SUPPORTING INFORMATION

for

Simply accessible platinum(II) complexes enabling alkene hydrosilylation at ppm catalyst loadings

Benon P. Maliszewski,[a] Eleonora Casillo,[a] Perrine Lambert,[a] Fady Nahra,*[a,b] Catherine S. J. Cazin*[a] and Steven P. Nolan*[a]

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[a] *Department of Chemistry and Centre for Sustainable Chemistry, Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium. E-mail: steven.nolan@ugent.be*

[b] *VITO (Flemish Institute for Technological Research), Separation and Conversion Technology, Boeretang 200, 2400 Mol, Belgium. E-mail: fady.nahra@vito.be*

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1. Synthetic procedures and characterisation data

1.1. General information

All chemical syntheses were performed in glass vials under air. Solvents and all other reagents were purchased and used as received without any additional purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Bruker 300 and 400 MHz spectrometers. All chemical shifts are quoted in parts per million referenced to the $CHCl_3$ solvent residue (δ_H = 7.26 ppm, δ_C = 77.16 ppm). ^{1}H NMR splitting patterns are abbreviated as follows: broad signal (br), singlet (s), doublet (d), triplet (t), doublet of doublets (dd), doublet of triplets (dt), triplet of triplets (tt), quartet (q), quintet (quint), heptet (hept), multiplet (m). The general hydrosilylation procedure (**A**) was used for catalyst screening (Table 1) and the general hydrosilylation procedure (**B**) was used to synthesise the products presented in Scheme 2. In catalysis, complex **1a** obtained *via* **method B** was used.

1.2. *Cis/trans*-[Pt(DMS)$_2$Cl$_2$] (1a) CAS 55449-91-7

Method A: A 4.0 mL vial was charged with $PtCl_2$ (50.0 mg, 0.188 mmol, 1.0 equiv.) and CH_2Cl_2 (1.0 mL). DMS (55.6 µL, 0.752 mmol, 4.0 equiv.) was added, the vial was closed with a septum screw cap and the resulted mixture was stirred at 20 °C for 60 min. After this time, a complete consumption of the dark $PtCl_2$ was observed, leading to the formation of a clear yellow gold solution. The volatiles were removed under vacuum, affording the desired complex **1a** as a yellow crystalline solid (73.4 mg, >99%).

Method B:[1] A 1000 mL round-bottom flask was charged with a solution of K_2PtCl_4 (15.500 g, 37.34 mmol, 1.00 equiv.) in demineralised water (600 mL) and placed in an ice bath. DMS (15.50 mL, 209.56 mmol, 5.61 equiv.) was added, while stirring vigorously, resulting in a rapid formation of a pale pink precipitate (Magnus-type complex of the formula $[Pt(DMS)_4][PtCl_4]$). The flask was then equipped with a reflux condenser, the resulted mixture was heated up to 80 °C and stirred at this temperature for 10 min, until the solution became clear yellow. After this time, the mixture was cooled down to the room temperature and extracted with CH_2Cl_2 (4x200 mL) until colourless. The combined organic fractions were dried over anhydrous $MgSO_4$ and evaporated to dryness, affording the desired complex **1a** as a yellow crystalline solid (14.570 g, >99%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 2.56 (t, $^3J_{Pt\text{-}H}$ = 49.3 Hz, 1.00H, *cis*-**1a**, minor), 2.45 (t, $^3J_{Pt\text{-}H}$ = 41.4 Hz, 4.41H, *trans*-**1a**, major). *Cis/trans* ratio = 18:82 (approximated; the peaks are not entirely separated due to the large coupling constant $^3J_{Pt\text{-}H}$; the ratio changes from batch to batch, however, *trans*-**1a** remains the major isomer). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 23.12 (*cis*-**1a**, minor), 22.44 (*trans*-**1a**, major).

1.3. C*is/trans*-[Pt(THT)$_2$Cl$_2$] (1b) CAS 24940-43-0

A 20.0 mL vial was charged with $PtCl_2$ (250.0 mg, 0.940 mmol, 1.0 equiv.) and CH_2Cl_2 (5.0 mL). THT (500 µL, 5.671 mmol, 6.0 equiv.) was added, the vial was closed with a septum screw cap and the resulted mixture was stirred at 20 °C for 60 min. After this time, a complete consumption of the dark $PtCl_2$ was observed, leading to the formation of a clear orange solution. The volatiles were removed under vacuum, affording the desired complex **1b** as an orange powder (414.0 mg, >99%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 3.67 (br, 2H, S(C**H**$_2$)), 2.83 (br, 2H, S(C**H**$_2$)), 2.24 (br, 2H, S(CH$_2$)(C**H**$_2$)), 2.00 (br, 2H, S(CH$_2$)(C**H**$_2$)). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 38.87 (S(**C**H$_2$), minor), 37.40 (S(**C**H$_2$), major), 30.37 (S(CH$_2$)(**C**H$_2$), minor), 30.00 (S(CH$_2$)(**C**H$_2$), major).

1.4. General hydrosilylation procedure (A)

A 4.0 mL vial was charged with a platinum catalyst (20-100 µl of a solution of **1a–b** in CH_2Cl_2) and dodecane (internal standard, 138 µL, 0.605 mmol). 1,1,1,3,5,5,5-heptamethyltrisiloxane (**3a**) (546 µL, 2.00 mmol, 1.0 equiv.) and 1-octene (**2a**) (318 µL, 2.00 mmol, 1.0 equiv.) were added, the vial was closed with a septum screw cap and the resulted mixture was stirred at the temperature indicated in Table **1**. The reaction aliquots were analysed by gas chromatography (GC), calibrated on a commercial sample of the product (**4aa**). Figure S1 presents the physical appearance of selected model reaction mixtures after reaching completion.

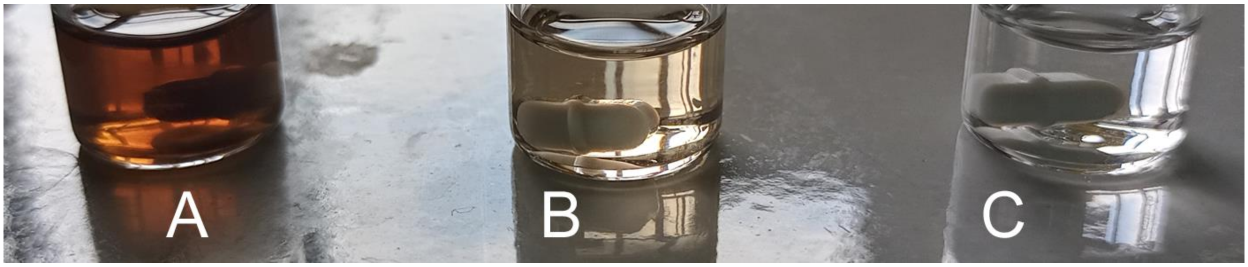


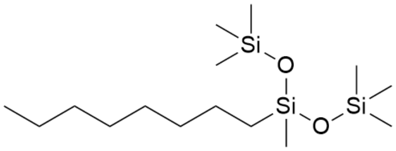
Figure S1 Model hydrosilylation reactions carried out with 1000 ppm (**A**), 100 ppm (**B**) and 10 ppm (**C**) of $[Pt(DMS)_2Cl_2]$ (**1a**).

1.5. General hydrosilylation procedure (B)

A 4.0 mL vial was charged with a solution of **1a** in CH_2Cl_2 (20 µL of a solution 0.390 mg/mL, 2.0×10^{-5} mmol, 10 ppm; 100 µL of the same solution in the case of the reactions carried out at 50 ppm catalyst loading). Silane (2.00 mmol, 1.0 equiv.) and subsequently alkene (2.00 mmol, 1.0 equiv.) were added, the vial was closed with a septum screw cap and the resulted mixture was stirred at 80 °C. The progress of the reaction was monitored by ^1H NMR spectroscopy. Caution: the hydrosilylation reactions are strongly exothermic and on a larger scale the reaction temperature must be carefully controlled. In the case of **4ja**, 1.00 mmol of 1,7-octadiene (**2j**) and 2.00 mmol of **3a** was used. In the case of **4ae**, 2.00 mmol of **2a** and 1.00 mmol of 1,1,3,3-tetramethyldisiloxane (**3e**) was used. In the case of **4af**, 2.00 mmol of **2a** and 0.50 mmol of 2,4,6,8-tetramethylcyclotetrasiloxane (**3f**) was used. The amount of pre-catalyst was calculated based on the number of Si-H groups involved in hydrosilylation (2.00 mmol).

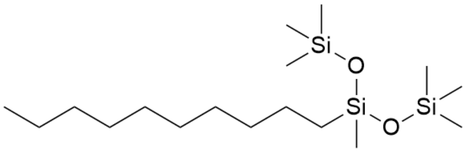
1.6. 1,1,1,3,5,5,5-Heptamethyl-3-octyltrisiloxane (4aa) CAS 17955-88-3

Following the general hydrosilylation procedure (**B**), **4aa** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 1.37 – 1.21 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H), 0.45 (t, *J* = 7.7 Hz, 2H), 0.09 (s, 18H), 0.00 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 33.43, 32.11, 29.51, 29.44, 23.23, 22.87, 17.78, 14.29, 2.01, -0.12. Analytical data match the values reported in the literature.[2]



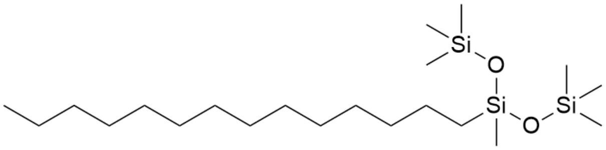
1.7. 3-Decyl-1,1,1,3,5,5,5-heptamethyltrisiloxane (4ba) CAS 54253-66-6

Following the general hydrosilylation procedure (**B**), **4ba** was obtained as a colourless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.39 – 1.17 (m, 16H), 0.88 (t, *J* = 6.4 Hz, 3H), 0.45 (t, *J* = 7.5 Hz, 2H), 0.09 (s, 18H), -0.01 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 33.40, 32.08, 29.82, 29.76, 29.54, 29.52, 23.22, 22.85, 17.78, 14.27, 2.01, -0.12. Analytical data match the values reported in the literature.[2]



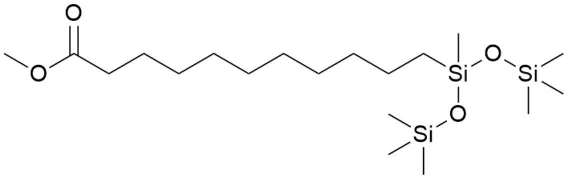
1.8. 1,1,1,3,5,5,5-Heptamethyl-3-tetradecyltrisiloxane (4ca) CAS 286938-65-6

Following the general hydrosilylation procedure (**B**), **4ca** was obtained as a colourless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 1.38 – 1.19 (m, 24H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.45 (t, *J* = 7.6 Hz, 2H), 0.09 (s, 18H), -0.00 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 33.43, 32.12, 29.89, 29.85, 29.79, 29.57, 29.55, 23.25, 22.87, 17.81, 14.28, 2.01, -0.11. Analytical data match the values reported in the literature.[2]



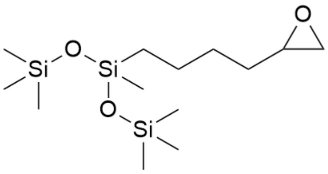
1.9. Methyl 11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecanoate (4da) CAS 60728-44-1

Following the general hydrosilylation procedure (**B**), **4da** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.66 (s, 3H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.53 (m, 2H), 1.38 – 1.16 (m, 14H), 0.52 – 0.35 (m, 2H), 0.08 (s, 18H), -0.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 174.51, 51.58, 34.26, 33.37, 29.65, 29.62, 29.48, 29.41, 29.30, 25.10, 23.20, 17.75, 1.99, -0.14. Analytical data match the values reported in the literature.[2]



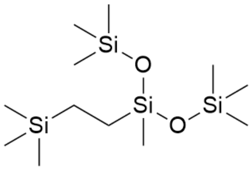
1.10. 1,1,1,3,5,5,5-Heptamethyl-3-(4-(oxiran-2-yl)butyl)trisiloxane (4ea) CAS 2123611-86-7

Following the general hydrosilylation procedure (**B**), **4ea** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 2.93 – 2.84 (m, 1H), 2.73 (dd, *J* = 5.0, 3.9 Hz, 1H), 2.45 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.58 – 1.30 (m, 6H), 0.51 – 0.41 (m, 2H), 0.08 (s, 18H), -0.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 52.48, 47.27, 32.36, 29.53, 23.11, 17.67, 1.98, -0.16. Analytical data match the values reported in the literature.[2]



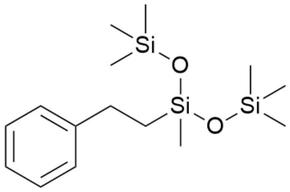
1.11. 1,1,1,3,5,5,5-Heptamethyl-3-(2-(trimethylsilyl)ethyl)trisiloxane (4fa) CAS 18077-53-7

Following the general hydrosilylation procedure (**B**), **4fa** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 0.44 – 0.29 (m, 4H), 0.09 (s, 18H), 0.00 (s, 3H), -0.03 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 9.68, 8.05, 2.03, -1.00, -2.08. Analytical data match the values reported in the literature.[2]



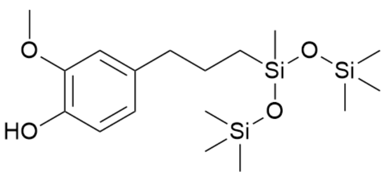
1.12. 1,1,1,3,5,5,5-Heptamethyl-3-phenethyltrisiloxane (4ga) CAS 3439-16-5

Following the general hydrosilylation procedure (**B**), **4ga** was obtained as a colourless oil. The product contains 16% of the branched side product. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.40 – 7.06 (m, 5H), 2.75 – 2.62 (m, 2H), 0.92 – 0.82 (m, 2H), 0.14 (s, 18H), 0.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 145.30, 128.43, 127.93, 125.62, 29.40, 19.87, 2.03, -0.17. Analytical data match the values reported in the literature.[2]



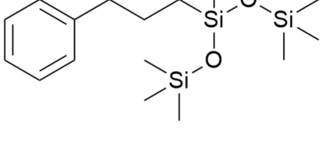
1.13. 4-(3-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)propyl)-2-methoxyphenol (4ha) CAS 889894-43-3

Following the general hydrosilylation procedure (**B**), **4ha** was obtained as a colourless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 6.88 – 6.77 (m, 1H), 6.73 – 6.59 (m, 2H), 5.45 (s, 1H), 3.88 (s, 3H), 2.55 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.54 (m, 2H), 0.59 – 0.41 (m, 2H), 0.09 (s, 18H), 0.00 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 146.41, 143.68, 134.90, 121.16, 114.22, 111.16, 55.96, 39.27, 25.59, 17.52, 2.01, -0.08. Analytical data match the values reported in the literature.[2]



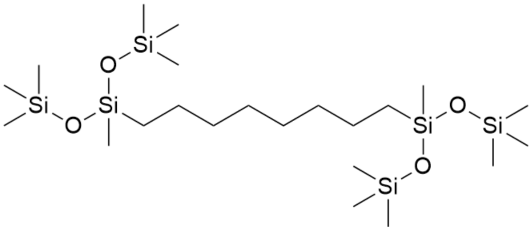
1.14. 1,1,1,3,5,5,5-Heptamethyl-3-(3-phenylpropyl)trisiloxane (4ia) CAS 101667-47-4

Following the general hydrosilylation procedure (**B**), **4ia** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.35 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.58 (m, 2H), 0.58 – 0.46 (m, 2H), 0.08 (s, 18H), 0.00 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 142.88, 128.63, 128.36, 125.74, 39.61, 25.34, 17.59, 2.01, -0.10. Analytical data match the values reported in the literature.[3]



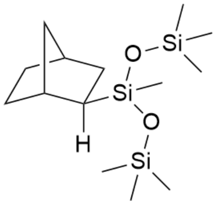
1.15. 1,8-Bis(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)octane (4ja) CAS 1688709-56-9

Following the general hydrosilylation procedure (**B**), **4ja** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 1.37 – 1.20 (m, 12H), 0.45 (t, *J* = 7.6 Hz, 4H), 0.09 (s, 36H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 33.43, 29.44, 23.21, 17.77, 2.01, -0.12. Analytical data match the values reported in the literature.[2]



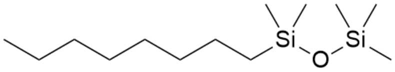
1.16. 3-(Bicyclo[2.2.1]heptan-2-yl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (4ka) CAS 1854132-67-4

Following the general hydrosilylation procedure (**B**), **4ka** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 2.28 – 2.15 (m, 2H), 1.55 – 1.48 (m, 2H), 1.48 – 1.41 (m, 1H), 1.38 – 1.24 (m, 2H), 1.24 – 1.13 (m, 2H), 1.13 – 1.02 (m, 1H), 0.51 – 0.38 (m, 1H), 0.08 (s, 18H), -0.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 37.78, 37.46, 36.82, 34.01, 31.72, 30.32, 29.19, 2.03, -1.29. Analytical data match the values reported in the literature.[4]



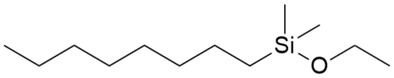
1.17. 1,1,1,3,3-Pentamethyl-3-octyldisiloxane (4ab) CAS 180006-15-9

Following the general hydrosilylation procedure (**B**), **4ab** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 1.37 – 1.20 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.50 (t, *J* = 7.4 Hz, 2H), 0.06 (s, 9H), 0.03 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 33.61, 32.12, 29.53, 29.45, 23.43, 22.86, 18.53, 14.29, 2.13, 0.50. Analytical data match the values reported in the literature.[2]



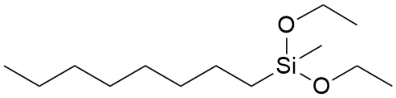
1.18. Ethoxydimethyl(octyl)silane (4ac) CAS 87281-31-0

Following the general hydrosilylation procedure (**B**), **4ac** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 3.65 (q, *J* = 7.0 Hz, 2H), 1.40 – 1.22 (m, 12H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.58 (t, *J* = 7.3 Hz, 2H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) = 58.32, 33.64, 32.09, 29.47, 29.41, 23.34, 22.83, 18.71, 16.49, 14.26, -1.95. Analytical data match the values reported in the literature.[2]



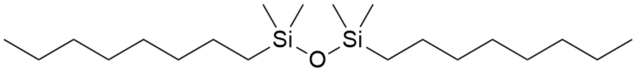
1.19. Diethoxy(methyl)(octyl)silane (4ad) CAS 2652-38-2

Following the general hydrosilylation procedure (**B**), **4ad** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 3.75 (q, *J* = 7.0 Hz, 4H), 1.40 – 1.17 (m, 12H), 1.20 (t, *J* = 7.0 Hz, 6H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.65 – 0.54 (m, 2H), 0.09 (s, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 58.16, 33.47, 32.06, 29.42, 29.37, 22.98, 22.81, 18.53, 14.24, 13.92, -4.77. Analytical data match the values reported in the literature.[2]



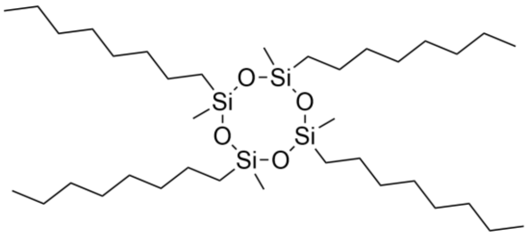
1.20. 1,1,3,3-Tetramethyl-1,3-dioctyldisiloxane (4ae) CAS 18642-94-9

Following the general hydrosilylation procedure (**B**), **4ae** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 1.42 – 1.16 (m, 24H), 0.89 (t, *J* = 6.8 Hz, 6H), 0.50 (t, *J* = 7.4 Hz, 4H), 0.03 (s, 12H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 33.64, 32.13, 29.55, 29.47, 23.46, 22.87, 18.58, 14.29, 0.54. Analytical data match the values reported in the literature.[2]



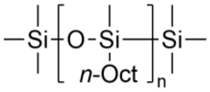
1.21. 2,4,6,8-Tetramethyl-2,4,6,8-tetraoctyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane (4af) CAS 15147-32-7

Following the general hydrosilylation procedure (**B**), **4af** was obtained as a colourless oil. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 1.43 – 1.17 (m, 48H), 0.89 (t, *J* = 6.7 Hz, 12H), 0.52 (t, *J* = 7.6 Hz, 8H), 0.06 (s, 12H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 33.36, 32.14, 29.49, 23.16, 23.13, 22.88, 17.36, 14.29, -0.49. Analytical data match the values reported in the literature.[2]



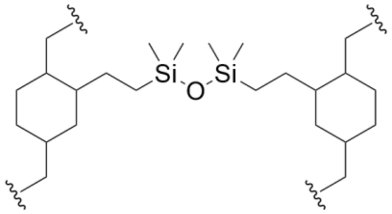
1.22. PMHS hydrosilylation (4ag)

PMHS used in the reaction was purchased from Sigma Aldrich (average M$_n$: 1700-3200; $n_{\text{avg.}} \approx 38$). The ratio $n_{\text{Si-H}}$ [mmol] / m$_{\text{PMHS}}$ [mg] was determined by ^{1}H NMR, using 1,3,5-trimethoxybenzene as an internal standard (1.382 mmol Si-H / 100 mg PMHS). The synthesis was carried out with 144.7 mg of PMHS (2.00 mmol Si-H, 1.0 equiv.) and 318 µL of 1-octene (2.00 mmol, 1.0 equiv.). Following the general hydrosilylation procedure (**B**), **4ag** was obtained as a viscous colourless oil. **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 4.69 (m, 0.15H, unreacted Si-**H**), 1.41 – 1.17 (m, 12.54H, C**H**$_2$), 0.88 (t, *J* = 6.7 Hz, 3.38H), 0.57 – 0.44 (m, 2.00H, Si(C**H**$_2$)), 0.18 – 0.00 (m, 4.09H, Si(C**H**$_3$)). **^{13}C NMR** (101 MHz, CDCl$_3$): δ (ppm) = 33.69, 33.61, 32.15, 29.59, 29.53, 23.24, 23.19, 23.12, 22.87, 17.84, 17.76, 17.67, 17.57, 14.26, -0.21, -0.47. Analytical data match the values reported in the literature.[5]



$$-\mathrm{Si}-\left[\mathrm{O}-\underset{n\text{-Oct}}{\mathrm{Si}}-\right]_n-\mathrm{Si}-$$

2. Hydrosilylation–polymerisation



A 4.0 mL vial was charged with a solution of **1a** in CH_2Cl_2 (60 µL of a solution 0.039 mg/mL, 6.0×10^{-6} mmol, 1 ppm). 1,1,3,3-Tetramethyldisiloxane (396.9 mg, 3.00 mmol, 1.5 equiv.) and subsequently 1,2,4-trivinylcyclohexane (mixture of isomers; 324.6 mg, 2.00 mmol, 1.0 equiv.) were added, the vial was closed with a septum screw cap and the resulted mixture was stirred at 75 °C. After 24 h, complete solidification of the reaction mixture was observed, resulting in a formation of a clear cross-linked polymer (Figure S2), insoluble in common organic solvents (including *n*-pentane, CH_2Cl_2 and acetone).

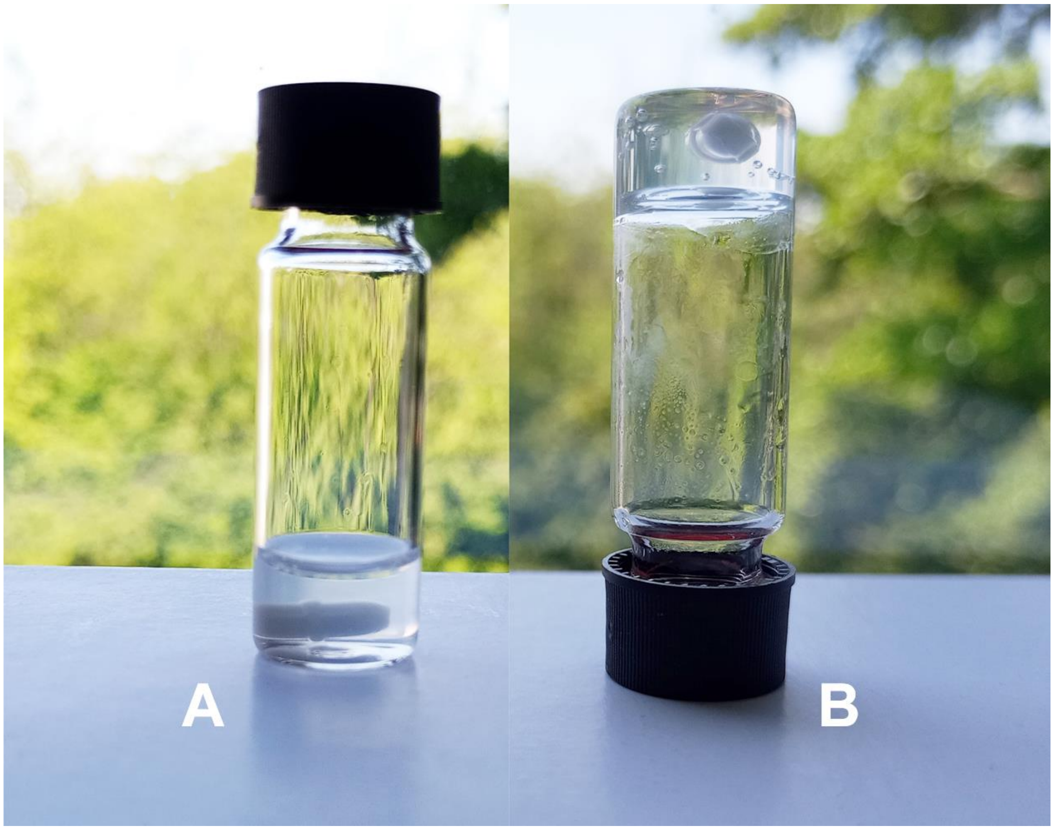


Figure S2 Hydrosilylation-polymerisation reaction mixture at t_0 (**A**) and after 24 h (**B**).

3. UV-VIS characterisation of colloidal [Pt]

Samples for the UV-VIS measurements were prepared following a modified general hydrosilylation procedure **(B)** (in 20 mL vials, at room temperature, with 8.00 mmol of the model substrates **2a** and **3a**), using 0.1 mol% of **1a** and **1b** (800 µL of a 0.01 mmol/mL solution in CH_2Cl_2; the solvent was evaporated before adding the substrates). After 15 min, the completion of the reaction was confirmed by GC. The samples were diluted 10x, using pure product **4aa**, and the UV-VIS spectra were measured at room temperature on a Perkin Elmer Lambda 900 spectrometer in quartz cuvettes (Figure S3). The baseline in both experiments was measured on a sample of pure **4aa**.

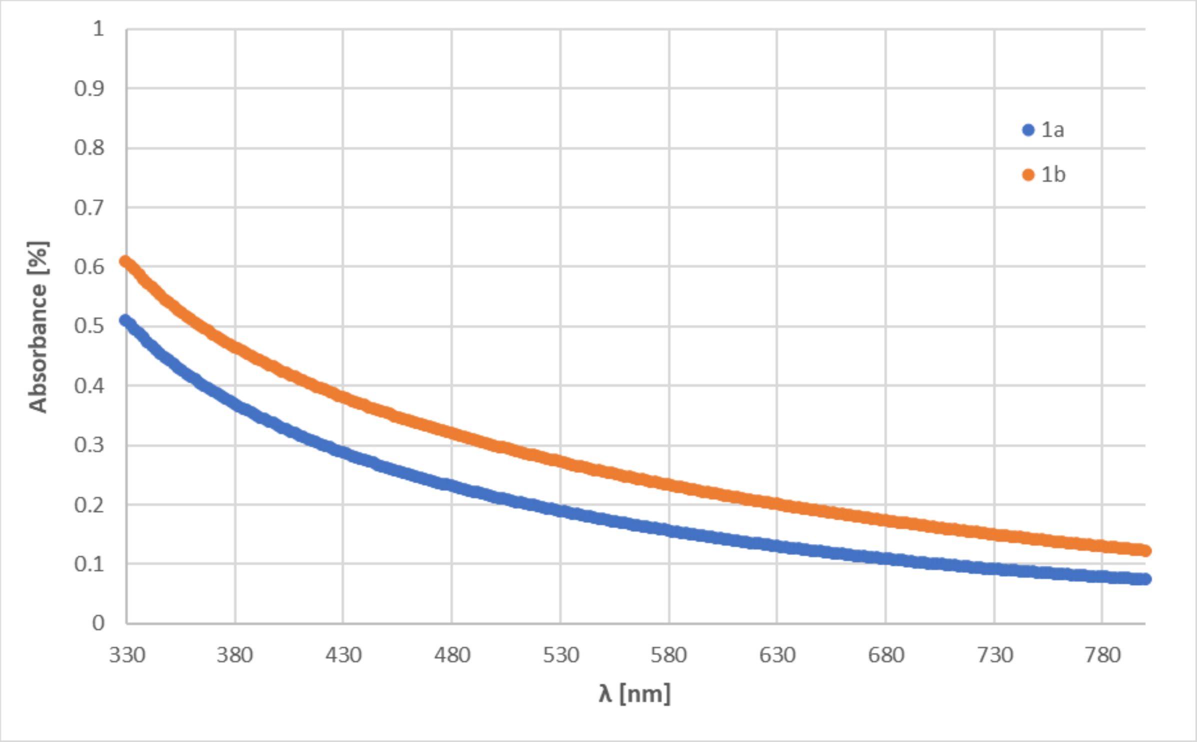


Figure S3 UV-VIS spectra of colloidal [Pt] species formed in a hydrosilylation reaction with 0.1 mol% of $[Pt(DMS)_2Cl_2]$ (**1a**) and $[Pt(THT)_2Cl_2]$ (**1b**).

4. *Cis/trans* isomerisation experiment

A 4.0 mL vial was charged with [Pt(DMS)$_2$Cl$_2$] (**1a**) (514 mg, 1.317 mmol). CHCl$_3$ (3.8 mL) was added, the vial was closed with a septum screw cap and the resulted clear yellow mixture was stirred at 75 °C. The isomerisation was monitored by ^{1}H NMR spectroscopy. After a few days at an elevated temperature, an appearance of a characteristic faint dark yellow tint in the sample was observed, suggesting the formation of colloidal [Pt] species. Samples for the NMR analysis were dried under vacuum and the spectra were recorded in CDCl$_3$. Three samples were analysed (Figure S4): **a)** at t$_0$, before dissolving **1a** in CHCl$_3$; **b)** after 167 h at 75 °C; and **c)** 20 h after cooling down the CHCl$_3$ solution back to the room temperature. The isomerisation appears to reach an equilibrium at 75 °C (*cis/trans* ratio = 11:89), and when cooled down, slowly reverses back towards the initial *cis/trans* ratio. This suggests that ***trans*-1a** is the thermodynamic product.

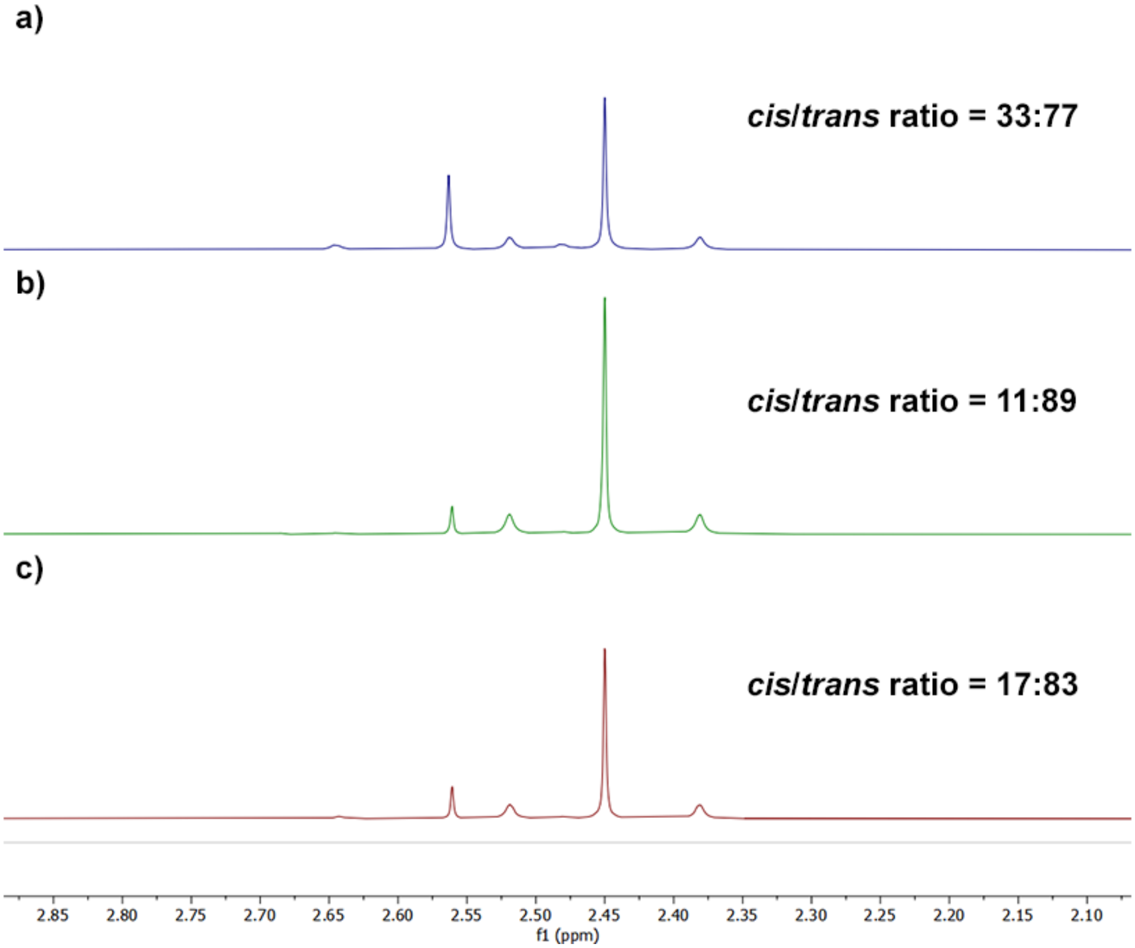
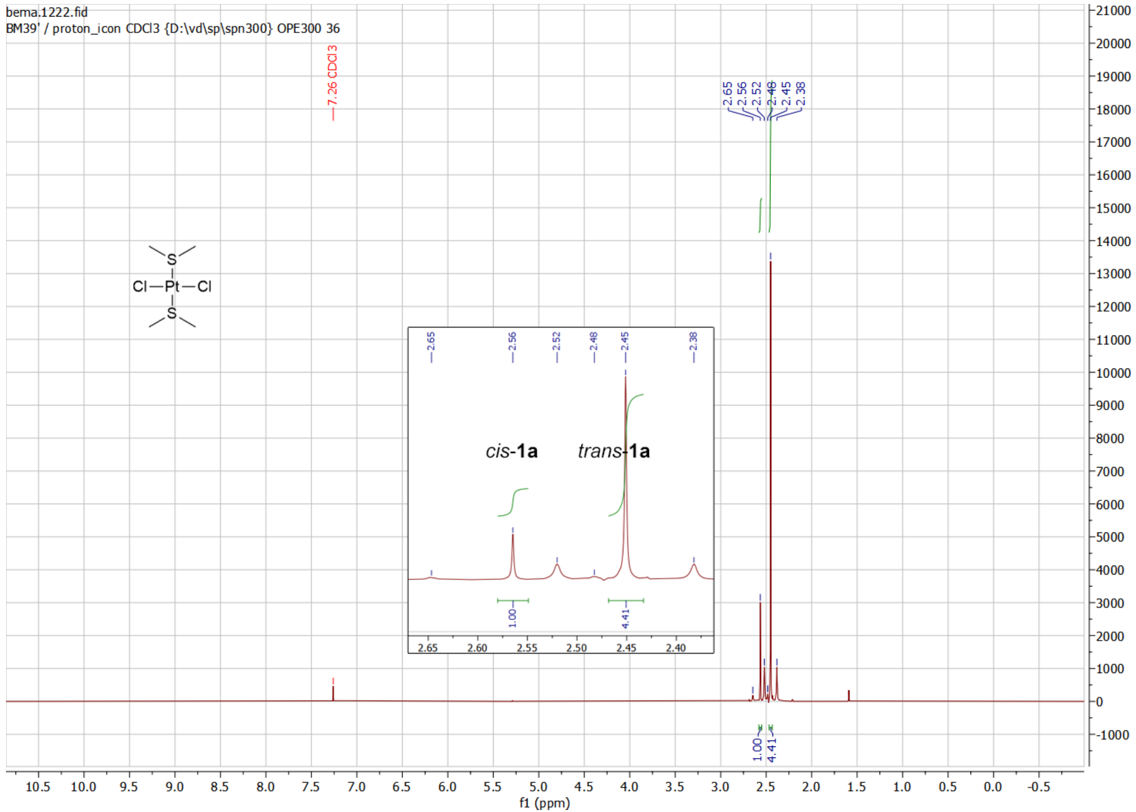
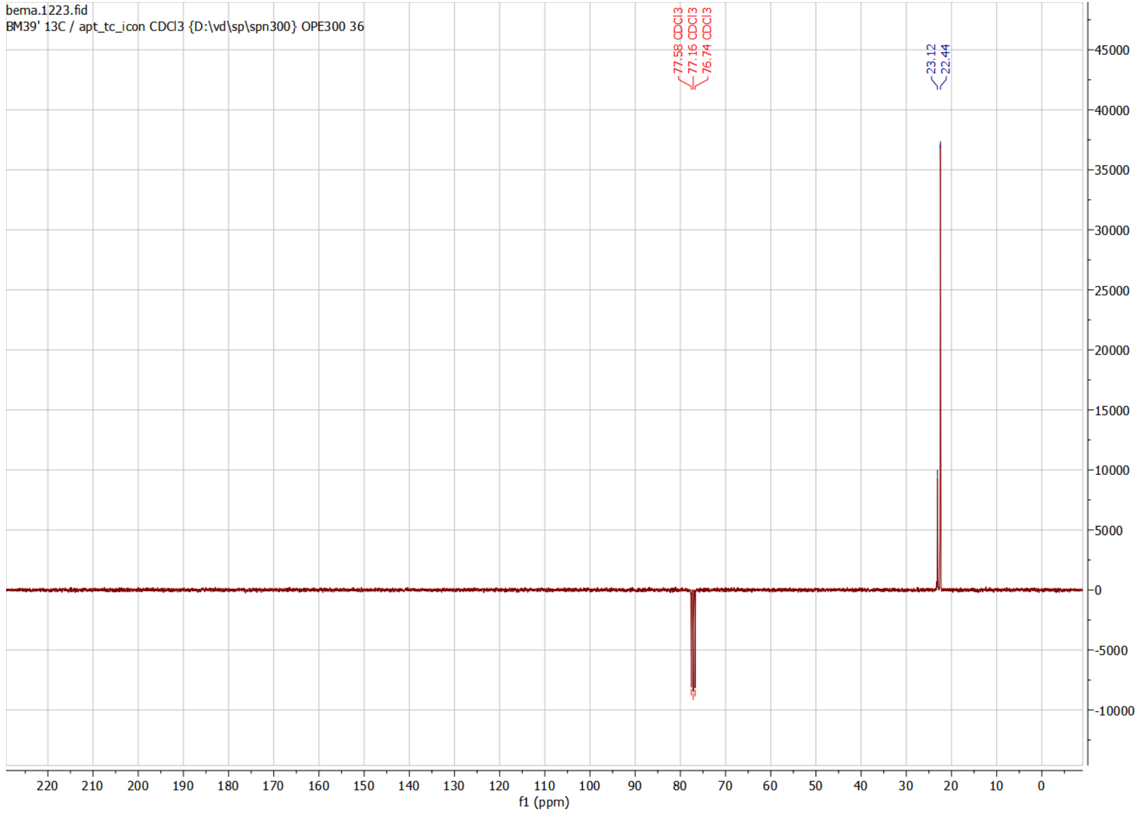


Figure S4 *Cis/trans* isomerisation of **1a**.

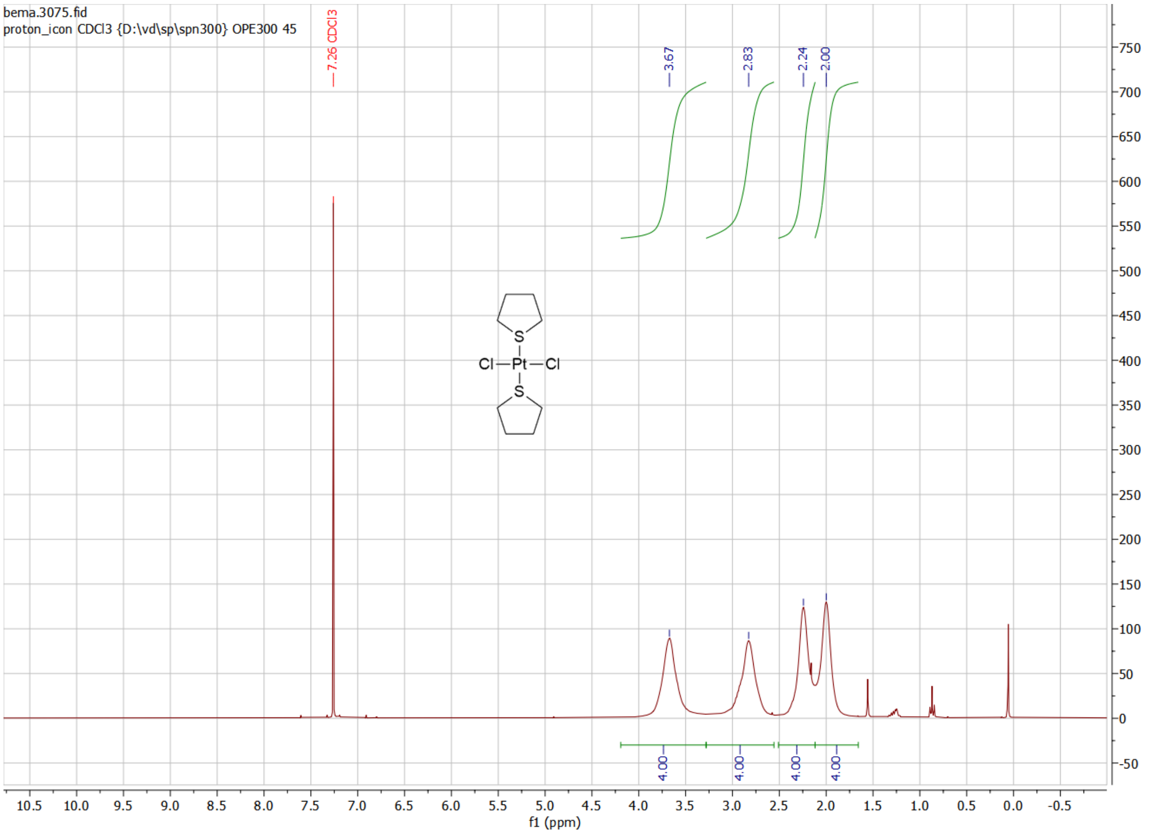
5. NMR spectra

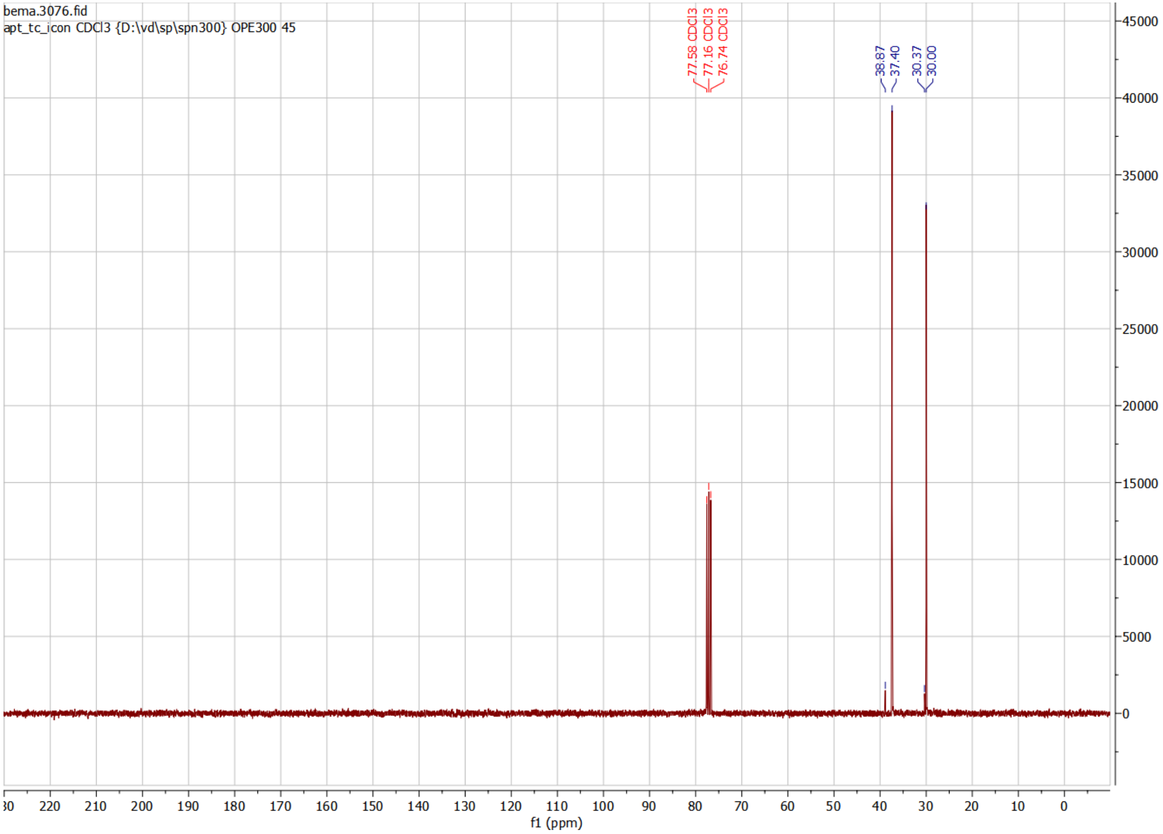
5.1. ^{1}H and ^{13}C{^{1}H} apt NMR of 1a



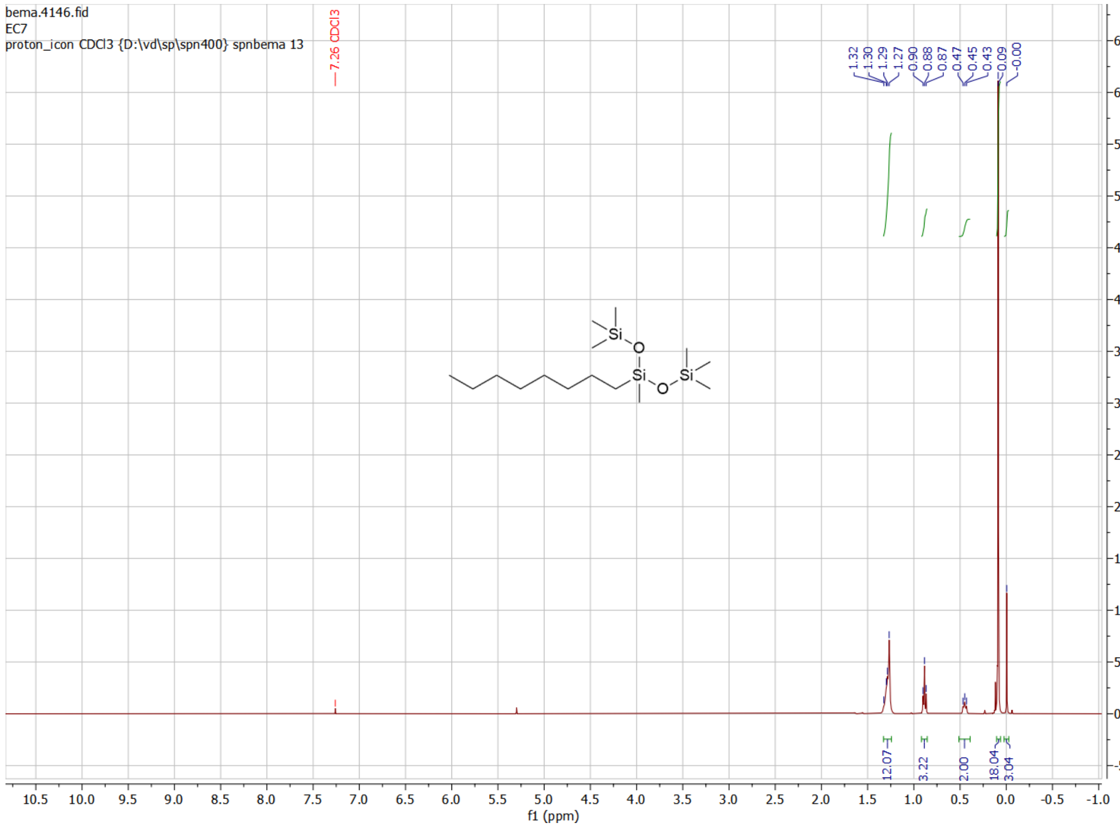


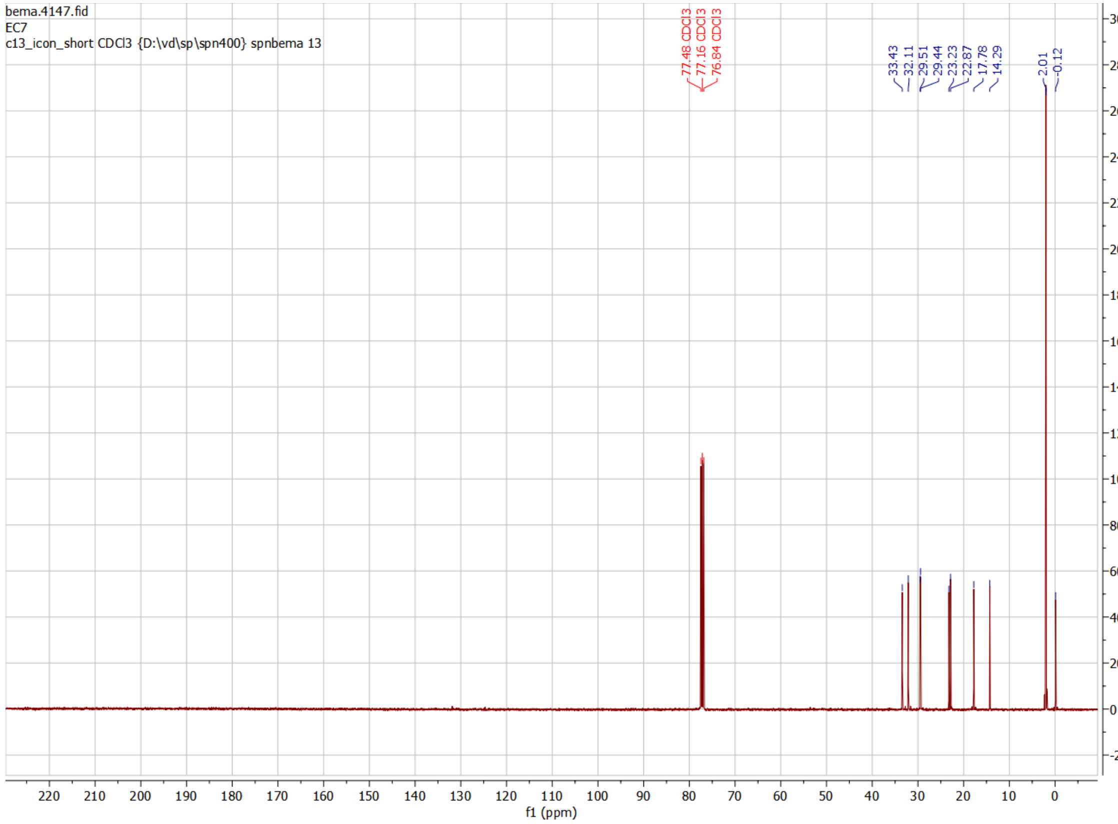
5.2. ^{1}H and ^{13}C{^{1}H} apt NMR of 1b



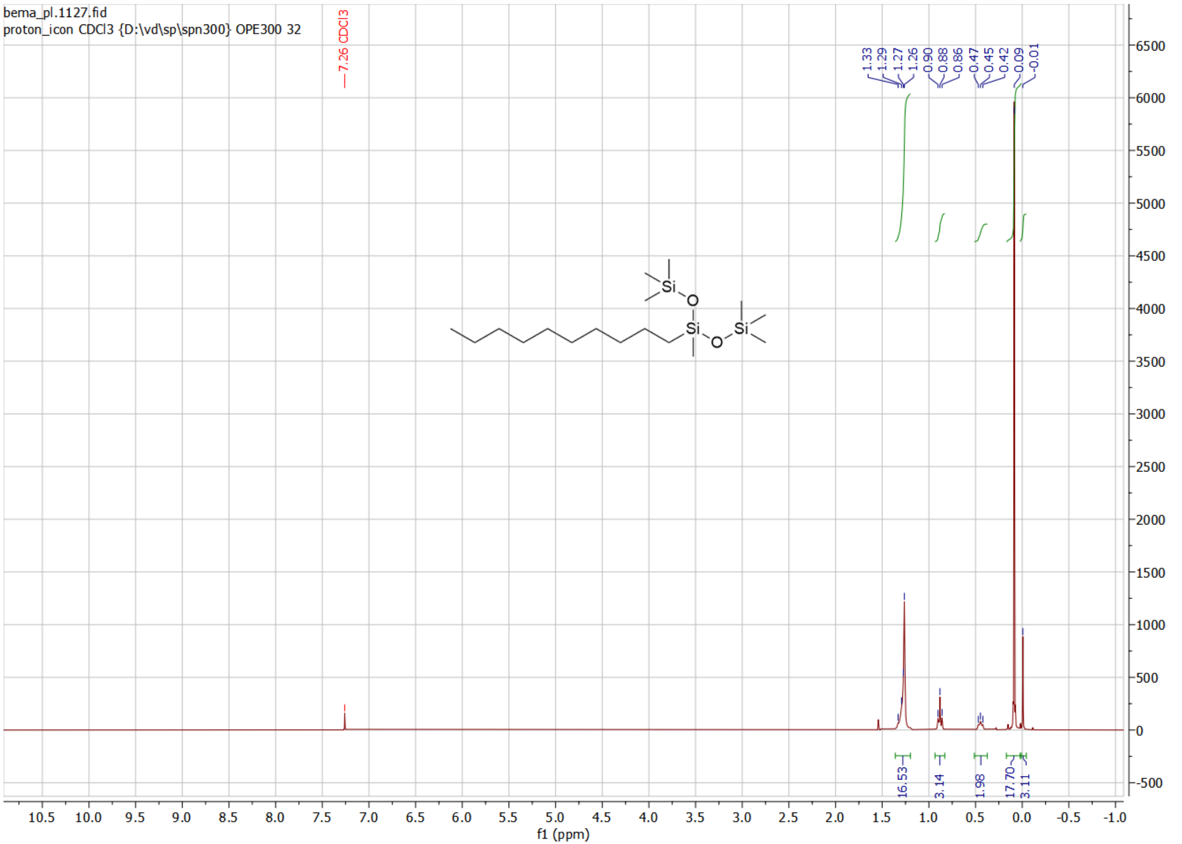


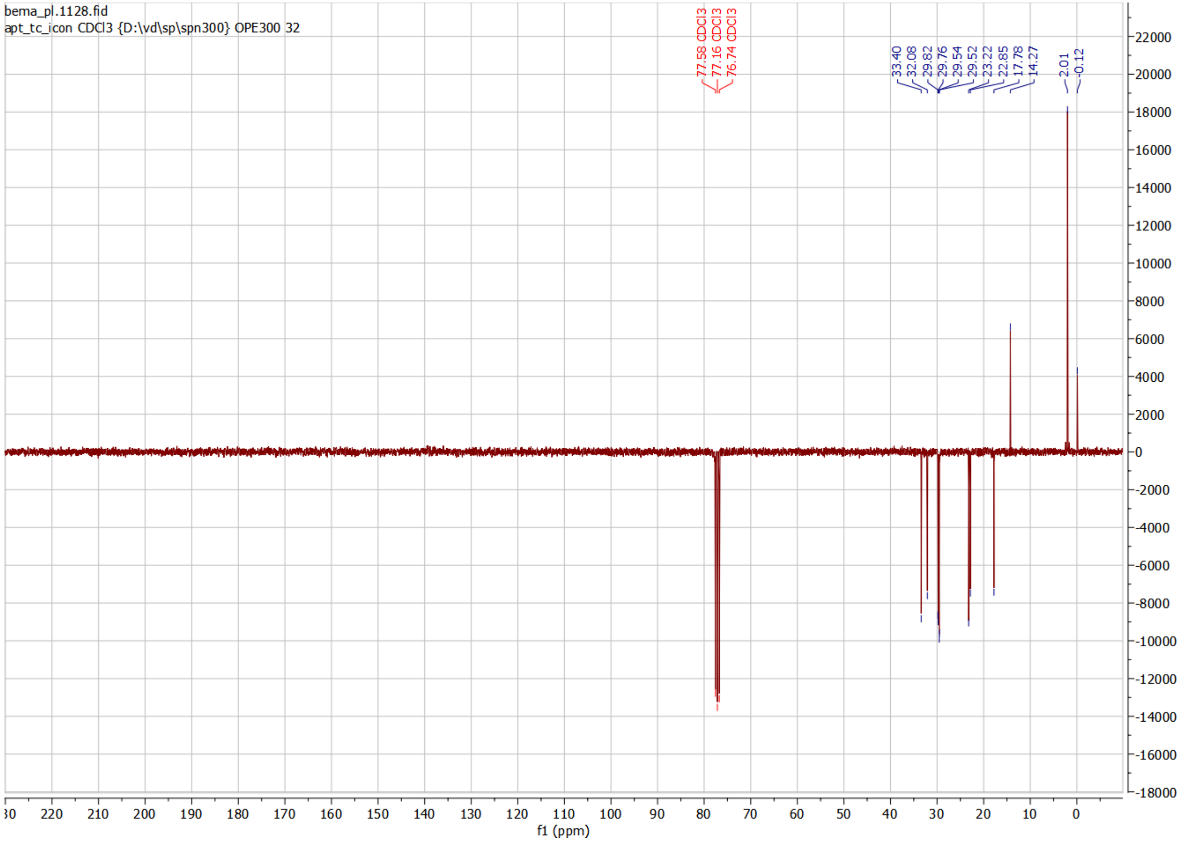
5.3. ^{1}H and ^{13}C{^{1}H} NMR of 4aa



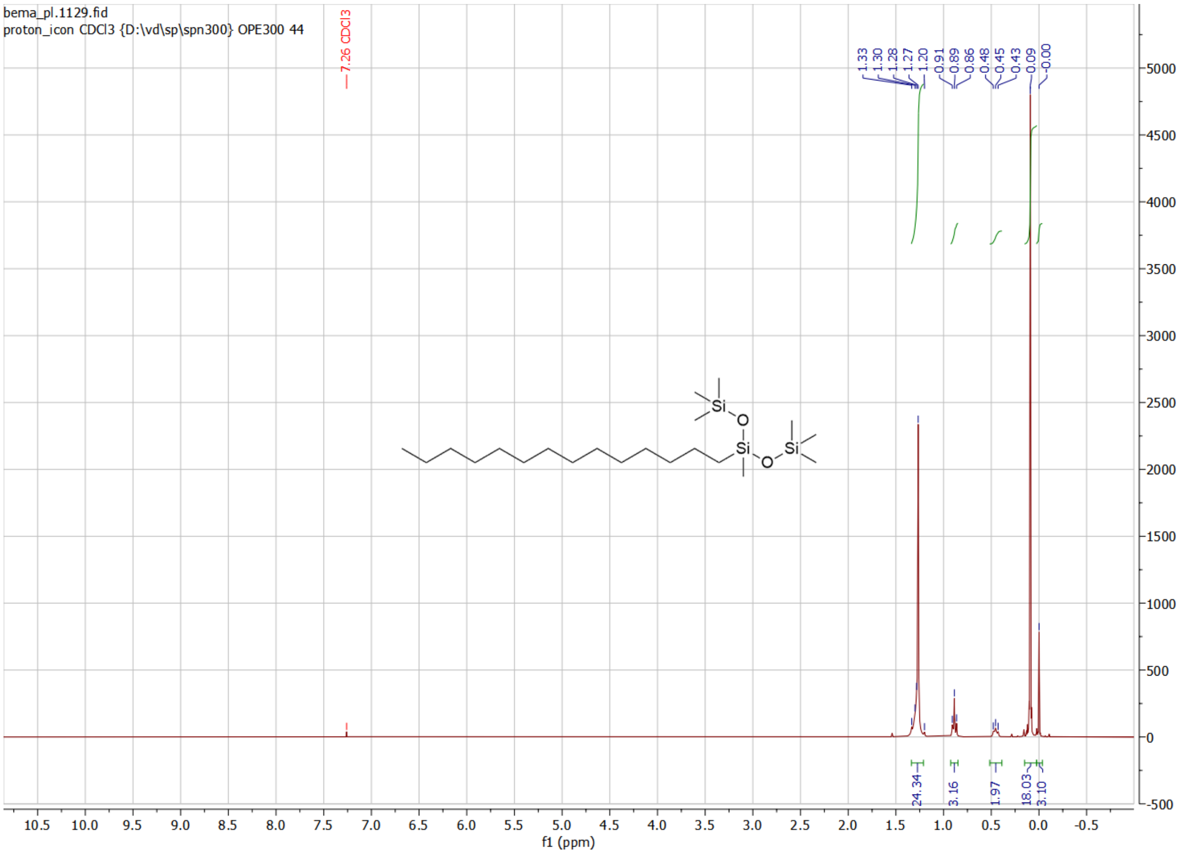


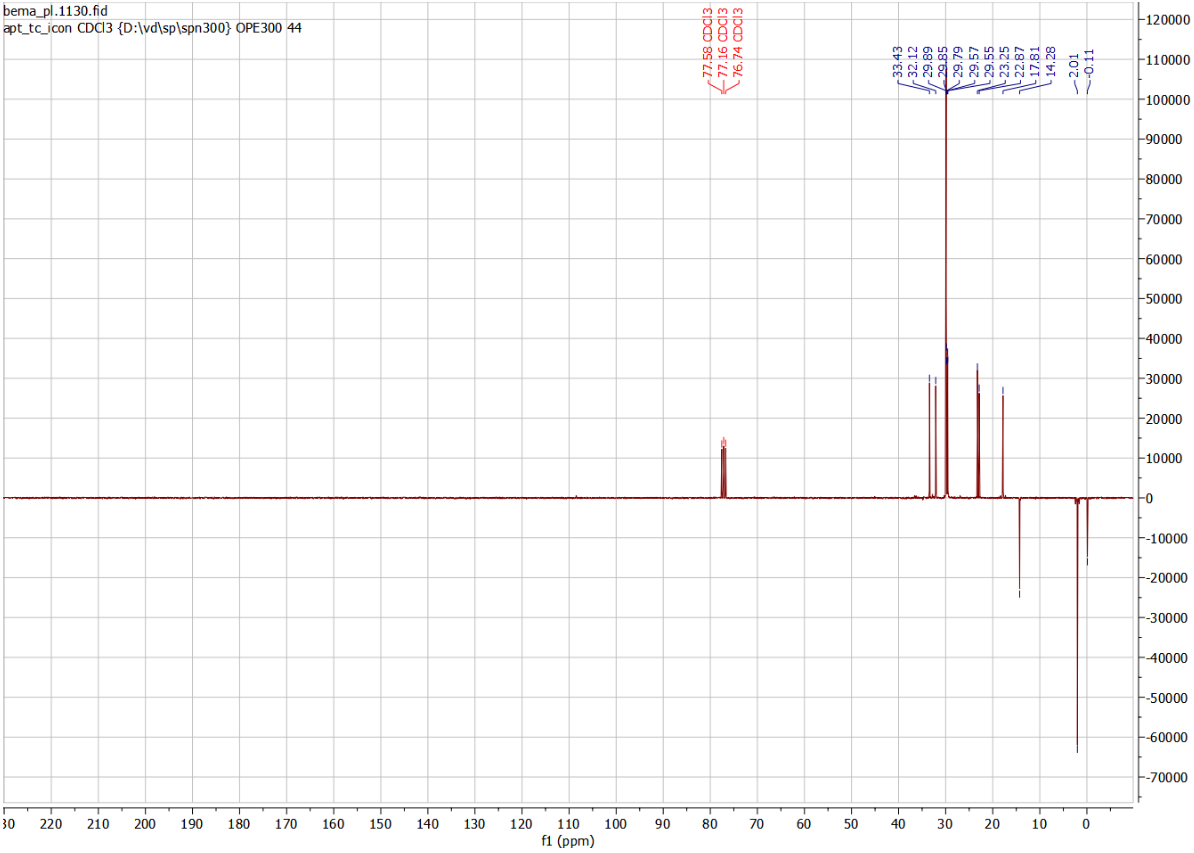
5.4. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ba



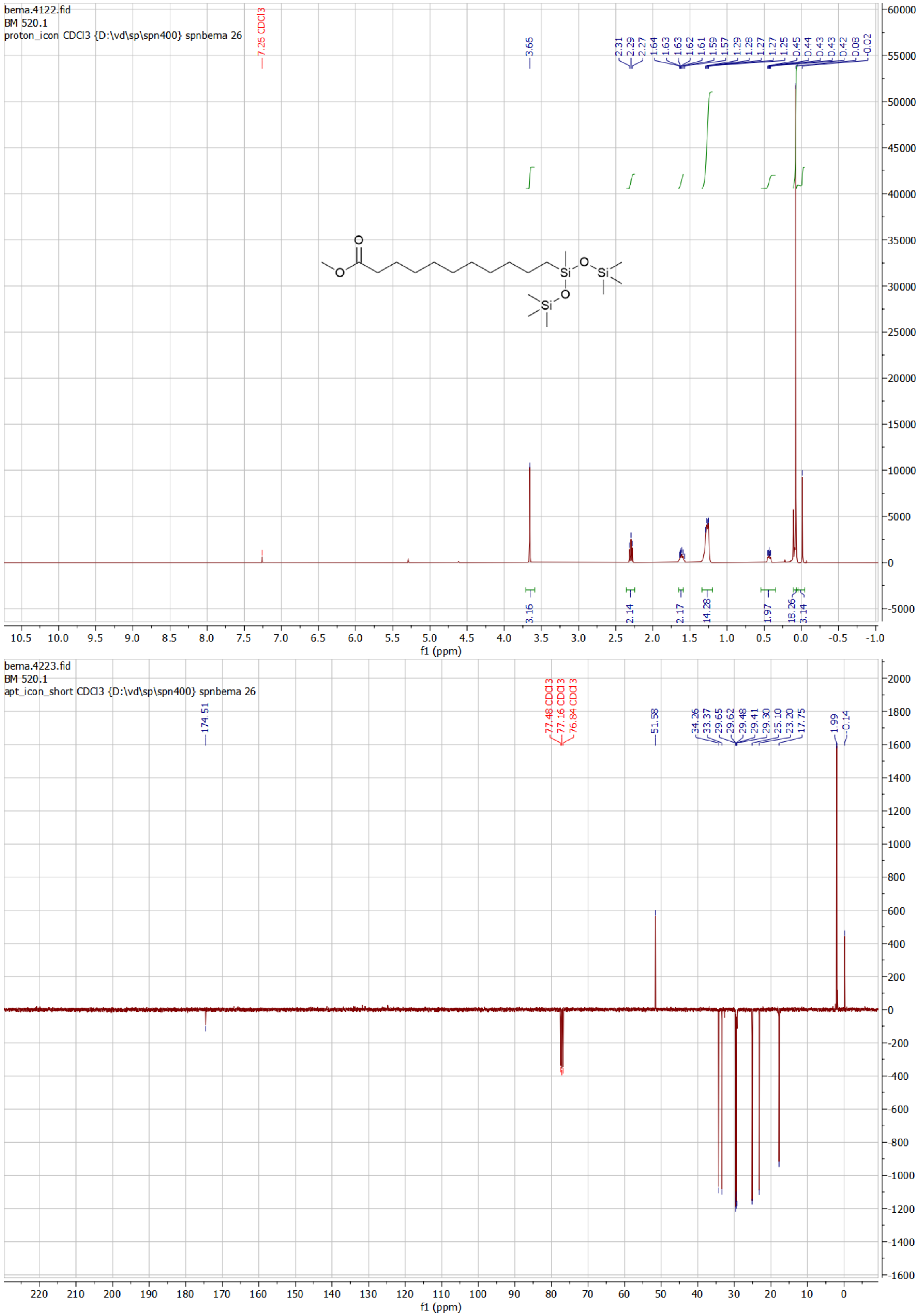


5.5. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ca

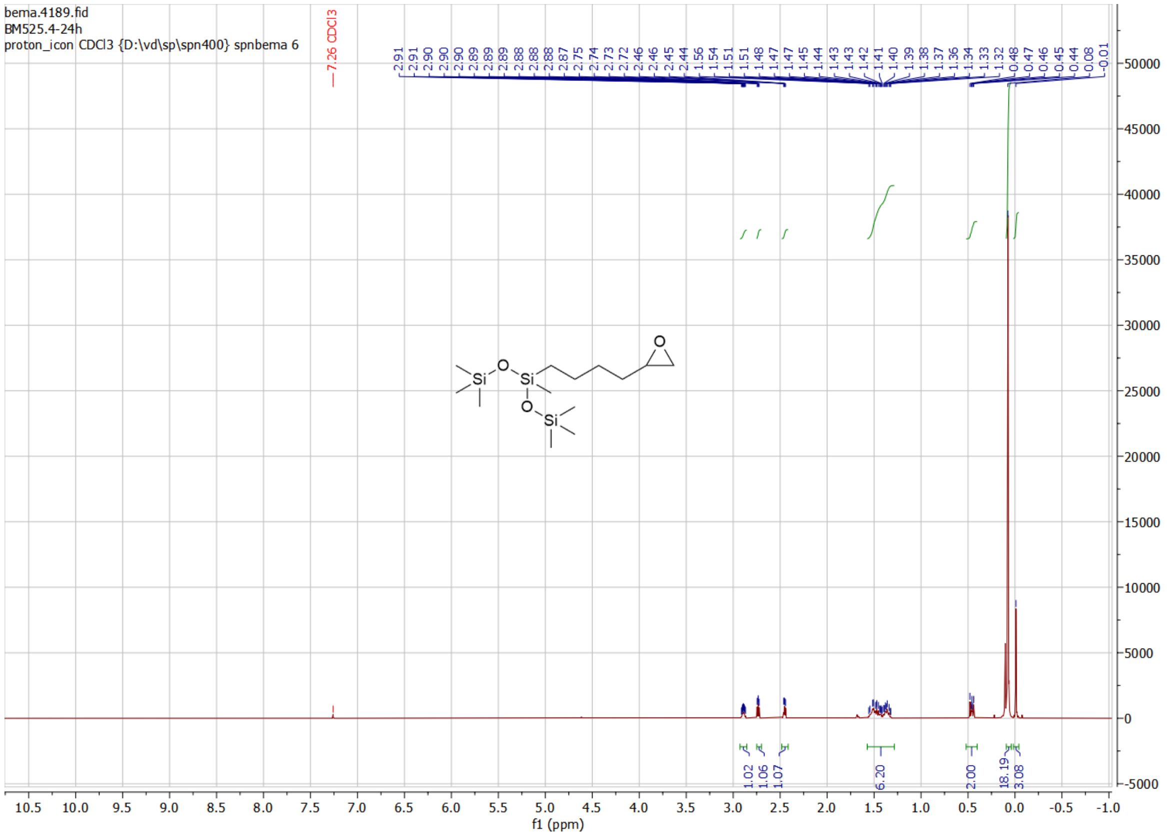


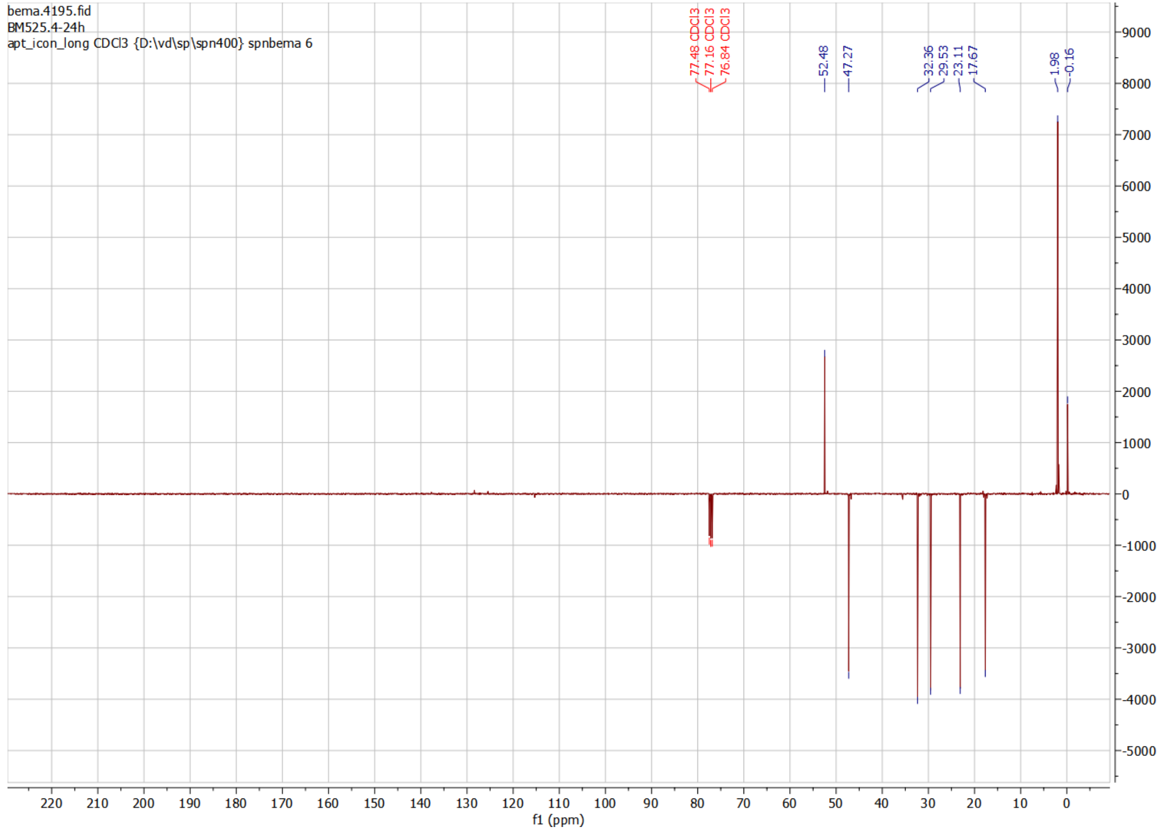


5.6. ^{1}H and ^{13}C{^{1}H} apt NMR of 4da

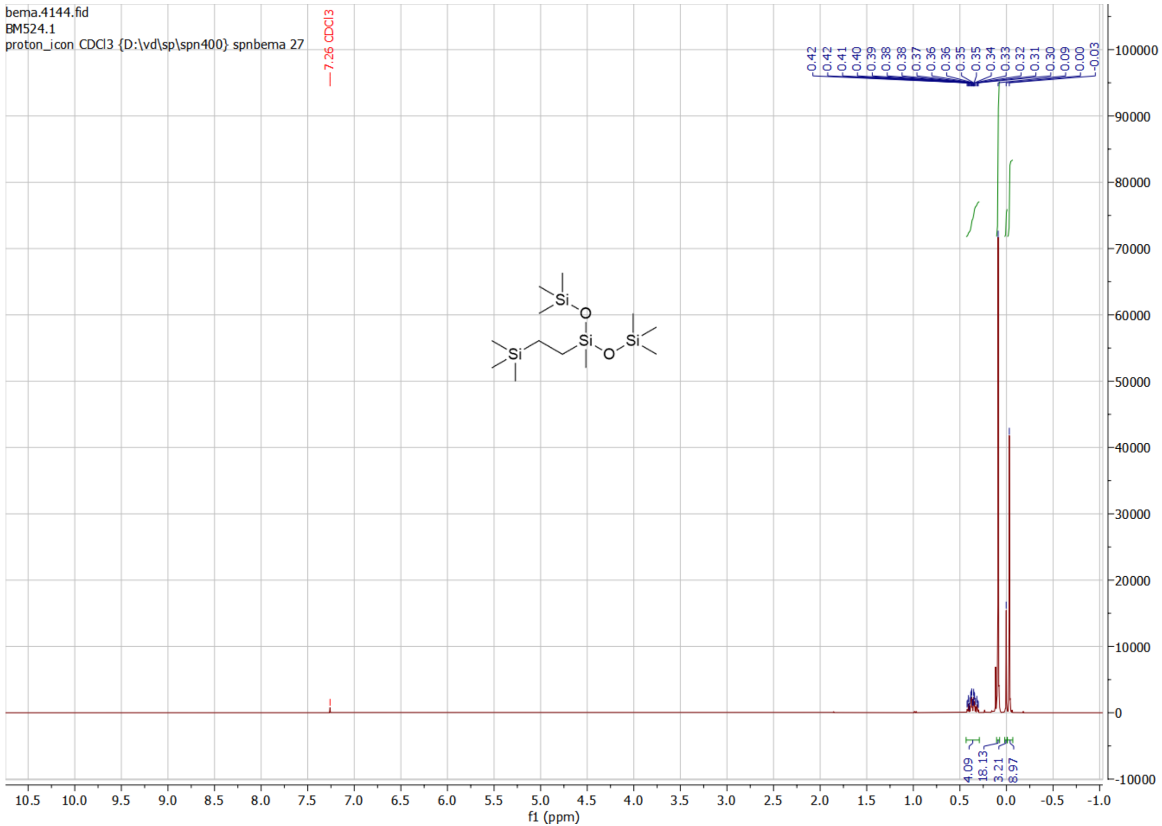


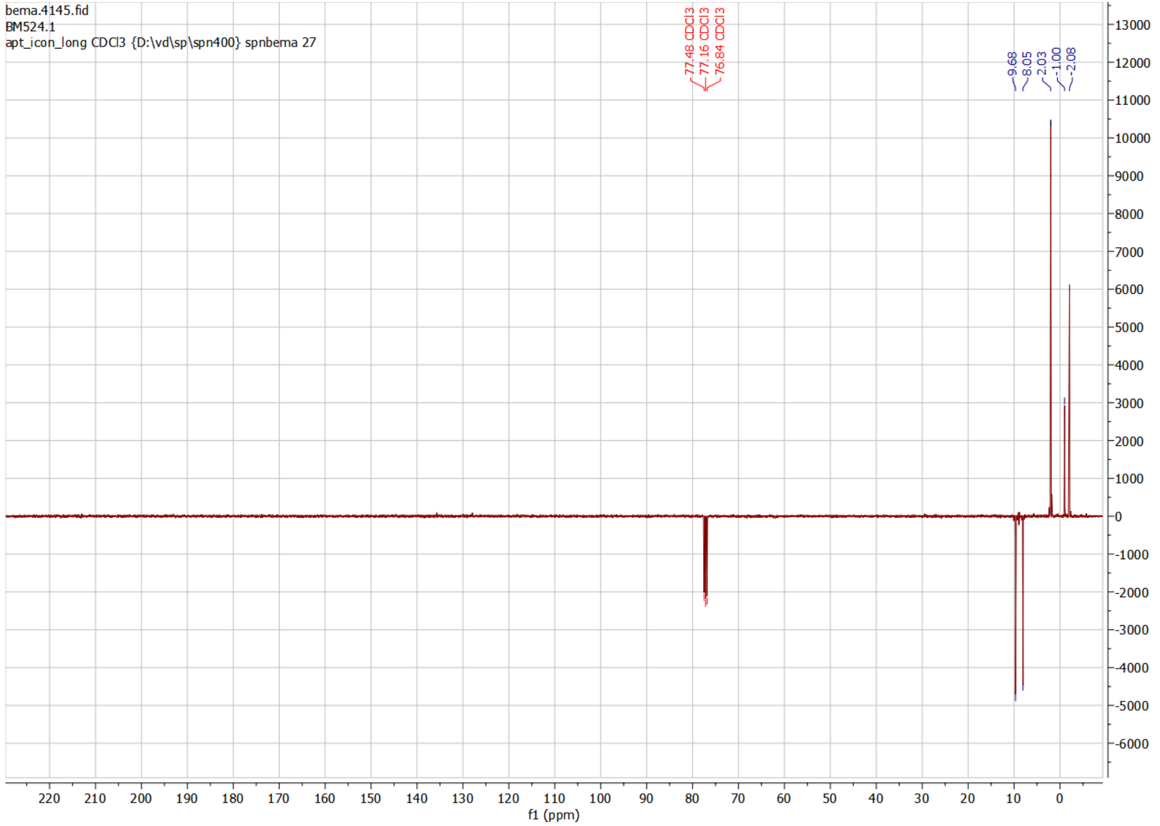
5.7. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ea



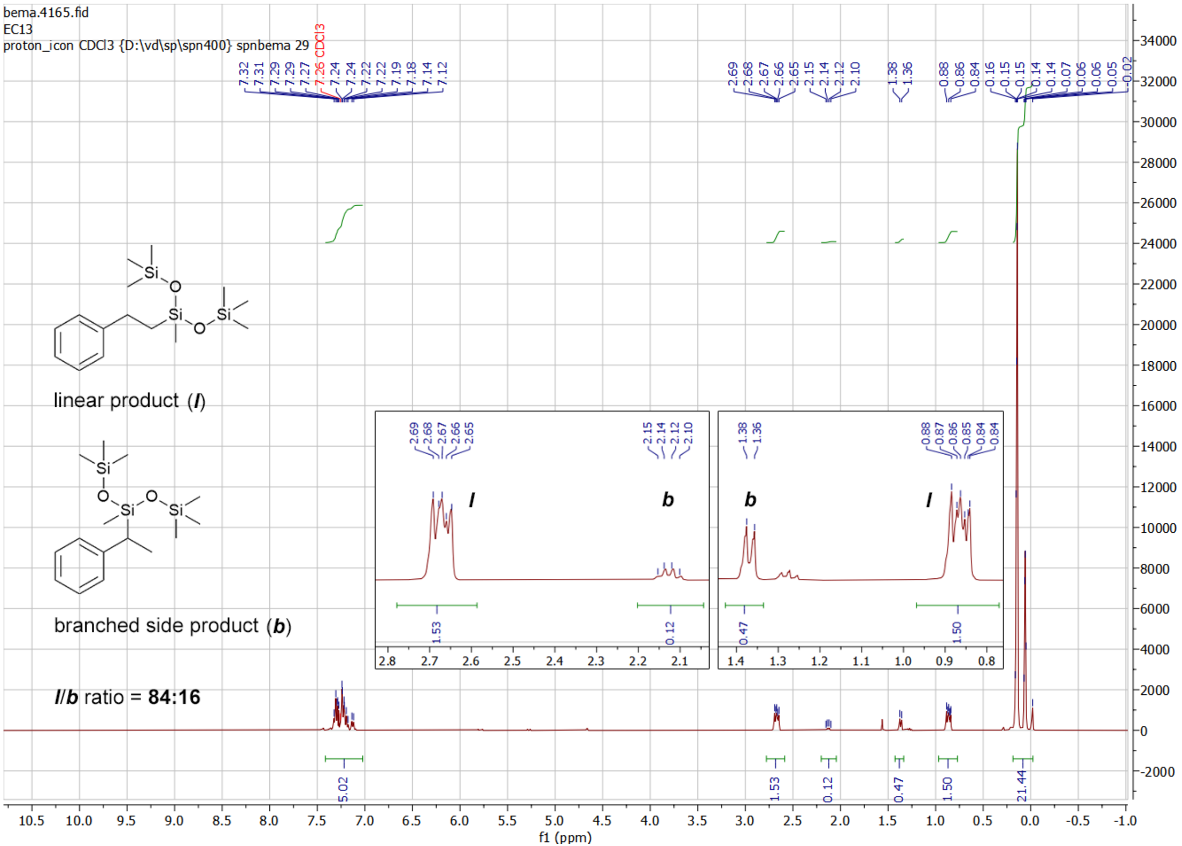


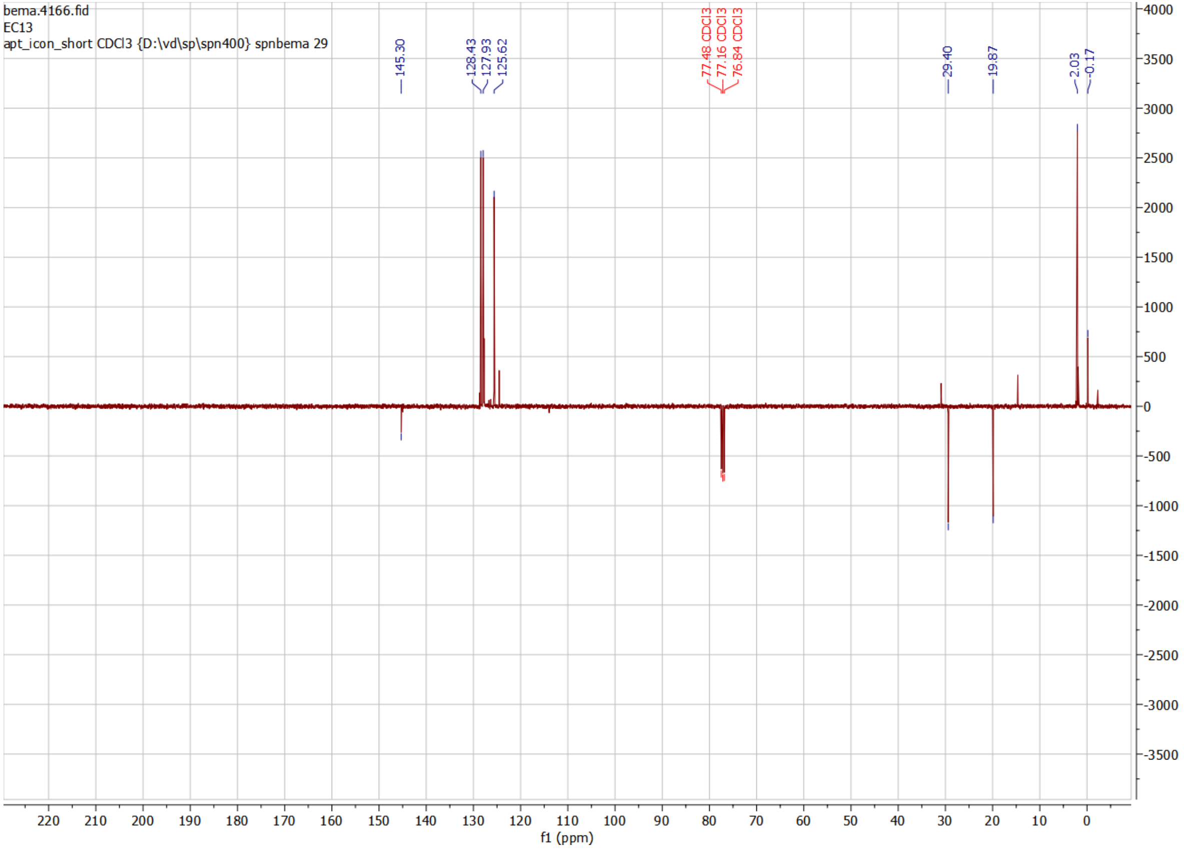
5.8. ^{1}H and ^{13}C{^{1}H} apt NMR of 4fa



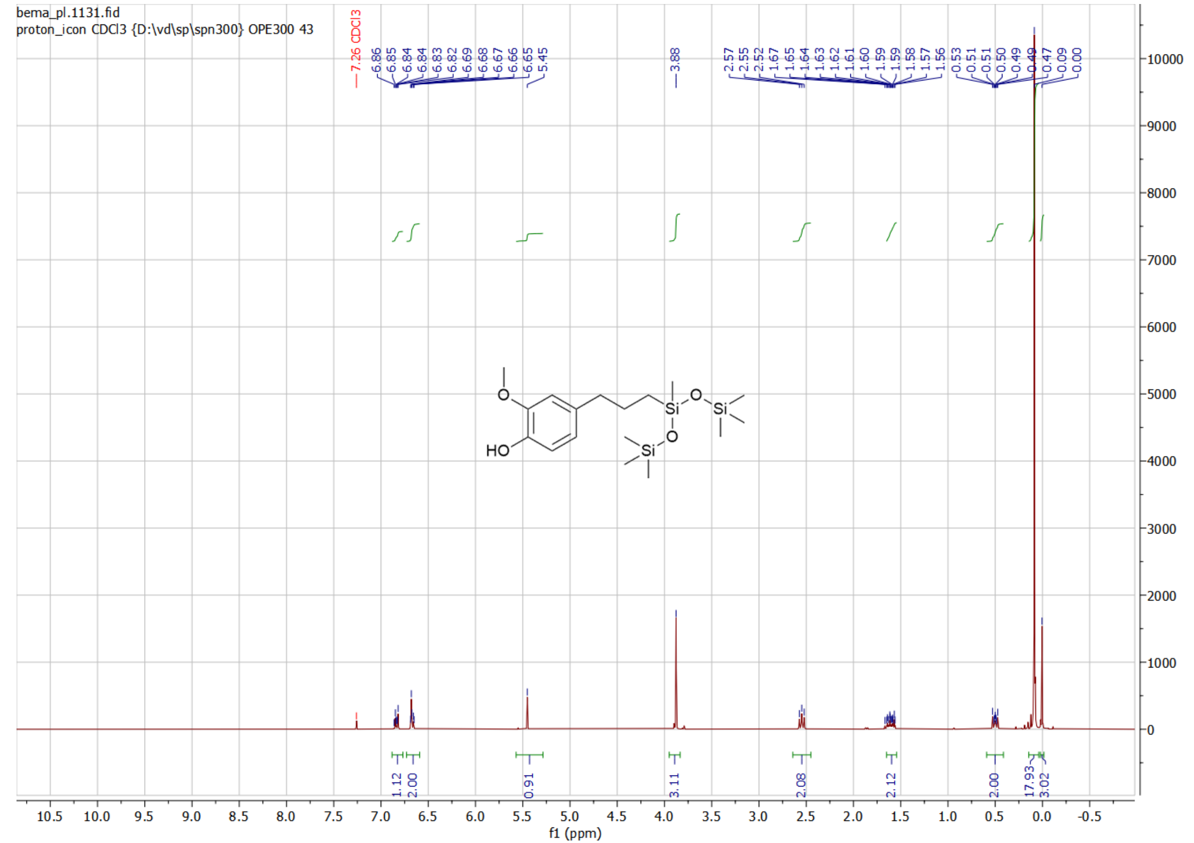


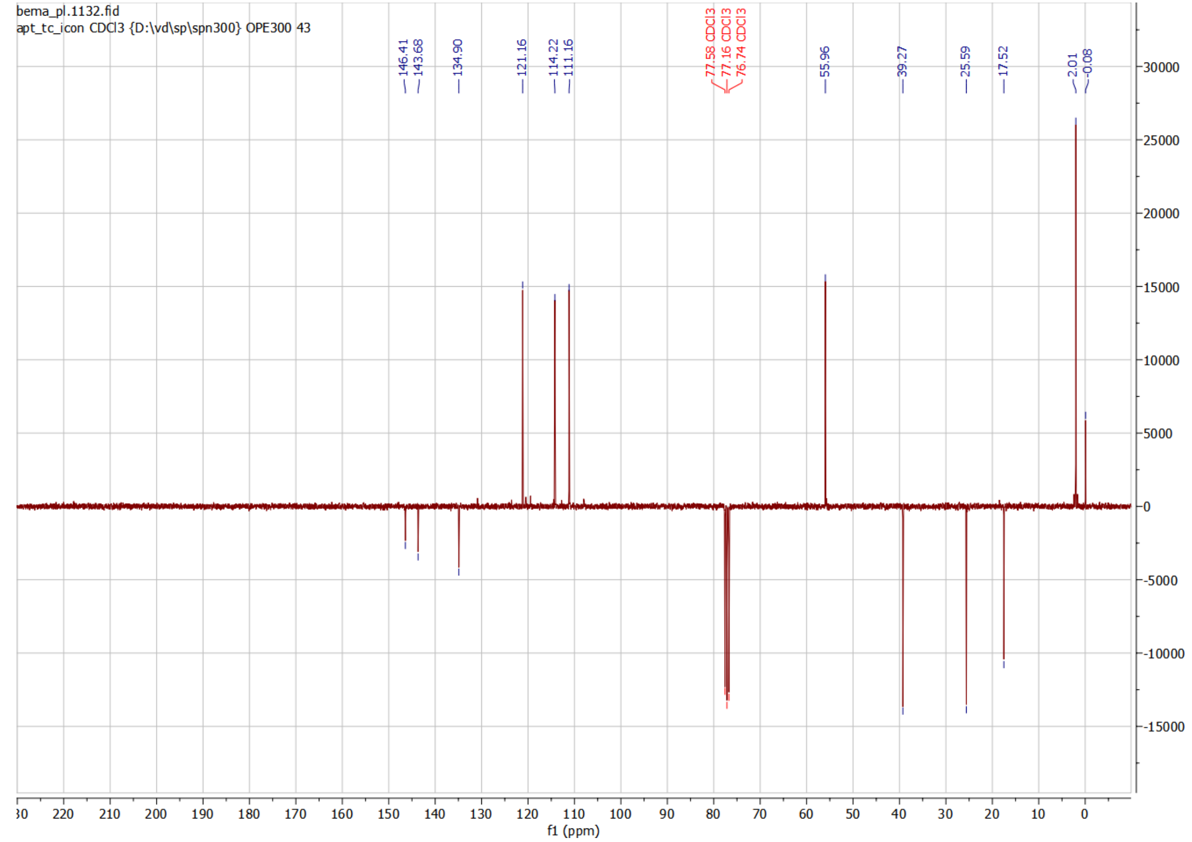
5.9. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ga



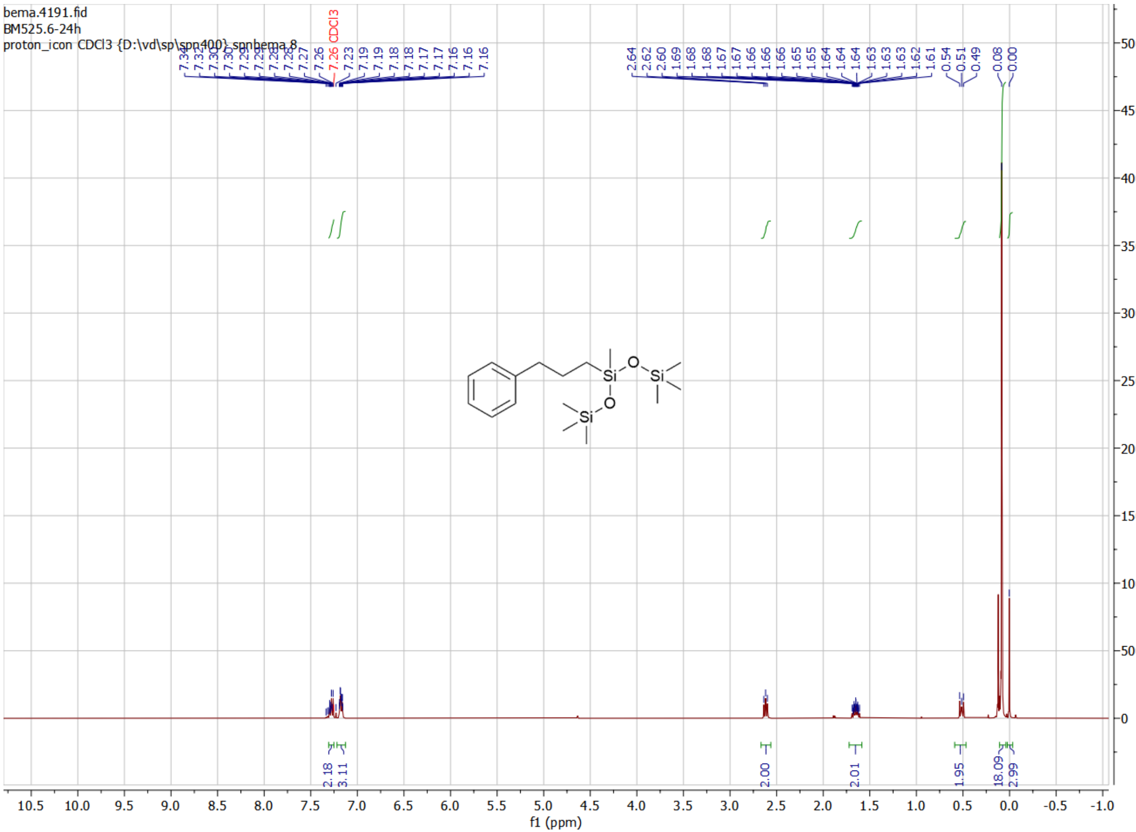


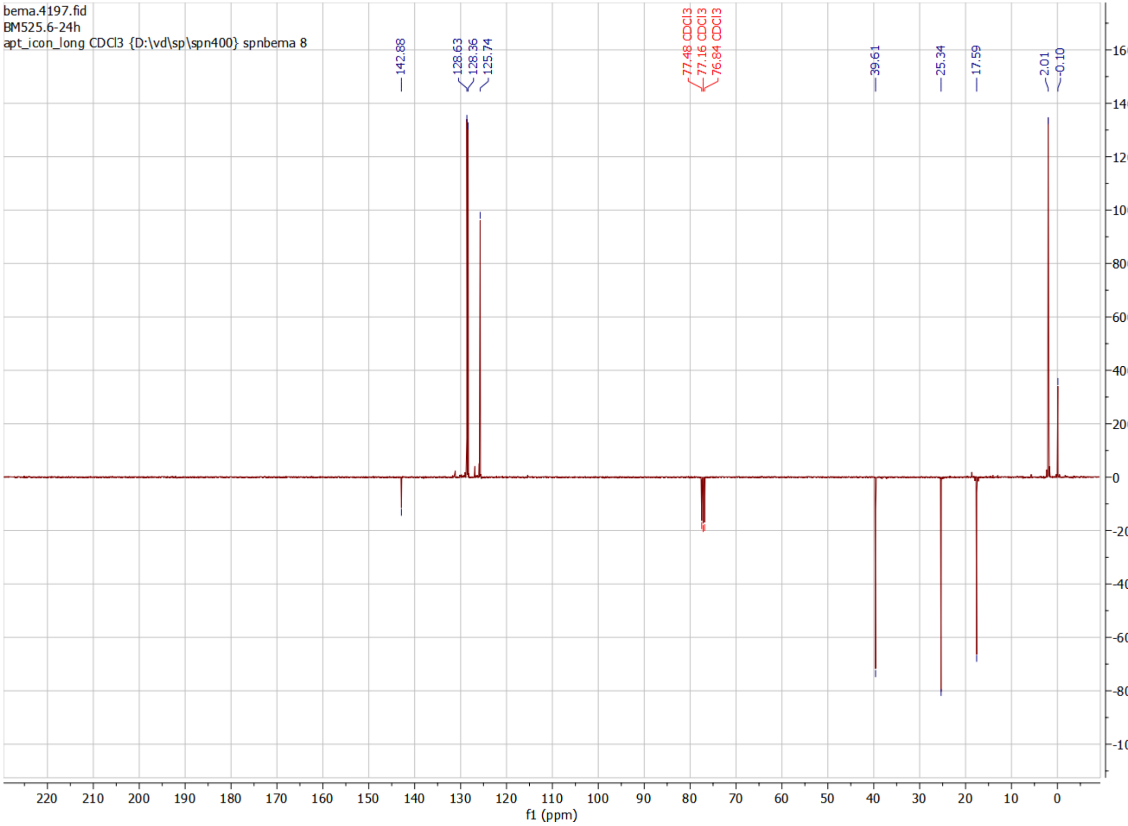
5.10. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ha



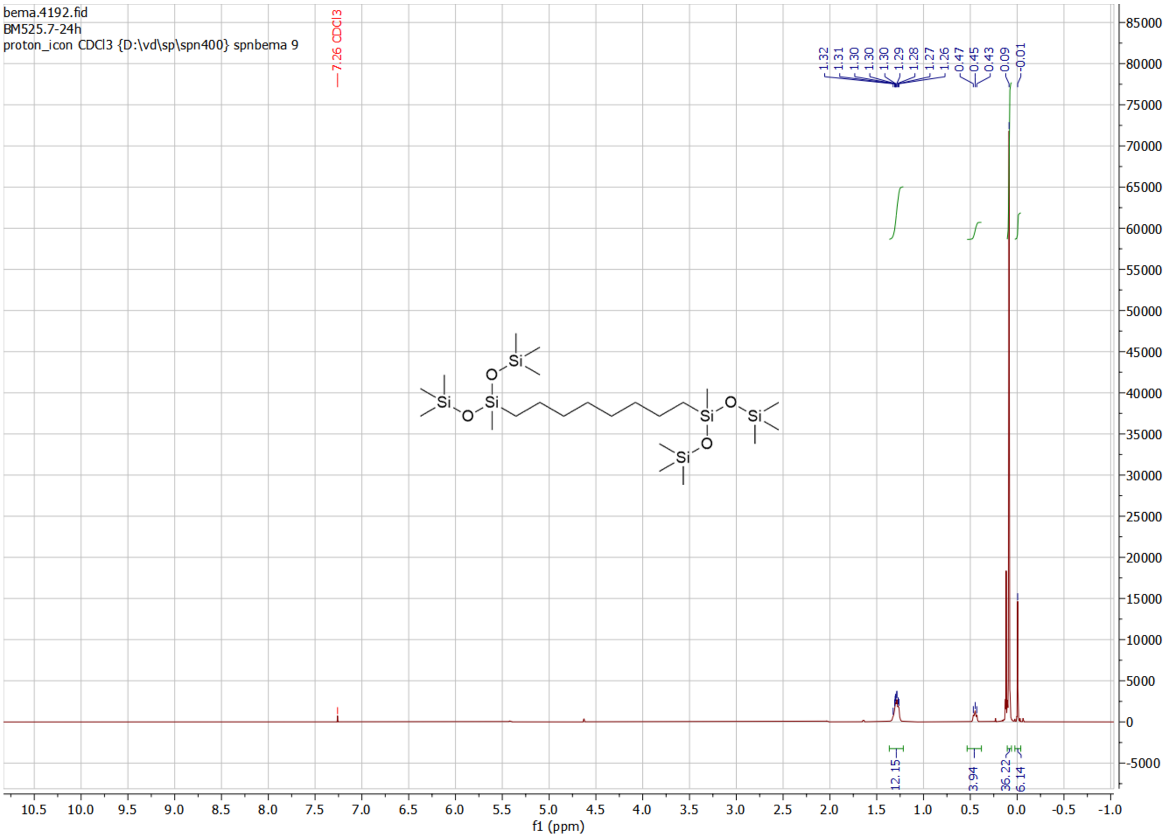


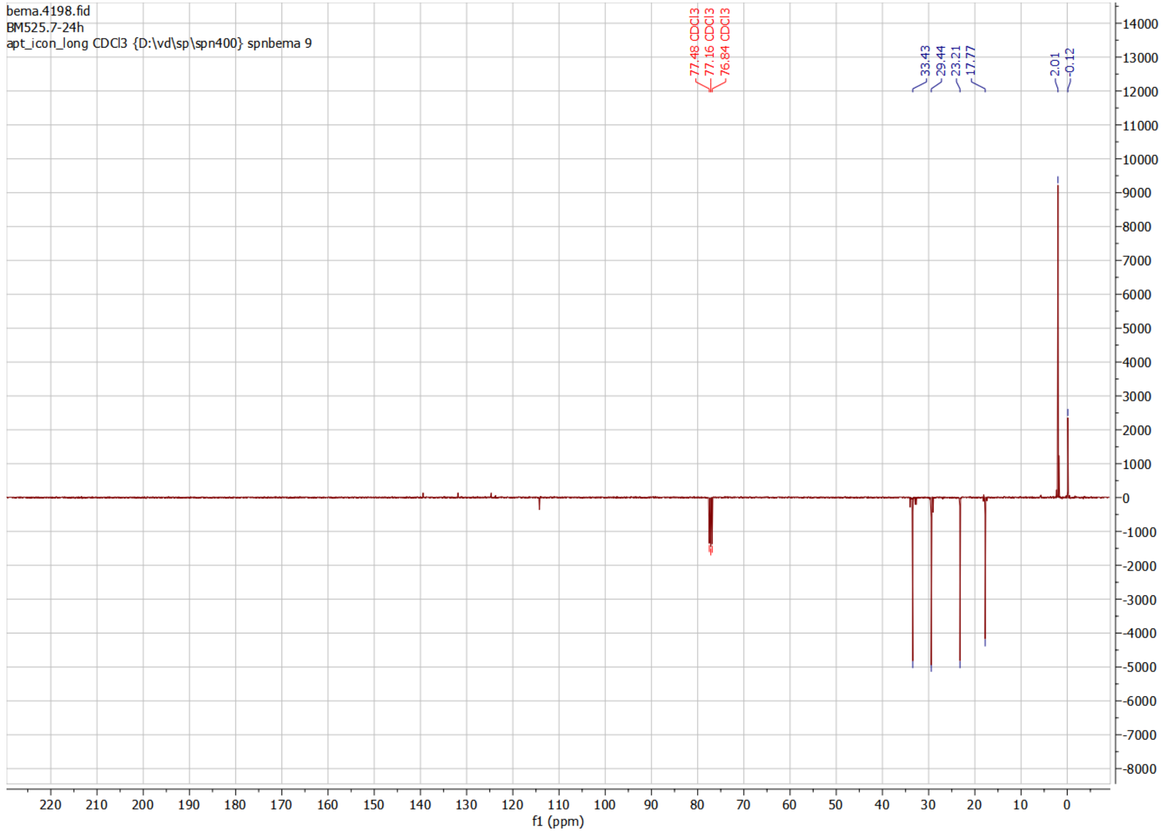
5.11. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ia



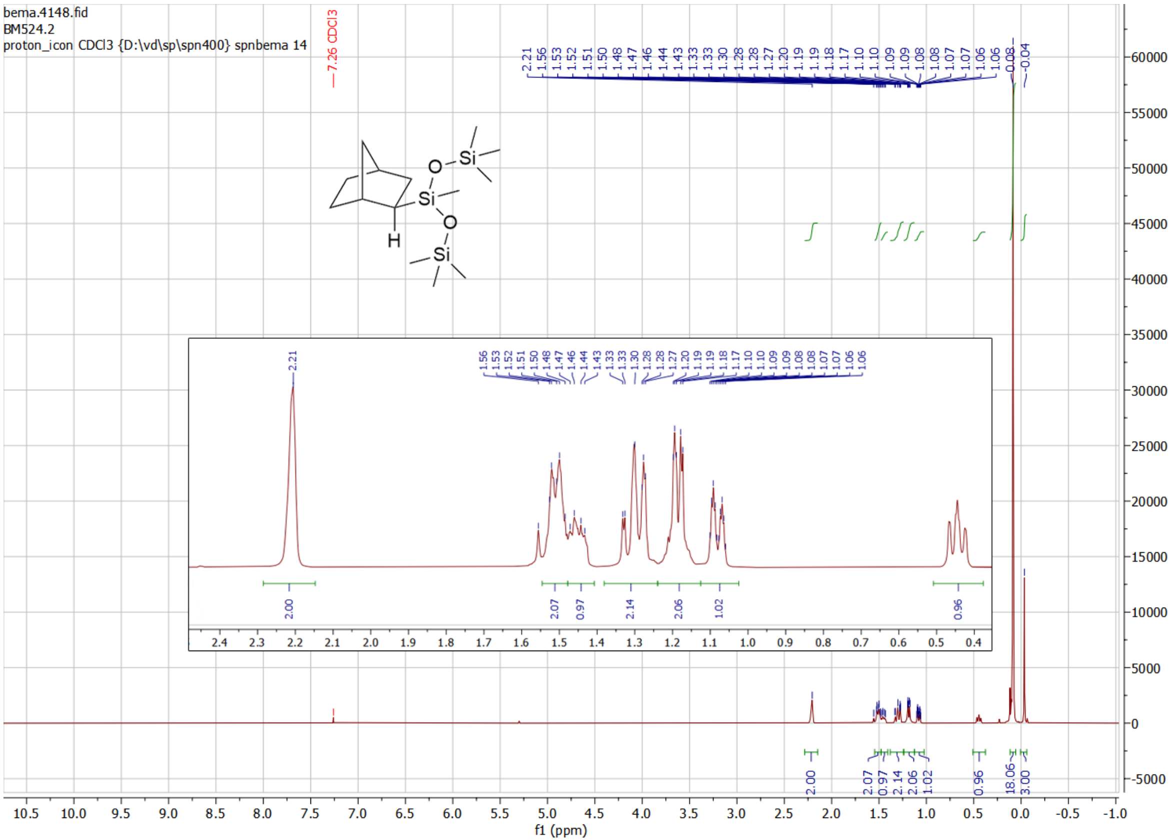


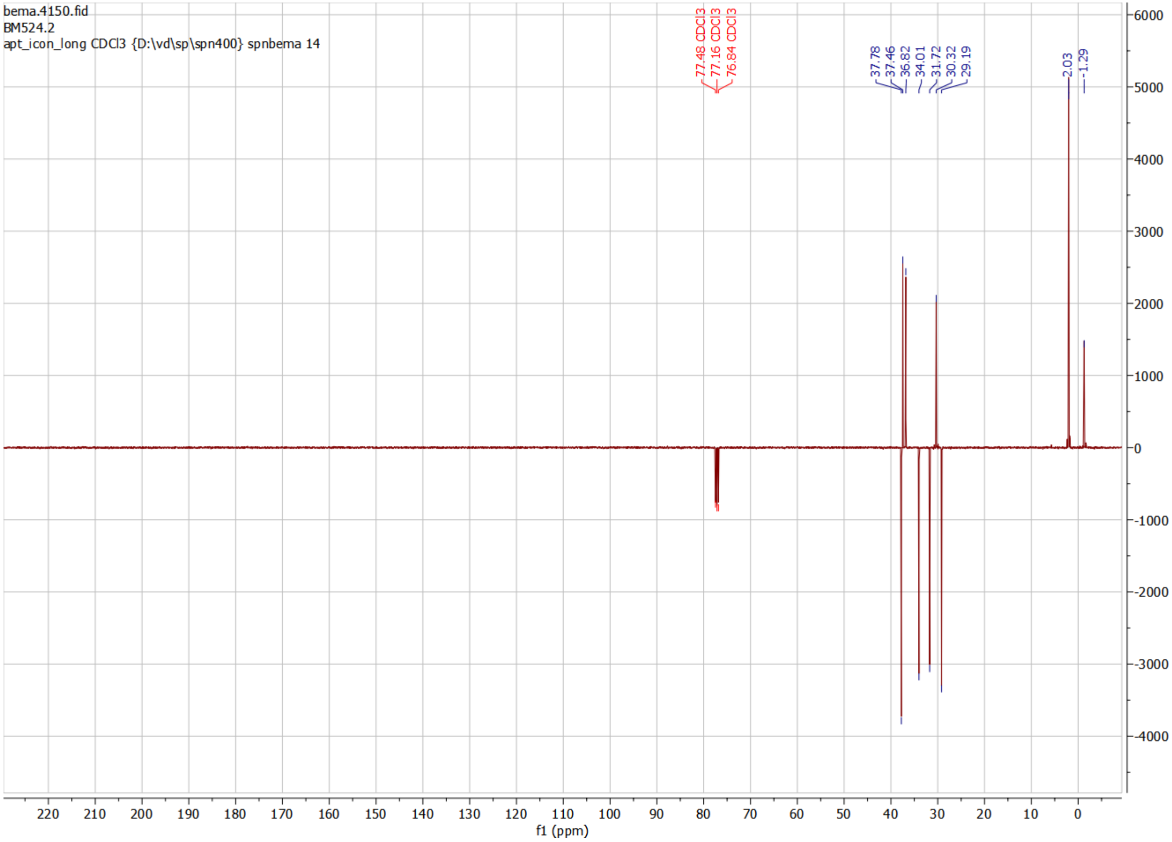
5.12. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ja



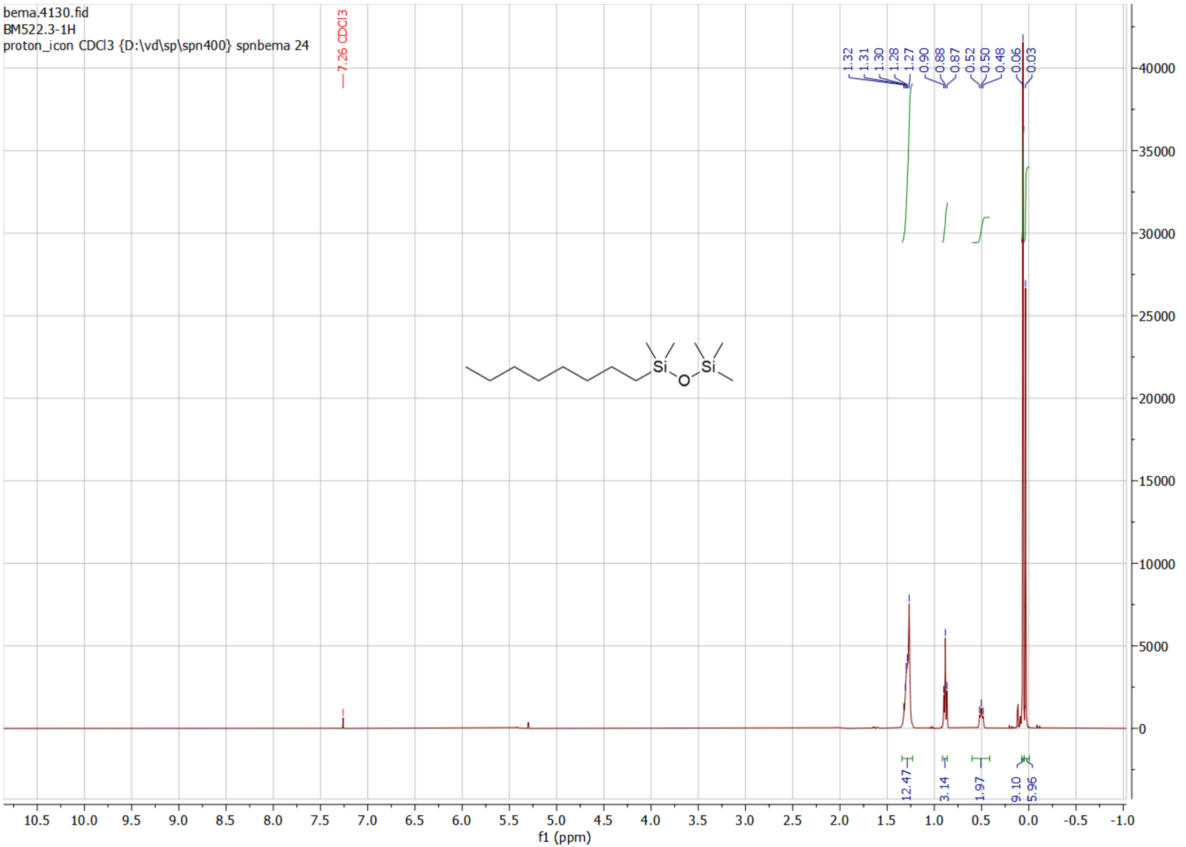


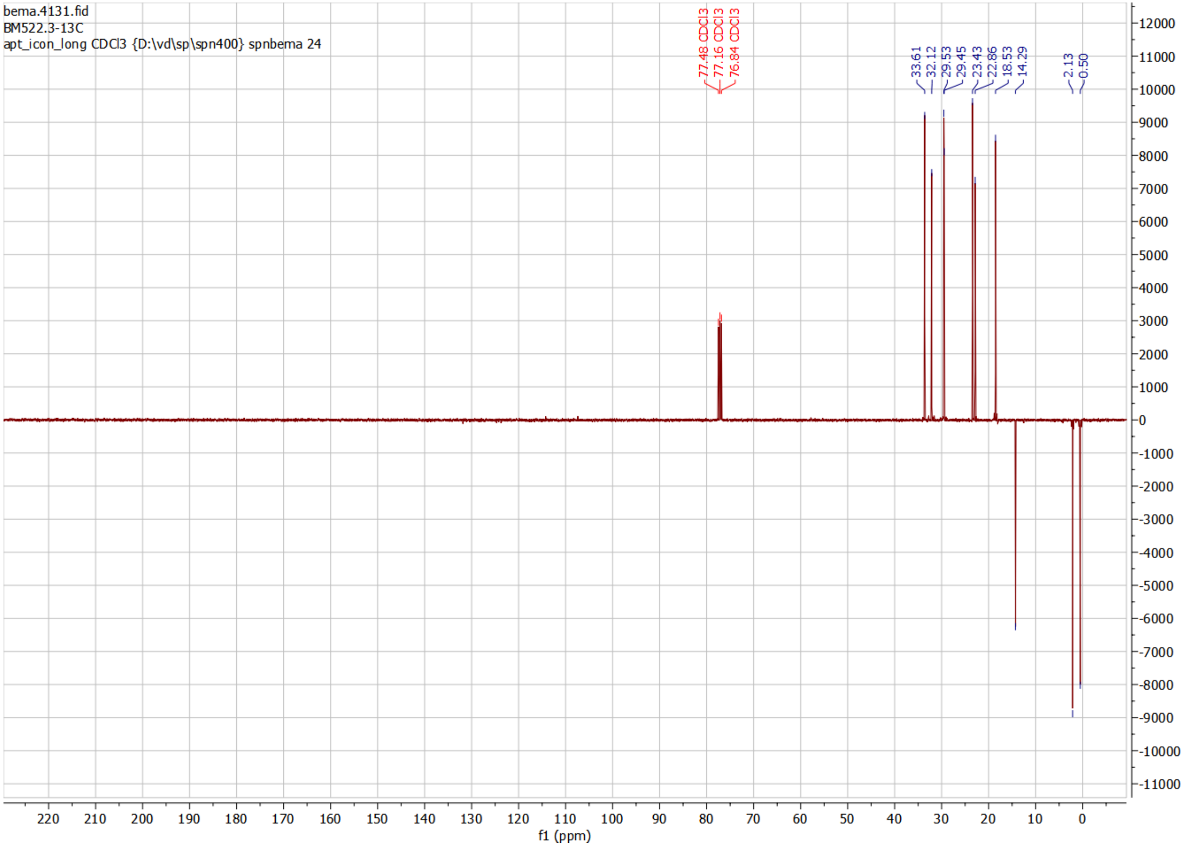
5.13. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ka



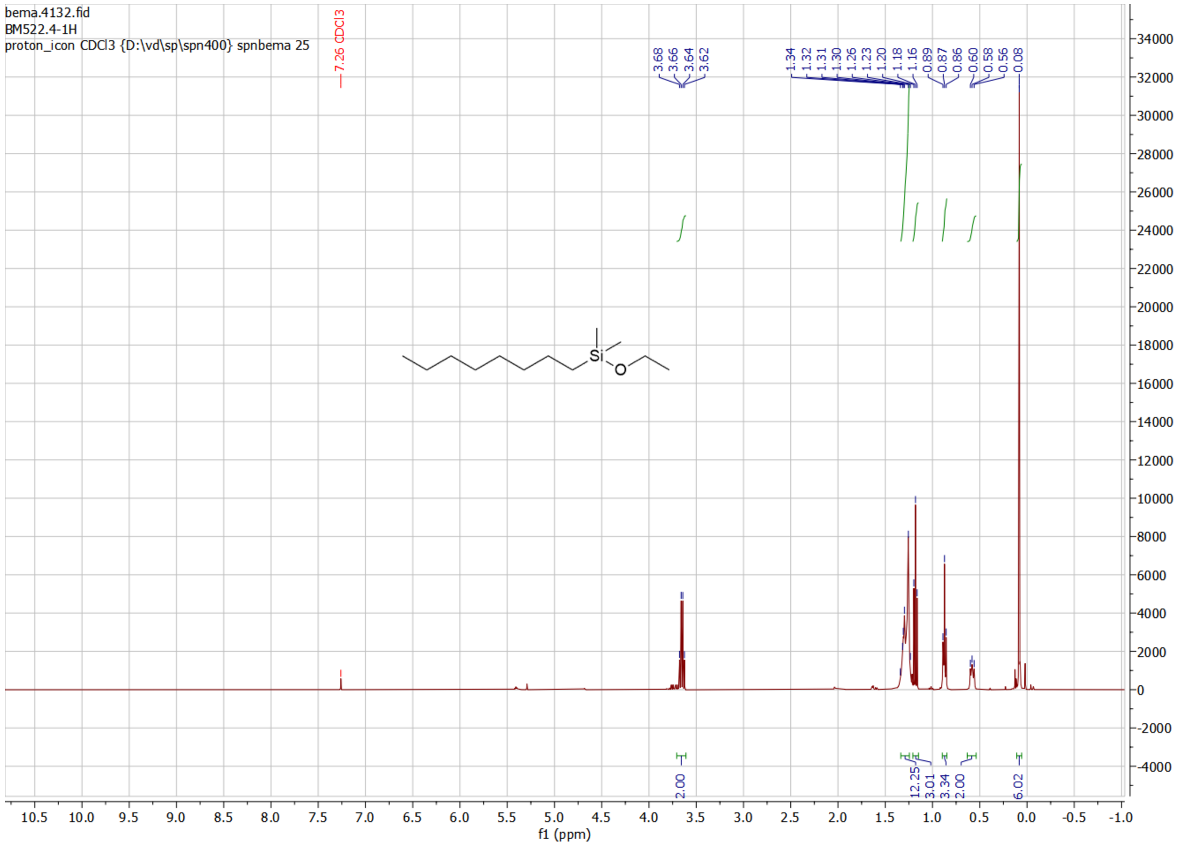


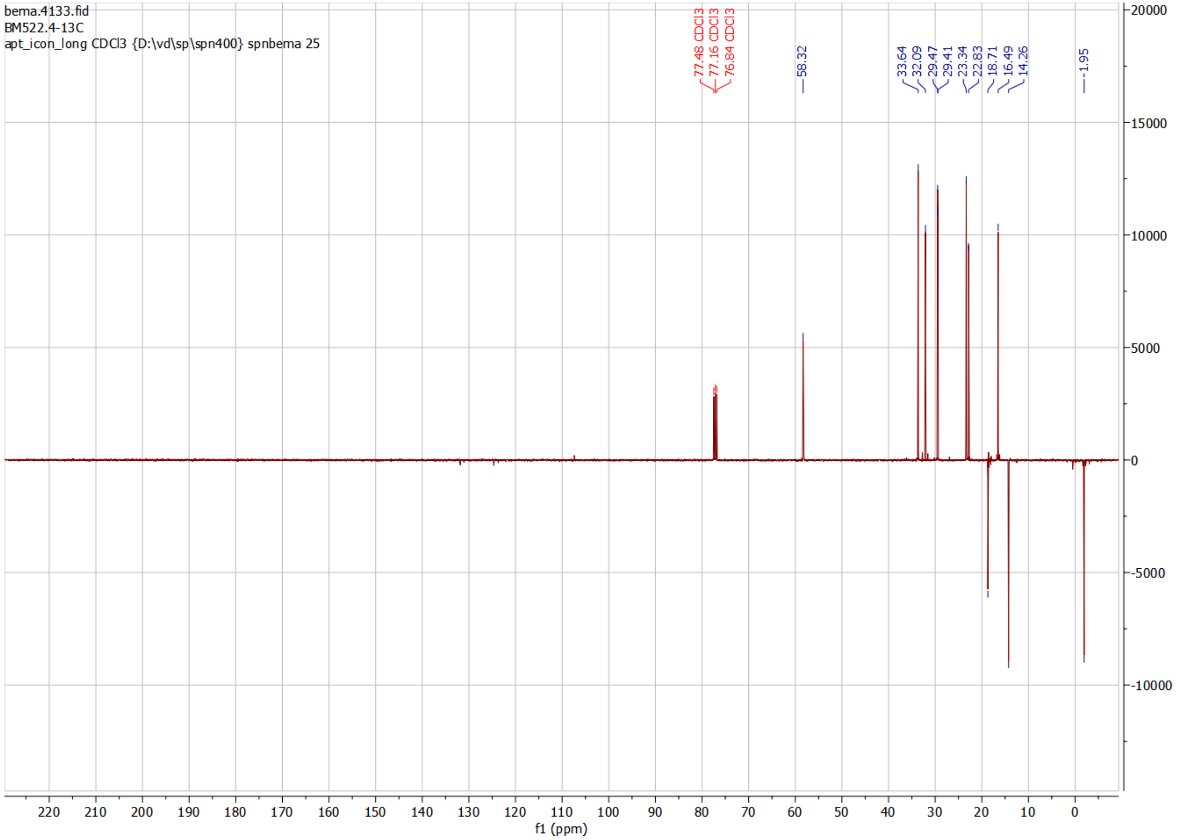
5.14. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ab



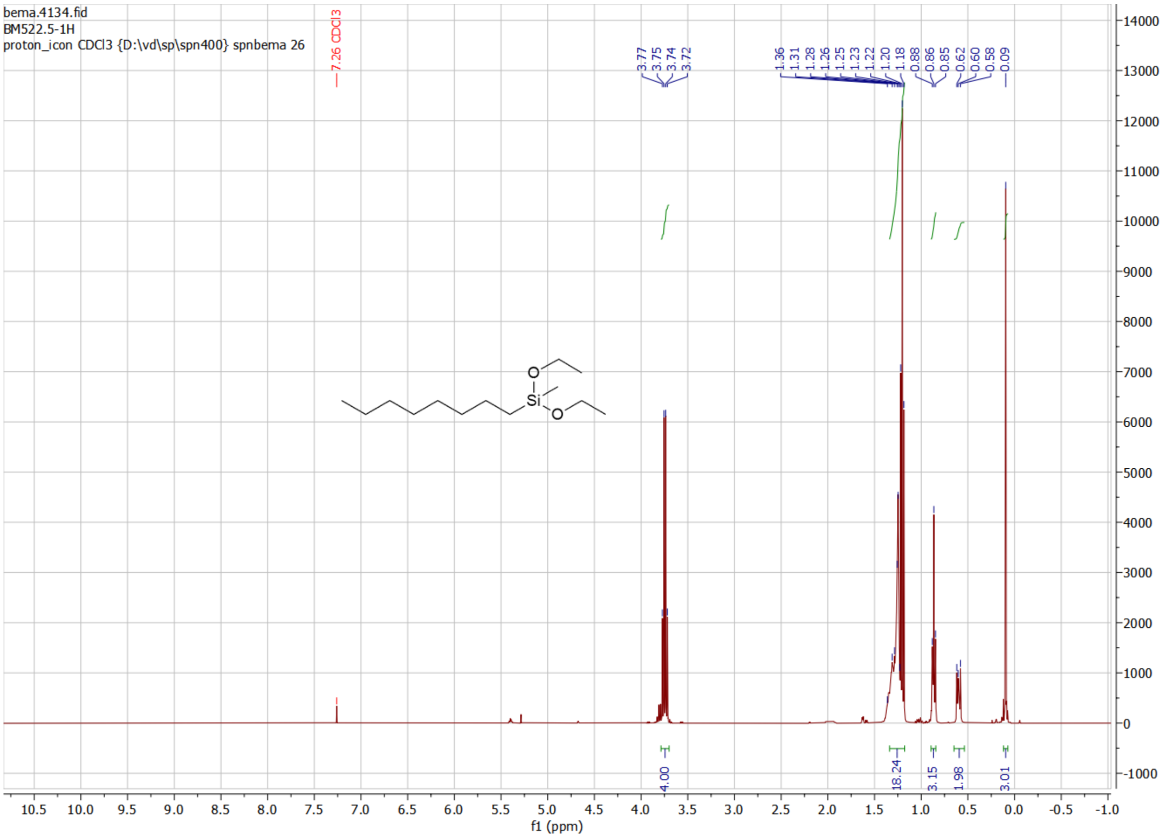


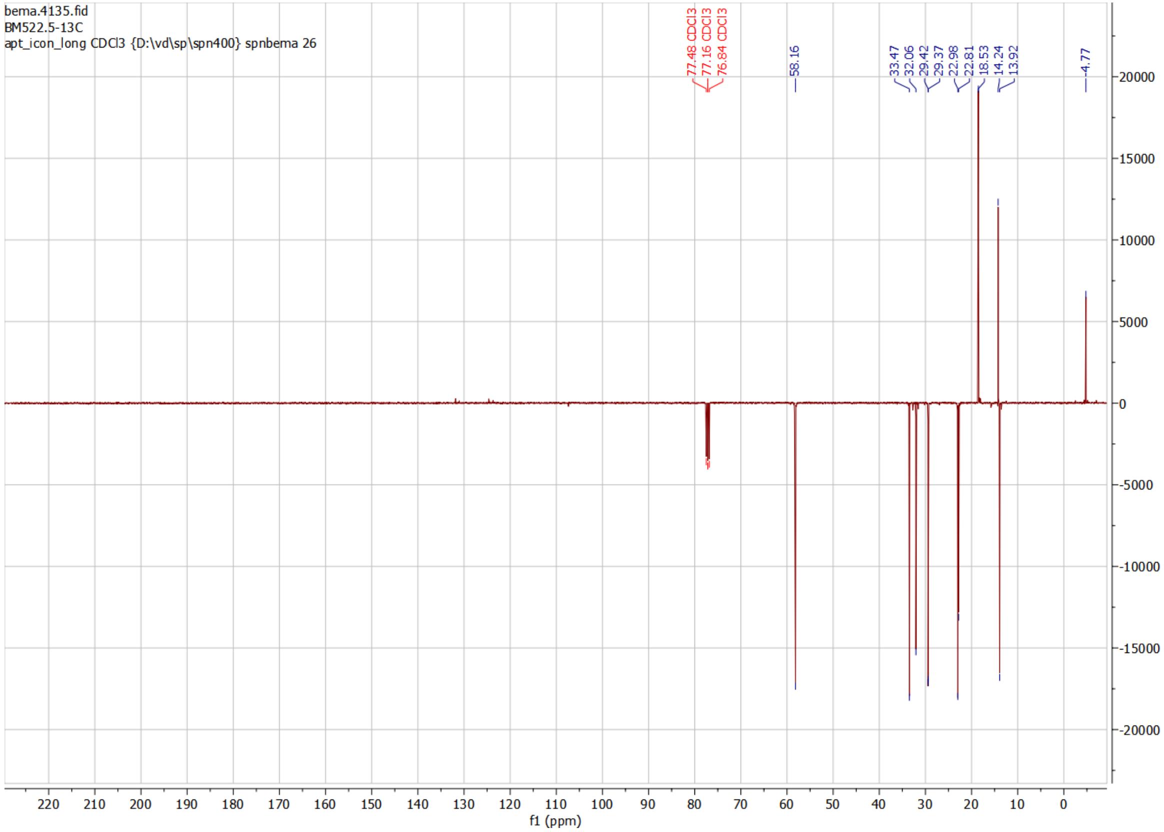
5.15. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ac



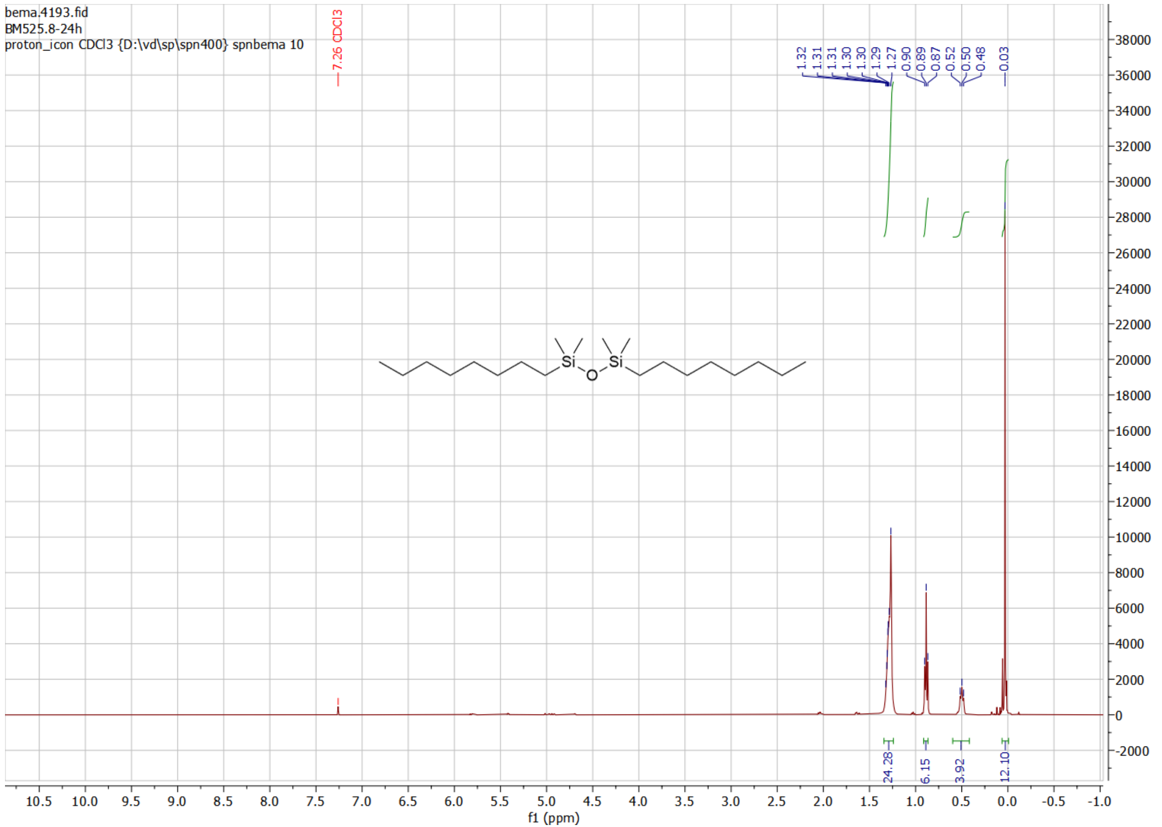


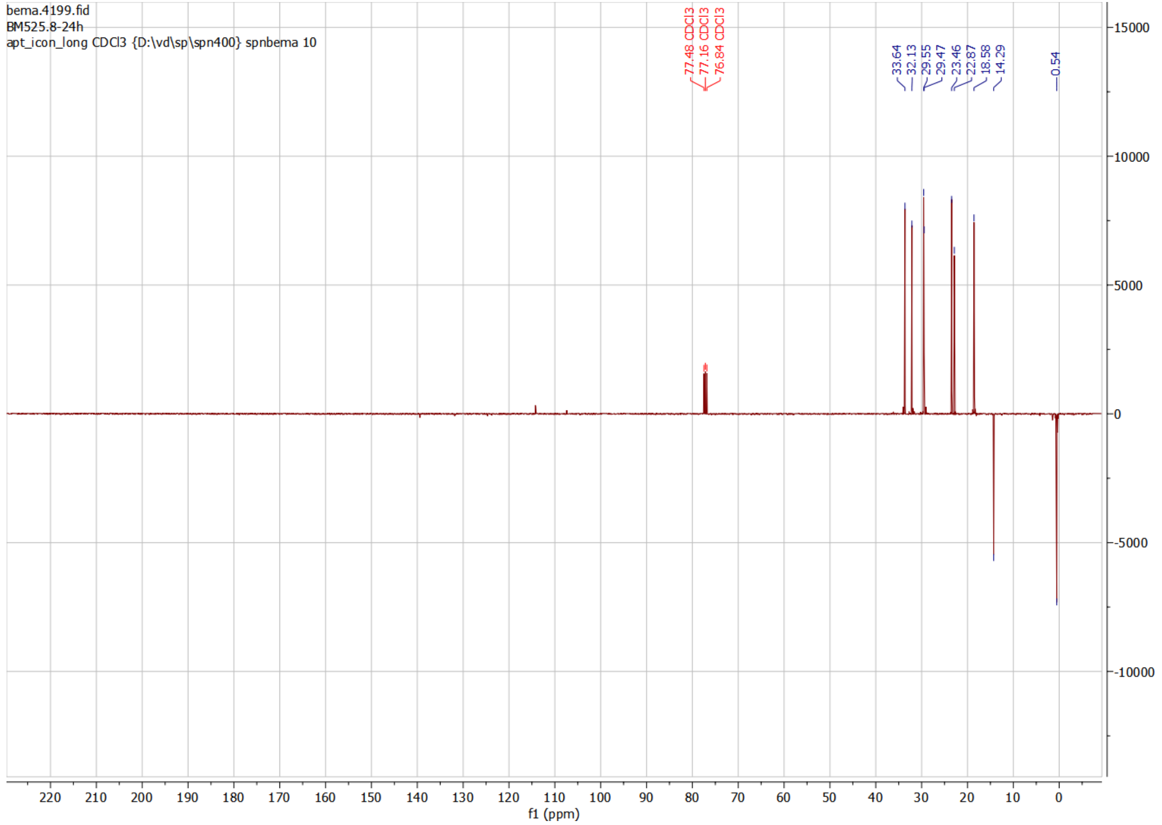
5.16. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ad



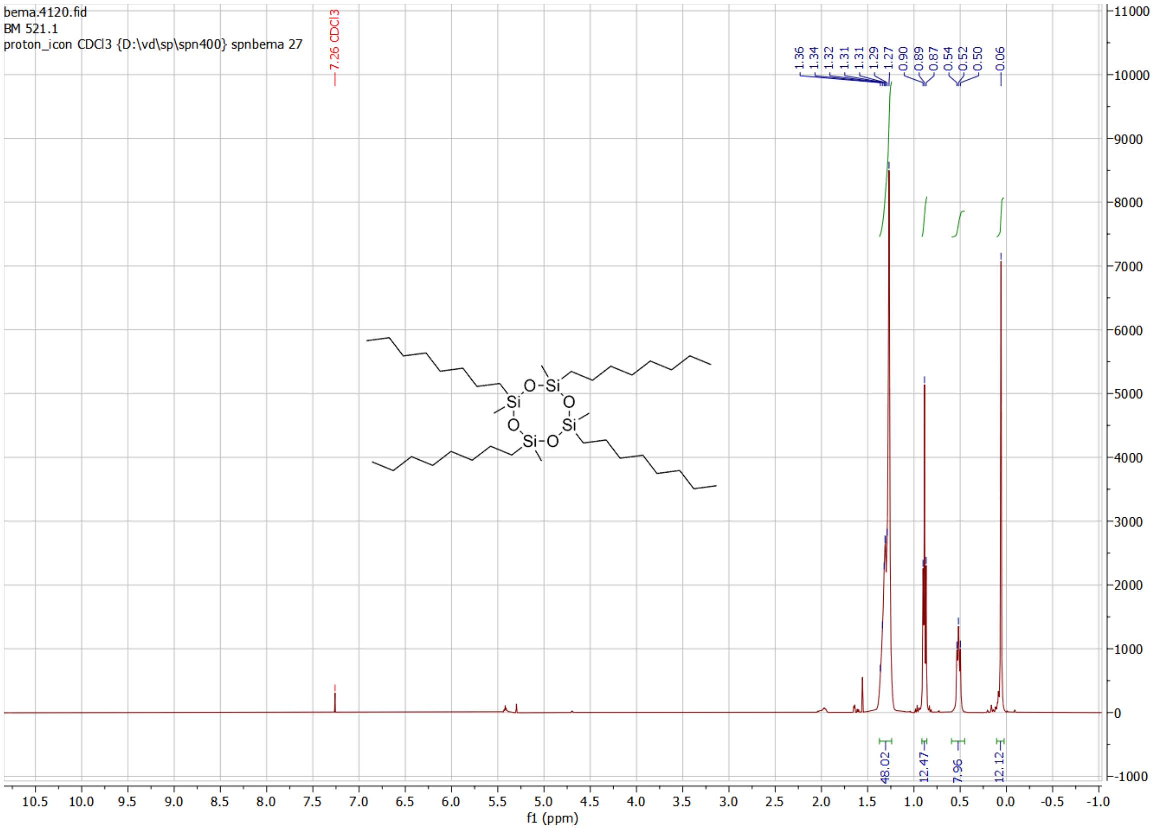


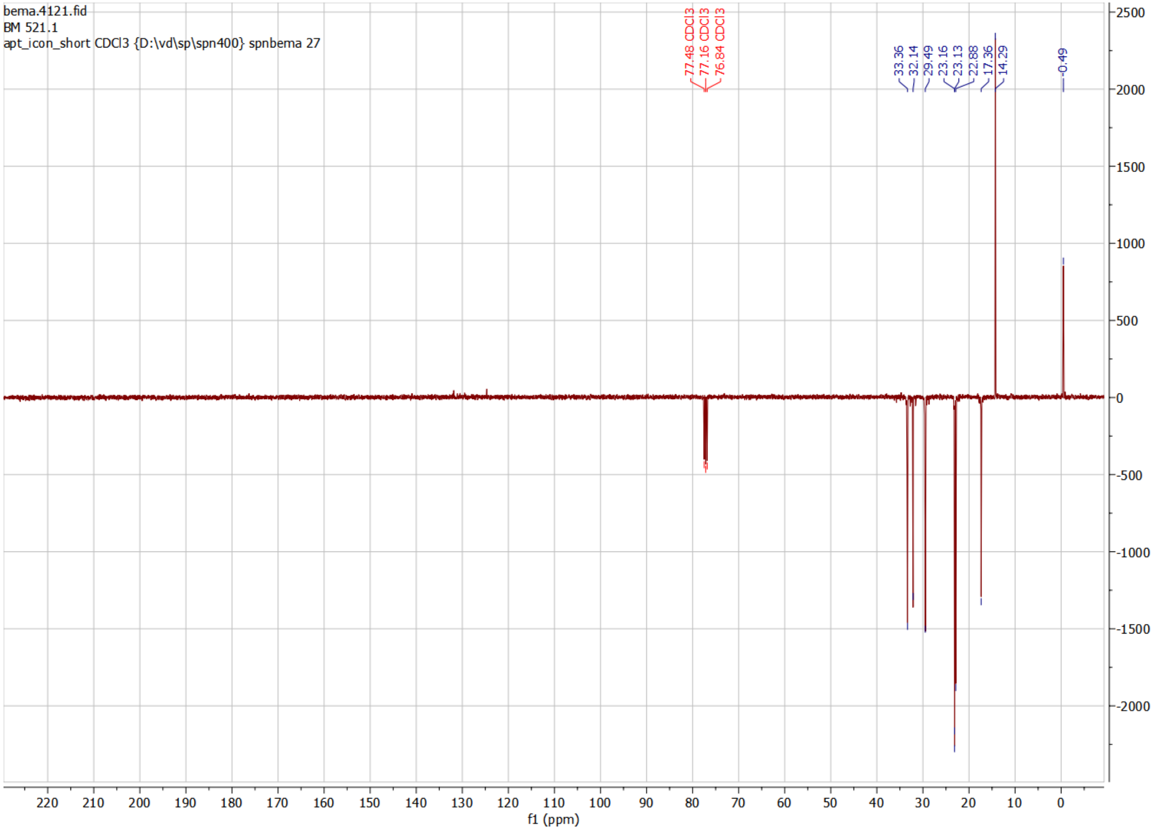
5.17. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ae



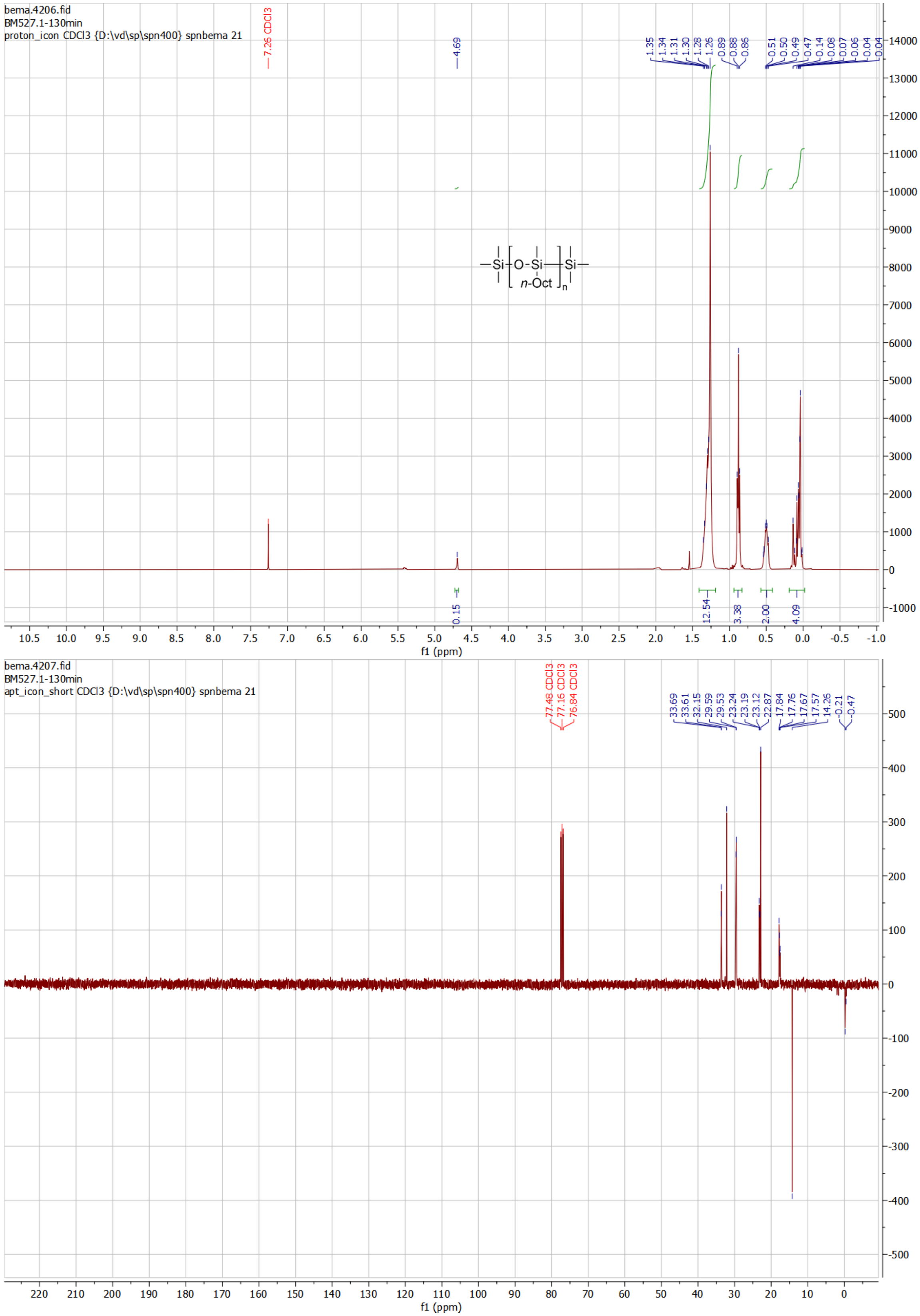


5.18. ^{1}H and ^{13}C{^{1}H} apt NMR of 4af





5.19. ^{1}H and ^{13}C{^{1}H} apt NMR of 4ag



6. Author contributions

Benon P. Maliszewski: conducted the experimental work; wrote and edited the manuscript.

Eleonora Casillo: conducted the experimental work.

Perrine Lambert: conducted the experimental work.

Fady Nahra: supervised the experimental work; wrote and edited the manuscript.

Catherine S. J. Cazin: supervised the work; wrote and edited the manuscript; secured funding.

Steven P. Nolan: concept originator; supervised project; wrote and edited the manuscript; secured funding.

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