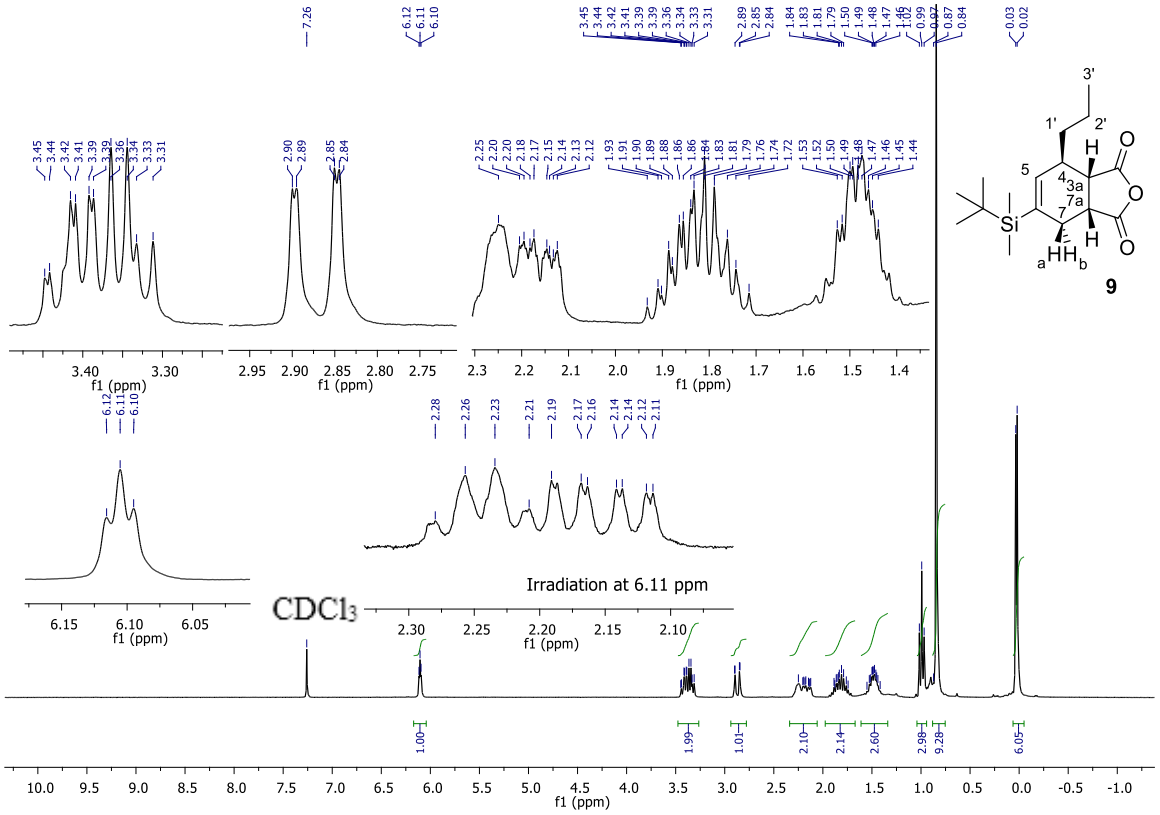


2D ^{1}H-^{13}C HSQC NMR

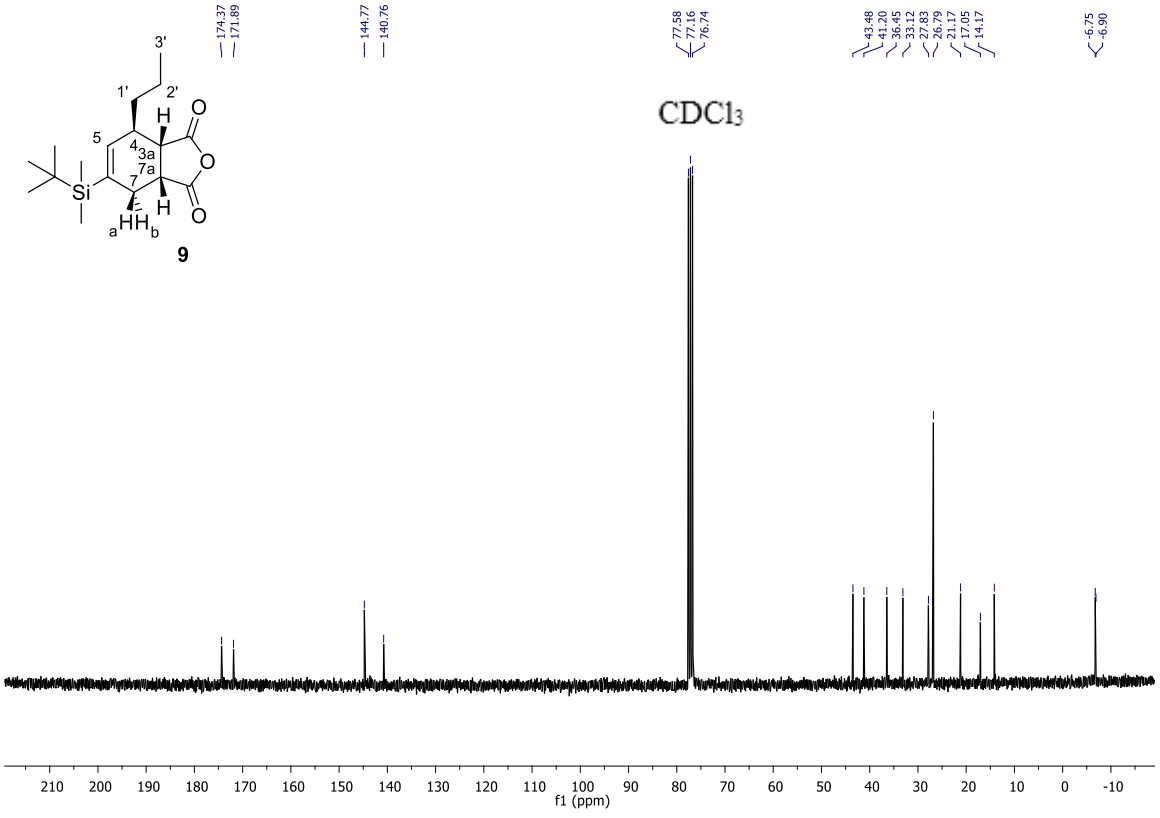


6-(*Tert*-butyldimethylsilyl)-4-propyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione **9**

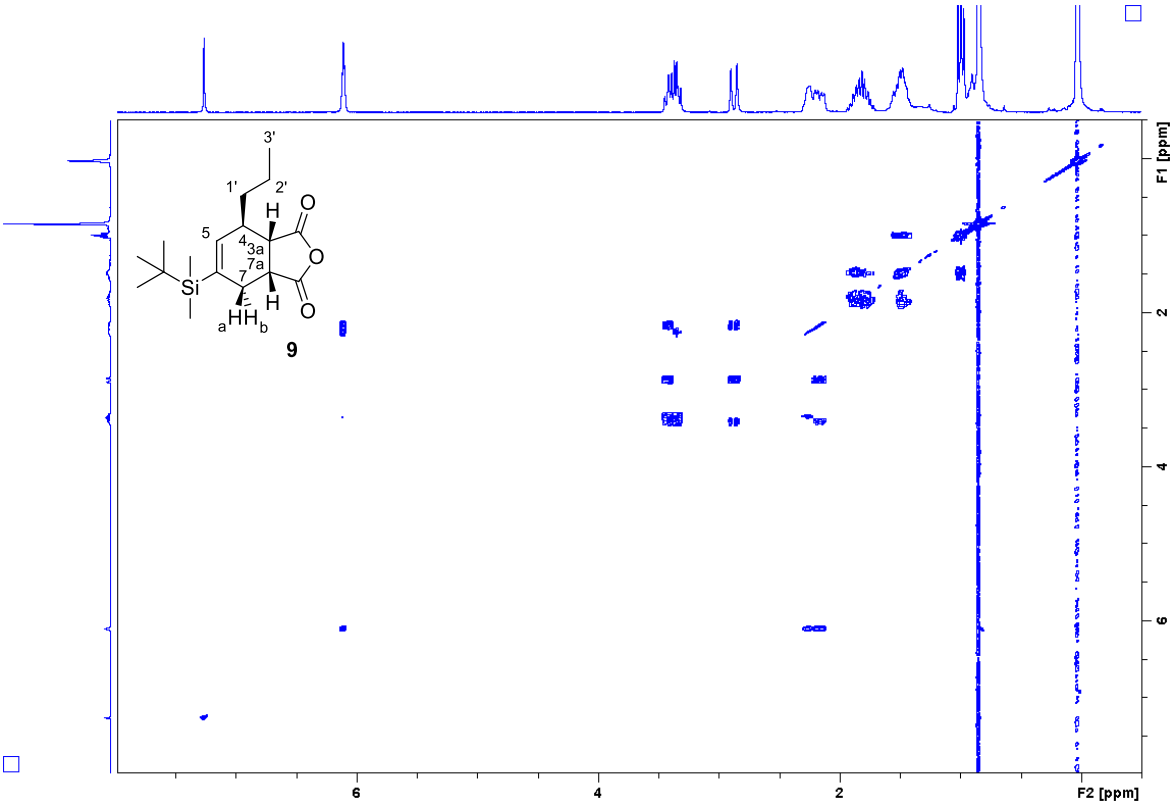
^{1}H NMR (300 MHz, $CDCl_3$)



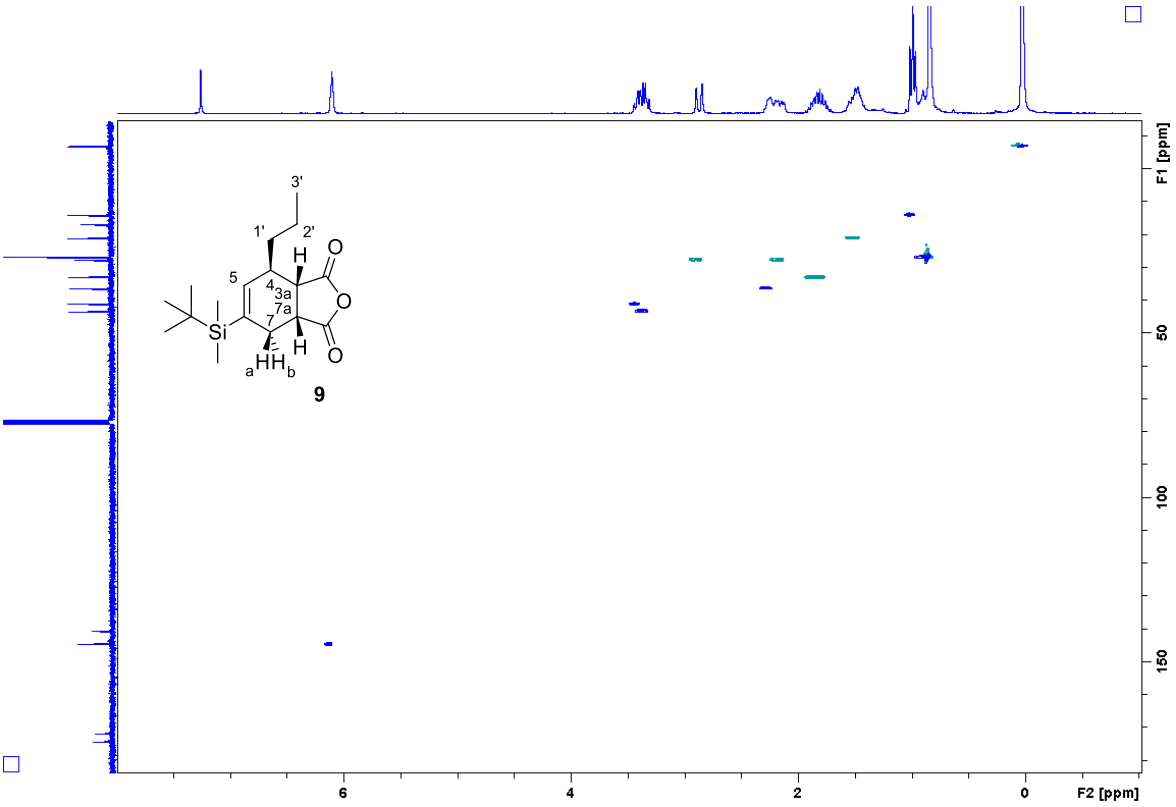
^{13}C NMR (75.5 MHz, $CDCl_3$)



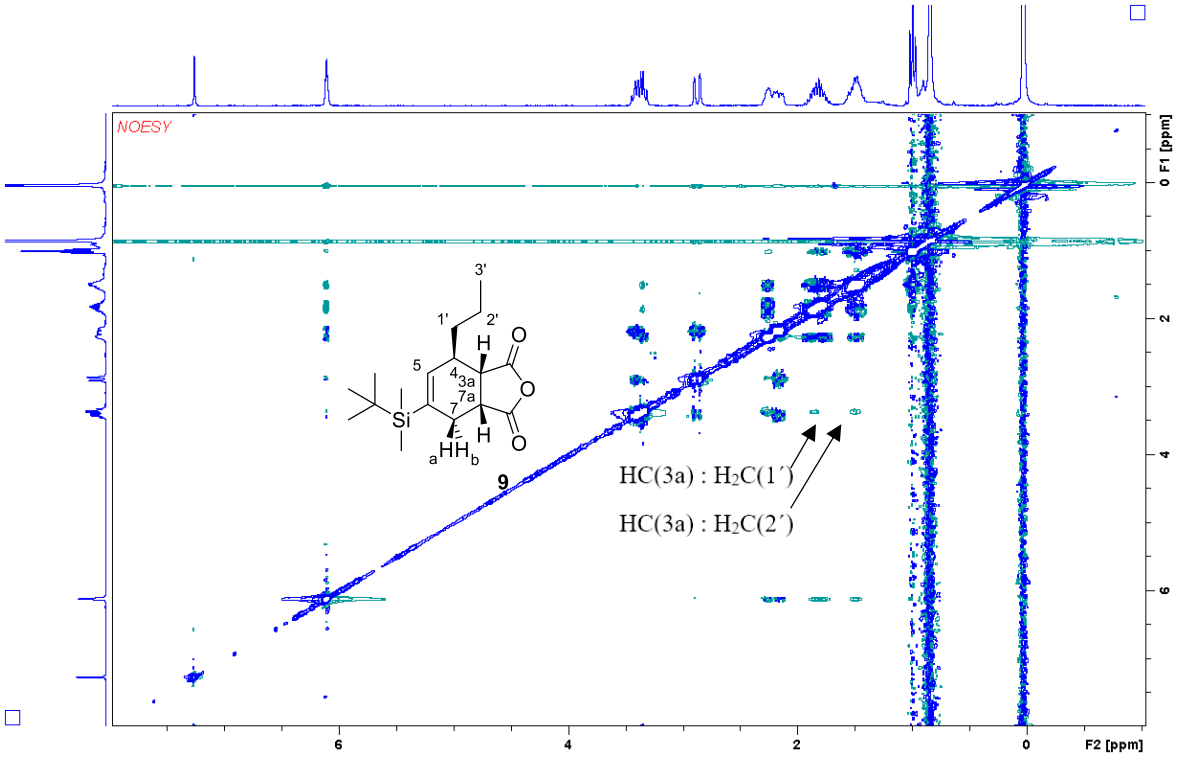
2D ^{1}H-^{1}H COSY NMR ($CDCl_3$)



2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)

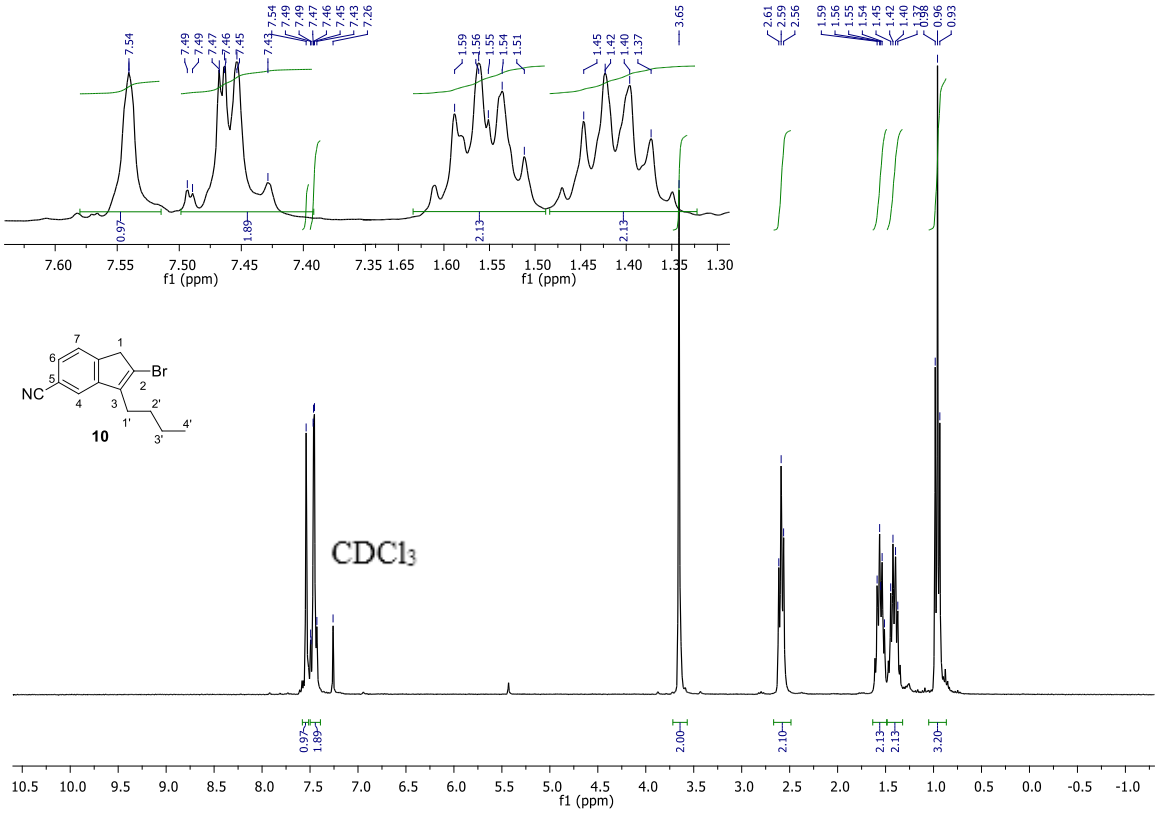


2D ^{1}H-^{1}H NOESY NMR ($CDCl_3$)

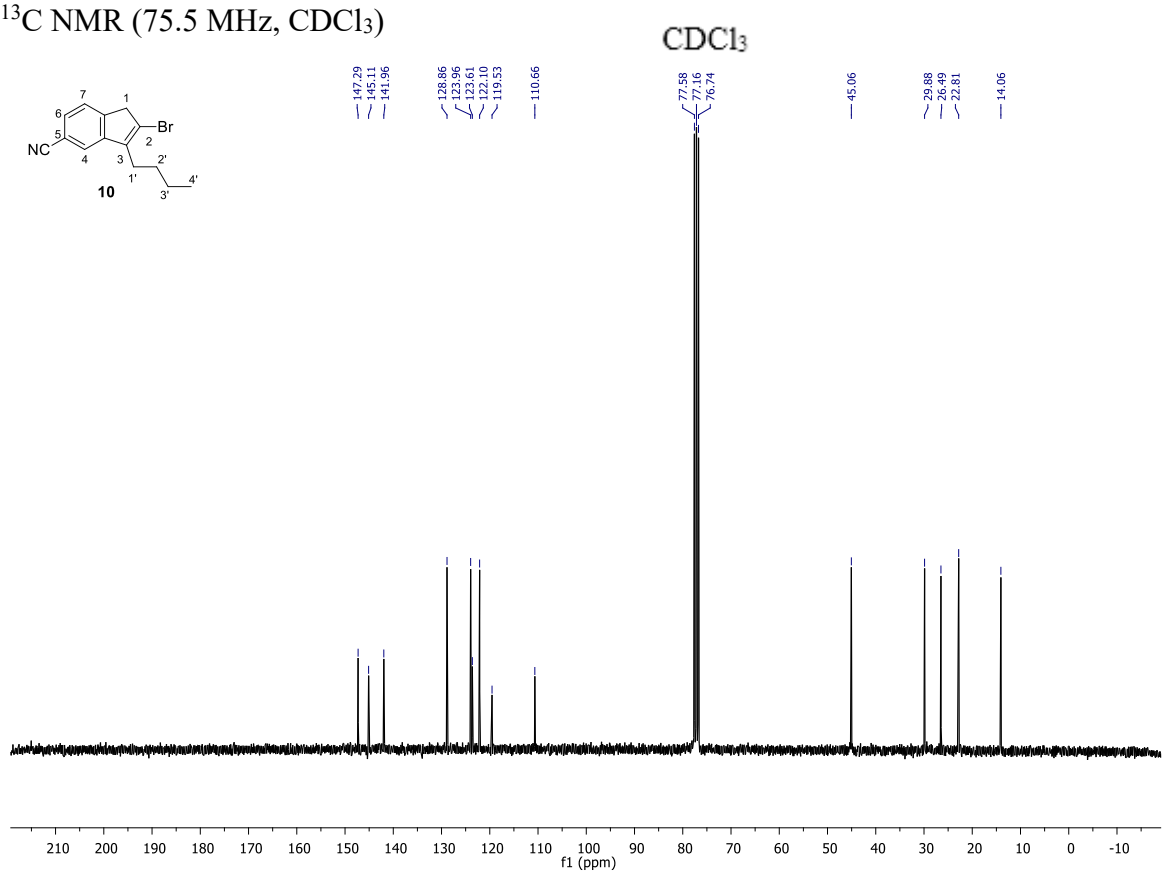


2-Bromo-3-butyl-1H-indene-5-carbonitrile **10**

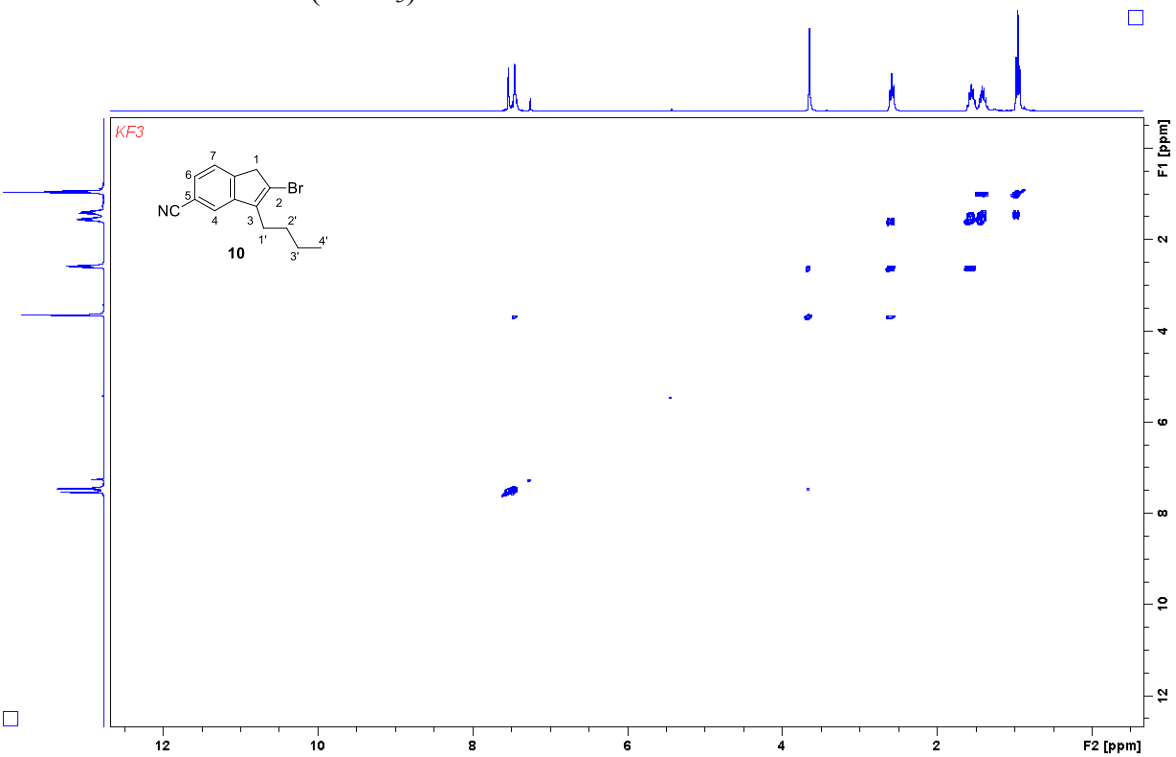
^{1}H NMR (300 MHz, $CDCl_3$)



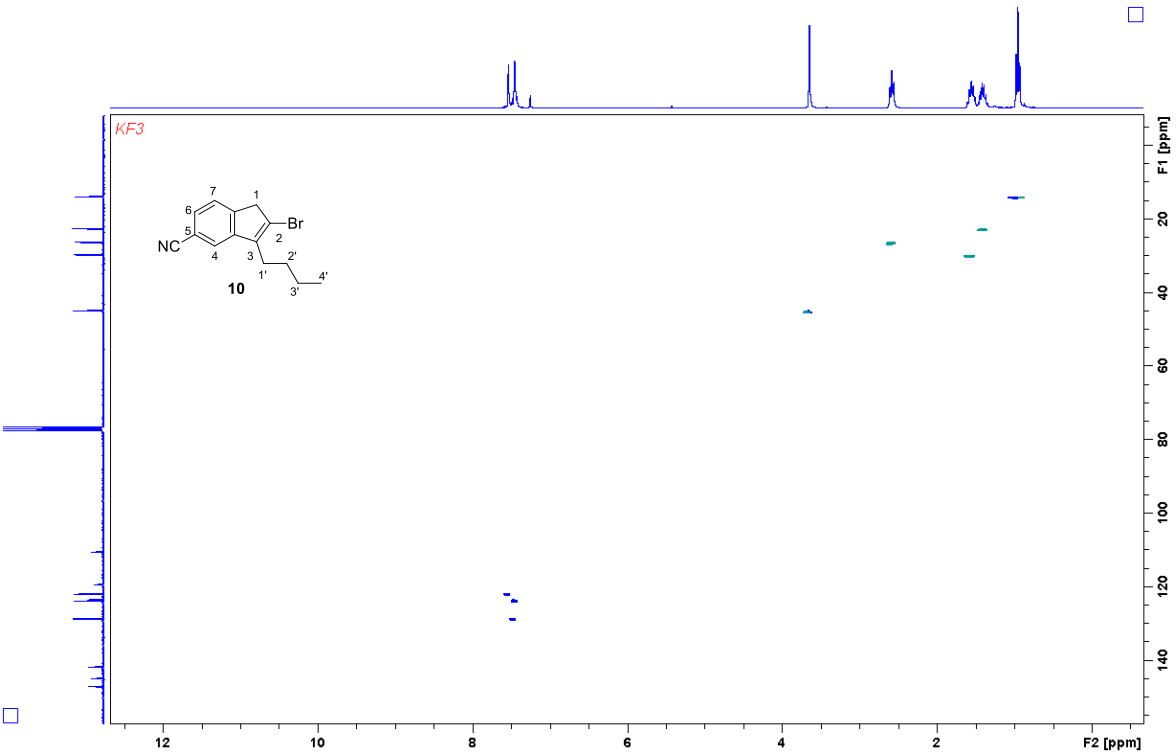
^{13}C NMR (75.5 MHz, $CDCl_3$)



2D ^{1}H-^{1}H COSY NMR ($CDCl_3$)



2D ^{1}H-^{13}C HSQC NMR ($CDCl_3$)



4. Crystallography data

4.1. ORTEP diagram

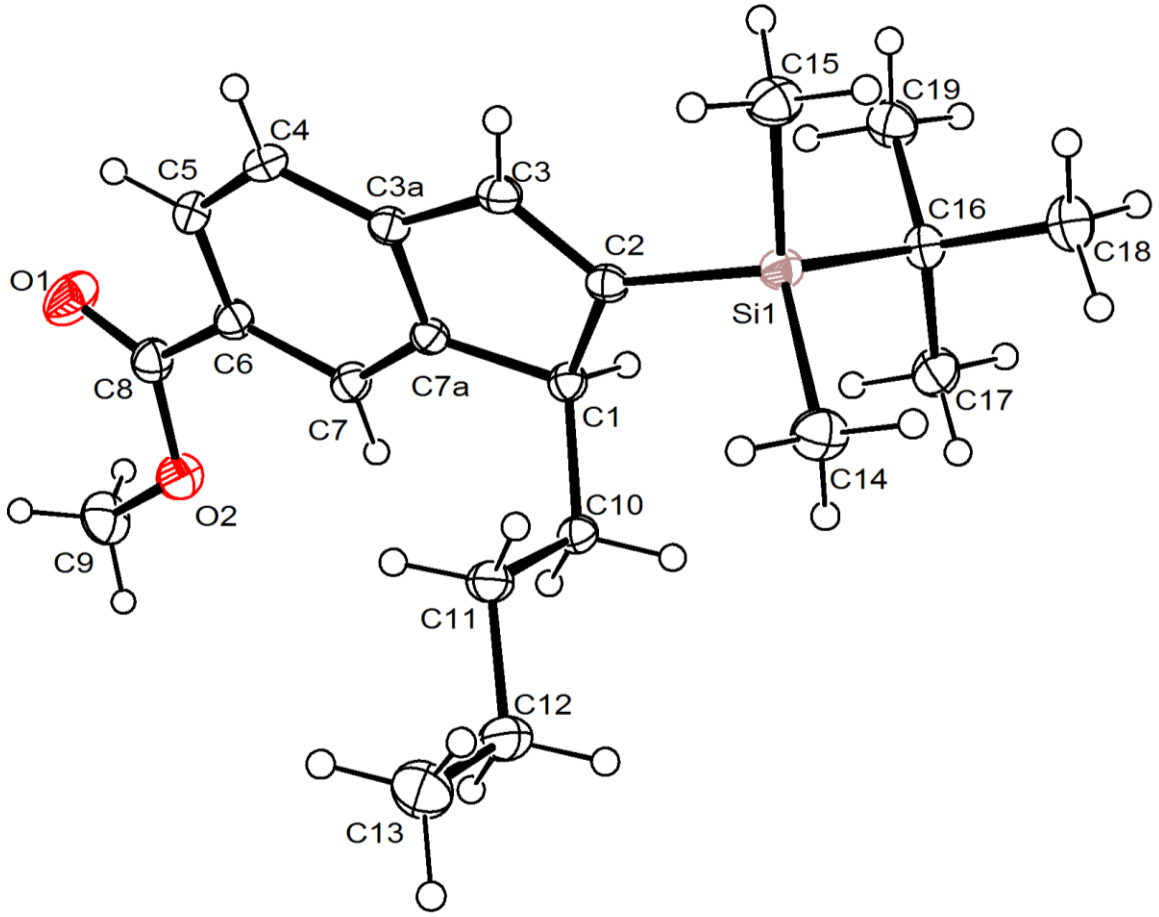


Figure S1. The molecular structure of the compound **6g**, showing 50% probability displacement ellipsoids.

4.2. Crystal parameter and refinement metrics

Solid silyl indene **6g** (approx. 15 mg) was heated in MeOH/MeCN 1:1 (1 ml) until complete disolution. Then the sample was allowed to cool to room temperature and left for 12 h. Then the sample was cooled to 0 °C for 6 h and formation of several monocrystals was observed.

Crystal data, data collection and structure refinement details are summarized in Table 1. Bruker-Nonius KappaCCD (λMoK$_\alpha$-radiation, graphite monochromator) diffractometer was used for experimental data acquisition. The crystal structure was solved by direct methods program SIR2004[1] and refined using SHELXL programs suite.[2] The C-bound H atoms were positioned geometrically and refined as riding on their parent atoms: C—H = 0.93–0.98Å with Uiso(H) = 1.5Ueq(C) for methyl H atoms and 1.2Ueq(C) for other H atoms.

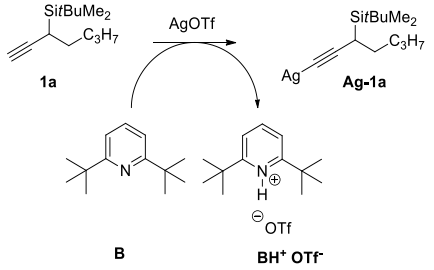
Table S1. Summary of crystal **6g** parameters.

Crystal data	
Chemical formula	$C_{21}H_{32}O_2Si$
M_r	344.55
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	190
a, b, c (Å)	10.7686 (3), 6.6244 (2), 15.1218 (5)
β (°)	110.361 (2)
V (Å^3)	1011.32 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.33 × 0.25 × 0.12
Data collection	
Diffractometer	KappaCCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6713, 4388, 3544
R_{int}	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.092, 1.04
No. of reflections	4388
No. of parameters	224
No. of restraints	1

H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.18, -0.21
Absolute structure	Flack x determined using 1216 quotients [(I+)-(I-)]/[(I+)+(I-)][3]
Absolute structure parameter	-0.04 (10)

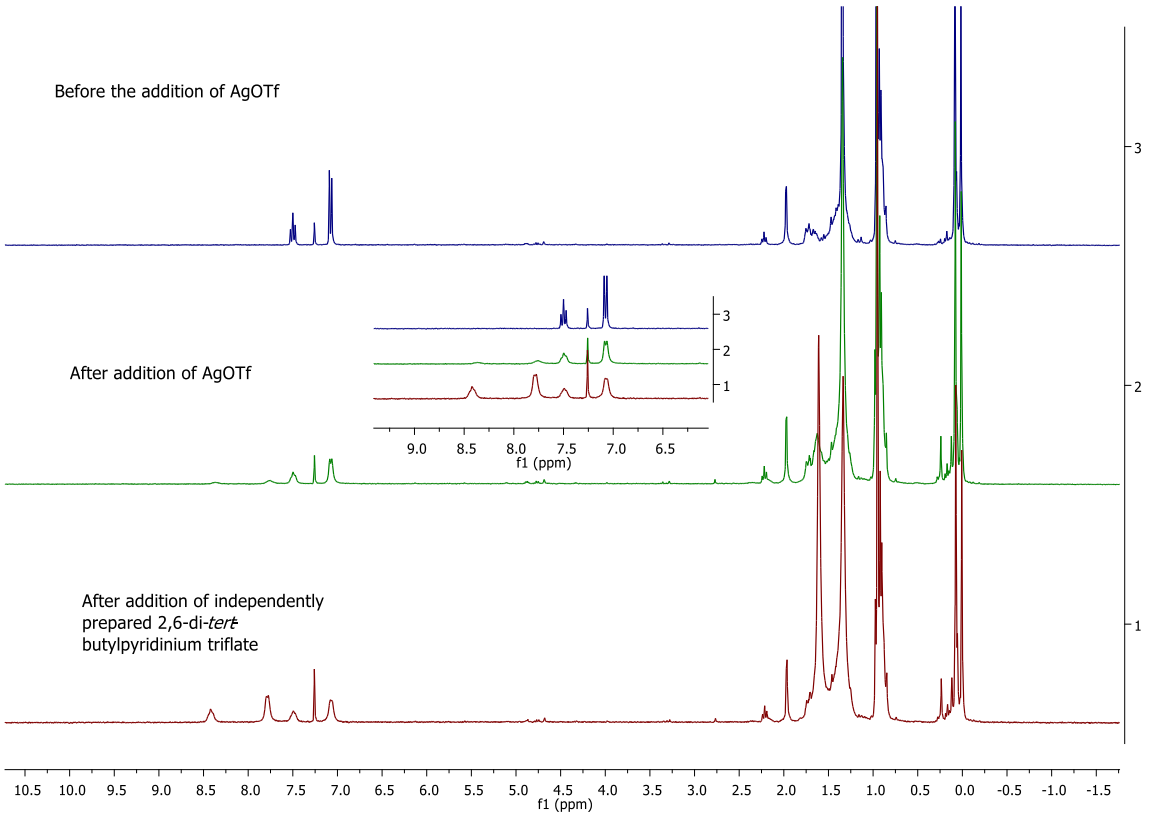
5. Observed side reactions

5.1. Generation of pyridinium triflate

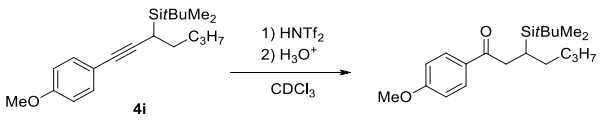


Scheme S1. Generation of Brønsted acid from AgOTf and propargyl silane **1a**.

^{1}H-NMR ($CDCl_3$, 300 MHz)

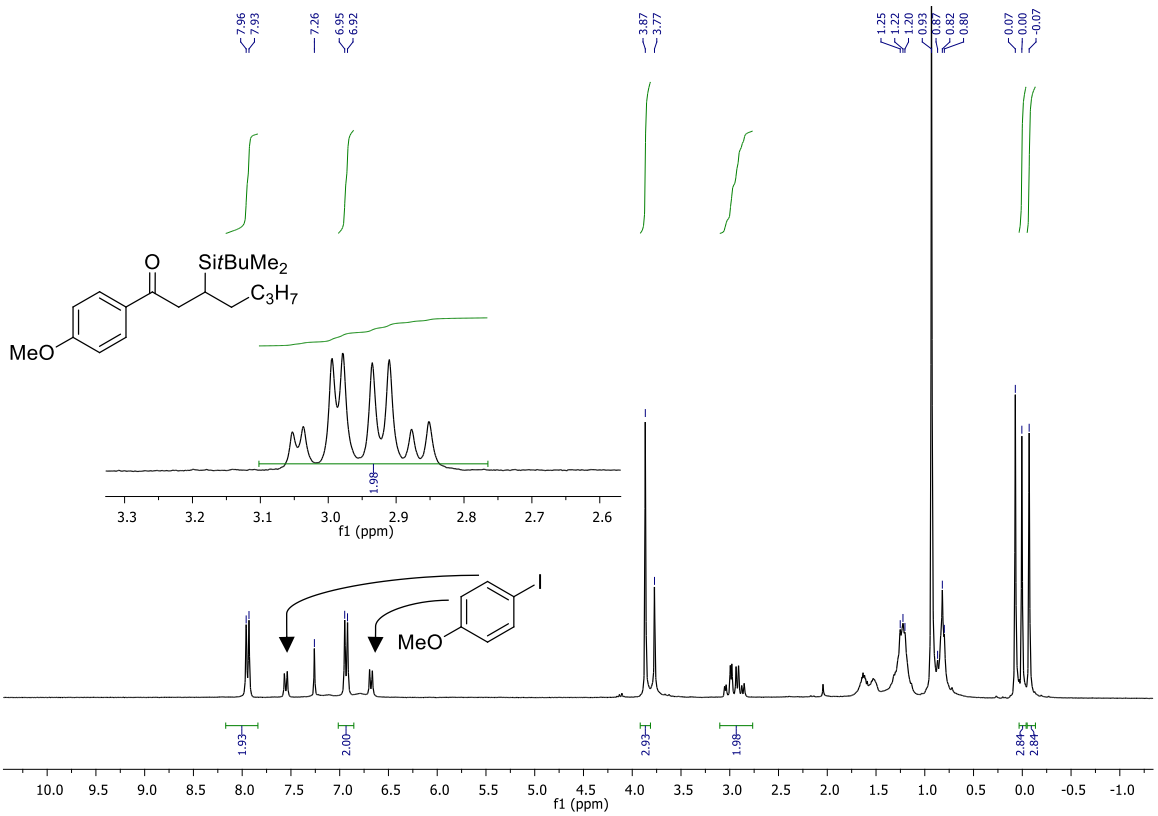


5.2. Hydration of propargyl silane

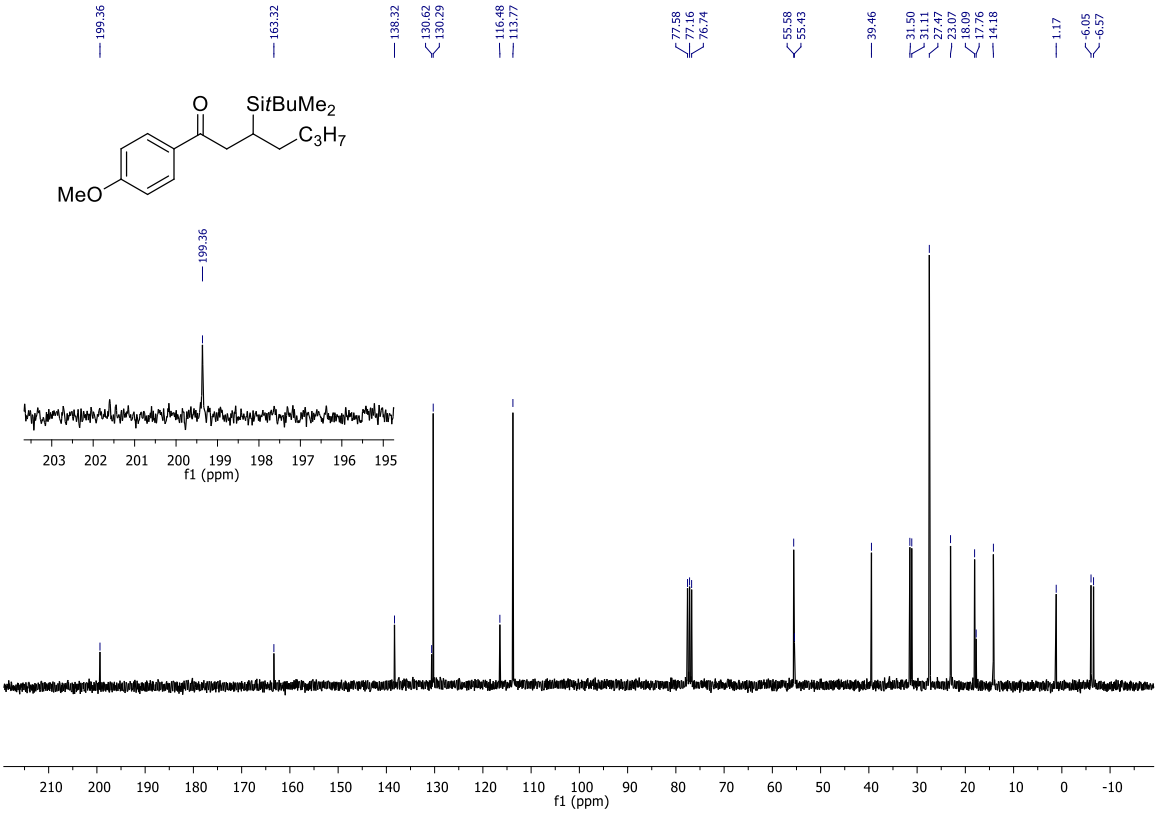


Scheme S2. Hydration of propargyl silane **4i**

^{1}H-NMR spectrum of crude product after filtration through silica (contains *para*-iodoanisole as internal standard) ($CDCl_3$, 300 MHz)



^{13}C-NMR spectrum of crude product after filtration through silica (contains *para*-iodoanisole as internal standard) ($CDCl_3$, 75.5 MHz)



References

(1) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. SIR2004 : An Improved Tool for Crystal Structure Determination and Refinement. *J. Appl. Crystallogr.* **2005**, *38* (2), 381–388.

(2) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71* (Md), 3–8.

(3) Parsons, S.; Flack, H. D.; Wagner, T. Use of Intensity Quotients and Differences in Absolute Structure Refinement. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2013**, *69* (3), 249–259.