

Supporting Information

Arylsilylation of Electron-Deficient Alkenes via Cooperative Photoredox and Nickel Catalysis

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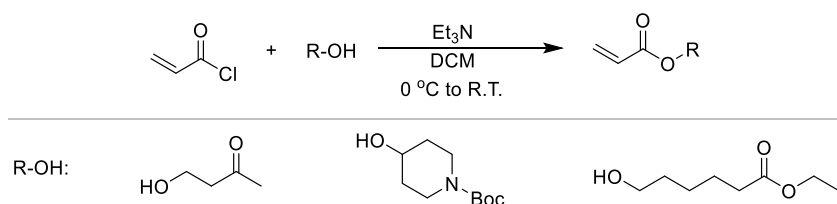
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1. General

All the reactions were performed under an inert N₂ (g) atmosphere and in dry reaction tubes. 1, 4-dioxane was purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) and transferred to a nitrogen filled glovebox without exposure to air. CDCl₃ were purchased from Cambridge Isotope Laboratories, Inc. and used directly. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. ¹H and ¹³C NMR spectra were recorded at 293 K on Bruker Advance 400 spectrometers. ¹H NMR chemical shifts were referenced to residual solvent as determined relative to Me₄Si (δ = 0 ppm) or CHCl₃ (δ = 7.26 ppm). The ¹³C (CPD) chemical shifts were reported in ppm relative to the carbon resonance of CDCl₃ (77.16 ppm). The data for NMR spectra were reported as follows: chemical shifts (δ) were reported in ppm, and coupling constants (*J*) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad spectrum. GC and GC-MS measurements were conducted on an Agilent Technologies 7890B GC system equipped with a 5977B mass detector. High-resolution mass (HRMS) measurements were conducted at the EPFL ISIC mass spectrometry service with a Micro Mass QTOF with Electrospray ionization (ESI). Single X-ray diffraction measurements were carried out on CrysAlisPro 1.171.40.53 (Rigaku Oxford Diffraction, 2019) with CuK_α radiation. Fluorescence quenching experiment was conducted on Varian Cary Eclipse machine. Blue LED type is A160WE Tuna Blue from Kessil Company. The fan to control the reaction temperature is Sonnenkönig Vind (Table Fan, 35W). The products were isolated with preparation thin-layer chromatography with TLC Silica gel 60 F₂₅₄ from Merck KGaA, Darmstadt, Germany or column chromatography filled with silica gel from SiliaFlash[®] P60 (40-60 μm, 230-400 mesh). Tris(trimethylsilyl)silane was from Fluorochem Company and methyl acrylate was from TCI Chemical Company. Sodium carbonate was from Sigma-Aldrich. Bis(1,5-cyclooctadiene)nickel(0) was from Strem Company. [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ was from Sigma-Aldrich.

2. Preparation of substrates.

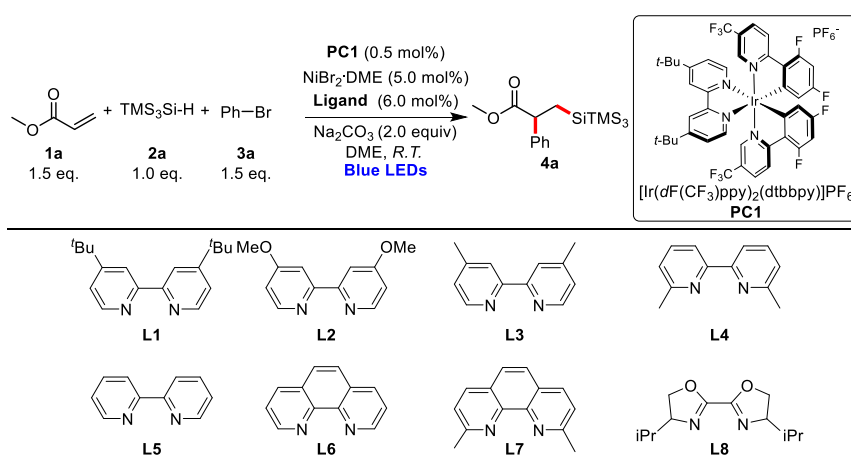
Substrates **1d**,^[1] **1e**^[2] and **1f**^[2] were prepared according to related reported procedures.



Scheme S1. Substrate preparation

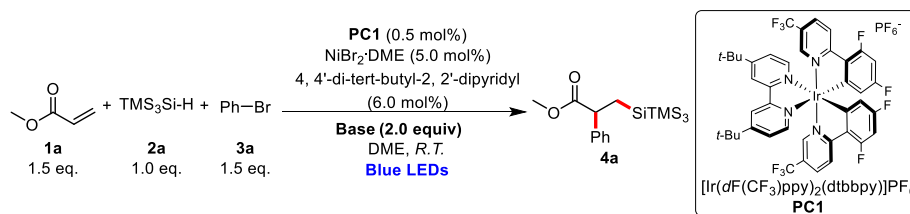
3. Screening of conditions

Table S1. Screen of ligands.^[a, b]



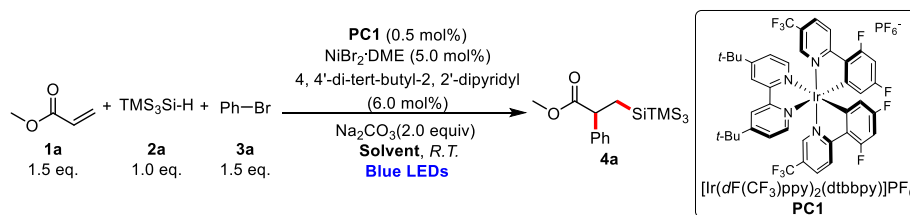
Entry	Ligand	Yield (%)
1	L1	15
2	L2	<5
3	L3	8
4	L4	<5
5	L5	<5
6	L6	<5
7	L7	<5
8	L8	<5

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. [b] Yields were determined by GC-FID analysis with dodecane as internal standard. TMS = trimethylsilyl, DME = dimethoxyethane, dtbbpy = 4, 4'-di-tert-butyl-2, 2'-dipyridyl, LED = light emitting diode, PC = photoredox catalyst.

Table S2. Screen of bases.^[a, b]

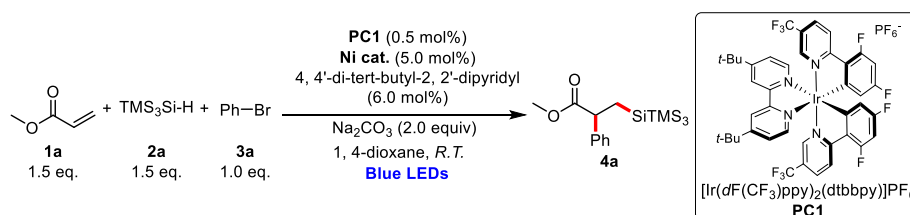
Entry	Base	Yield (%)
1	LiOMe	10
2	CS ₂ CO ₃	<5
3	LiO ^t Bu	<5
4	NaO ^t Bu	<5
5	K ₂ CO ₃	<5
6	K ₃ PO ₄	<5
7	NaOMe	<5
8	Na ₂ CO ₃	15

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. [b] Yields were determined by GC-FID analysis with dodecane as internal standard. TMS = trimethylsilyl, DME = dimethoxyethane, dtbbpy = 4,4'-di-tert-butyl-2,2'-dipyridyl, LED = light emitting diode, PC = photoredox catalyst.

Table S3. Screening of solvents.^[a, b]

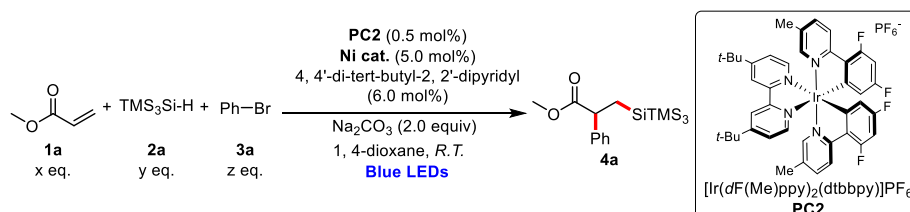
Entry	Solvent	Yield (%)
1	CH ₃ CN	12
2	^t BuOMe	<5
3	Tetrahydrofuran	31
4	Dimethylacetamide	8
5	1,4-Dioxane	54
6	Trifluorotoluene	<5
7	Diethyl ether	<5
8	Methyl cyclopentyl ether	<5

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. [b] Yields were determined by GC-FID analysis with dodecane as internal standard. TMS = trimethylsilyl, DME = dimethoxyethane, dtbbpy = 4,4'-di-tert-butyl-2,2'-dipyridyl, LED = light emitting diode, PC = photoredox catalyst.

Table S4. Screen of nickel salts.^[a, b]

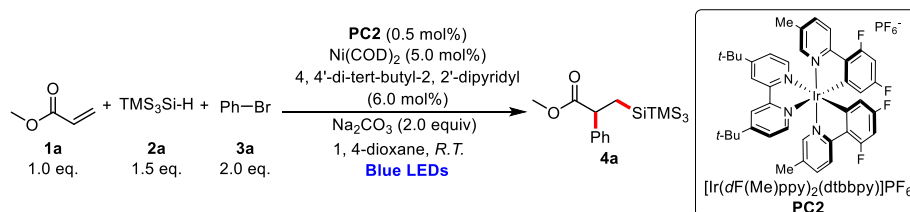
Entry	Ni salt	Yield (%)
1	$\text{NiCl}_2\cdot\text{DME}$	31
2	$\text{Ni}(\text{acac})_2$	35
3	$\text{Ni}(\text{COD})_2$	65
4	$\text{NiCl}_2\cdot\text{diglyme}$	39
5	$\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$	16
6	$\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	27

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. [b] Yields were determined by GC-FID analysis with dodecane as internal standard. TMS = trimethylsilyl, DME = dimethoxyethane, dtbbpy = 4, 4'-di-tert-butyl-2, 2'-dipyridyl, acac = acetylacetonate, COD = 1, 5-cyclooctadiene, diglyme = bis(2-methoxyethyl) ether, LED = light emitting diode, PC = photocatalyst.

Table S5. Screen of substrate ratios.^[a, b]

Entry	Ni cat.	x : y : z	Yield (%)
1	$\text{Ni}(\text{COD})_2$	1.5 : 1.5 : 1.0	76
2	$\text{Ni}(\text{COD})_2$	1.5 : 1.0 : 1.5	52
3	$\text{Ni}(\text{COD})_2$	1.0 : 1.5 : 1.5	64
4	$\text{Ni}(\text{COD})_2$	1.0 : 1.5 : 2.0	88 (80)
5 ^c	$\text{Ni}(\text{COD})_2$	1.0 : 1.5 : 2.0	82

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. [b] Yields were determined by GC-FID analysis with dodecane as internal standard. [c] 2.5 mol% Ni and 3.0 mol% ligand were used. TMS = trimethylsilyl, DME = dimethoxyethane, dtbbpy = 4, 4'-di-tert-butyl-2, 2'-dipyridyl, LED = light emitting diode, PC = photoredox catalyst.

Table S6. Control experiments.^[a, b]

Entry	Variation	Yield (%)
1	Without Ni cat. and ligand	N.P.
2	Without photocatalyst and light	N.P.
3	Without photocatalyst, but with light	N.P.
4	Replace Ph-Br with Ph-Cl	N.P.
5	Replace Ph-Br with Ph-I	<5%
6	Without Na ₂ CO ₃	24%
7	With 1.0 equiv TBAB	77%

[a] The reaction scale was 0.2 mmol. Loadings and substrate ratios were shown in the Table. Volume of solvent was 2 mL. Reactions were conducted under nitrogen at room temperature for 12 hours. [b] Yields were determined by GC-FID analysis with dodecane as internal standard. TMS = trimethylsilyl, dtbbpy = 4, 4'-di-tert-butyl-2, 2'-dipyridyl, LED = light emitting diode, PC = photoredox catalyst.

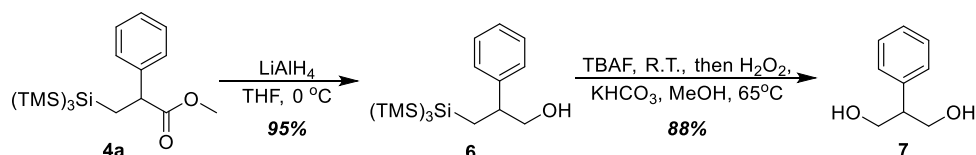
4. Substrate scope and further transformations

General procedures for exploration of substrate scope: In a glovebox, Ni(COD)₂ (2.8 mg, 0.01 mmol, 5 mol%) and 4,4'-di-tert-butyl-2,2'-dipyridyl (3.2 mg, 0.012 mmol, 6 mol%) were added to a dry vial with a magnetic stir, then 1, 4-dioxane (2.0 mL) was added to the above vial through a syringe. The reaction mixture was stirred for 10 minutes until no solid remained and the solution became dark purple. To another vial with a magnetic stir, Na₂CO₃ (42.4 mg, 0.40 mmol) and [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ (1.0 mg, 0.001 mmol, 0.5 mol%) were added in a glovebox. If a substrate is solid, then it was added at this time. After that, the Ni (0) complex solution was added to the vial containing the Ir photocatalyst, followed by addition of bromide (0.4 mmol, 2.0 equiv). The reaction mixture turned in orange to wine red colour. Then TMS₃SiH (93 μL, 0.3 mmol, 1.5 equiv) and alkene (0.2 mmol, 1.0 equiv) were added. The vial was capped and took out from the glovebox. Electrical tape was used to seal the cap to make sure no air will get inside of the vial. The vial was then irradiated with two blue LEDs in a distance of 5 cm on a reactor with a small table fan to cool down the temperature. Normally, two reaction vials can share two blue LEDs. If several reactions are run simultaneously, then a same nickel (0) complex solution can be used for them.

After 12 hours, the reaction was stopped and quenched by 5.0 mL of ethyl acetate. The solution was analyzed by GC-MS-FID with dodecane as internal standard. The mixture was filtered through a pad of silica gel eluted by ethyl acetate. The solvent was removed using a rotary evaporator. The arylsilylation product was isolated by column chromatography or preparation thin-layer chromatography with silica gel.

Procedures for 5.0 mmol scale synthesis of 4I: In a glovebox, Ni(COD)₂ (70 mg, 0.25 mmol, 5 mol%) and 4,4'-di-tert-butyl-2,2'-dipyridyl (80 mg, 0.30 mmol, 6 mol%) were added to a dry vial with a magnetic stir, then 1, 4-dioxane (10.0 mL) was added to the above vial through a syringe. The mixture was stirred for 15 minutes until no solid remained and the solution became dark purple. To a 200 mL Schlenk flask with a magnetic stir, methyl 4-bromobenzoate (**3I**, 2.15 g, 10 mmol, 2.0 equiv), Na₂CO₃ (1.06 g, 10 mmol, 2.0 equiv) and [Ir(*d*F(Me)ppy)₂(dtbbpy)]PF₆ (25 mg, 0.025 mmol, 0.5 mol%) were added in a glovebox. 40 mL of 1, 4-dioxane was then added to the Ir solution. The Ni (0) complex solution was then add to the Schlenk flask with stirring. The reaction mixture became orange after one minute. TMS₃SiH (**2a**, 2.32 mL, 7.5 mmol, 1.5 equiv) and methyl acrylate (**1a**, 0.45 mL, 5.0 mmol, 1.0 equiv) were added to the above mixture. The flask was capped and took out from the glovebox. Electrical tape was used to seal the cap to make sure no air will get inside of the flask. The flask was then irradiated with two blue LEDs in the distance of 5 cm on a reactor with a small table fan to cool down the temperature

After 24 hours, the reaction was stopped and quenched by 20 mL of ethyl acetate. The solution was analyzed by GC-MS-FID. The mixture was filtered through a pad of silica gel eluted by ethyl acetate. The solvent was removed using a rotary evaporator. The arylsilylation product **4I** was isolated by column chromatography with silica gel. 1.70 g product was obtained with a yield of 73%.

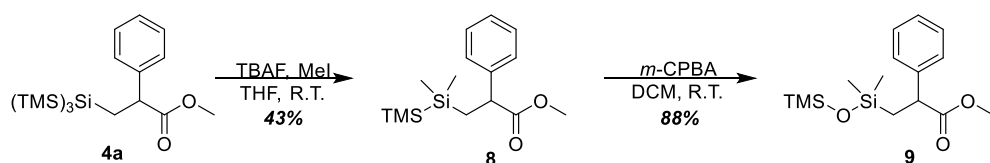


Scheme S2. Synthesis of 2-phenyl-1, 3-propanediol from **4a**

Procedures for further transformation to compound **6** and **7**:

Synthesis of 6: An arylsilylation product (**4a**, 52.3 mg, 0.127 mmol) was dissolved in dry THF (2.0 mL) under the protection of N₂. 32 μL of 4.0 M LiAlH₄ solution in diethyl ether was added to this solution at 0 °C. After the disappearing of substrate **4a** through TLC monitor, the reaction was quenched with drops of water at 0 °C. Then the mixture was filtered through a pad of silica gel eluted by ethyl acetate. The solvent was removed using a rotary evaporator. **6** was isolated by preparative thin-layer chromatography with silica gel. 46.2 mg product was obtained with a yield of 95%.

Synthesis of 7: This procedure was modified from a reported process.^[3] Substrate **6** (76.5 mg, 0.2 mmol, 1.0 equiv) was dissolved in 5 mL THF, then 1.2 mL of 1.0 M Bu₄NBr (TBAF) solution in THF(1.2 mmol, 6.0 equiv) was added to this solution at room temperature. Some gas evolved. After 5 minutes, 50% H₂O₂ (342 μL, 30.0 equiv) was added to the reaction mixture, followed by 5 mL MeOH and KHCO₃ (120 mg, 1.2 mmol, 6.0 equiv). After stirring at 60 °C for 12 hours, 10 mL 1.0 M sodium thiosulfate aqueous solution was added at room temperature to quench the reaction. The reaction mixture was extracted with ethyl acetate (20 ml × 3). The combined organic phase was dried by anhydrous Na₂SO₄, followed by evaporation of solvent and separation by preparative thin-layer chromatography with silica gel. 26.6 mg **7** was obtained in 88% yield.



Scheme S3. Synthesis of disilane and siloxane from **4a**

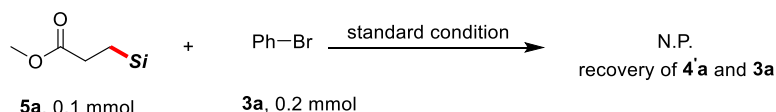
Procedures for transformation of **4a** to compounds **8** and **9**:

Synthesis of disilane **8**: Compound **4a** (0.93 g, 2.27 mmol) was added to 20 mL THF, followed by addition of MeI (6.45 g, 45.4 mmol, 20.0 equiv). A 1.0 M TBAF solution in THF (7.94 mL, 7.94 mmol, 3.5 equiv) was then added dropwise through syringe pump over 1.0 hour. After the disappearing of **4a** monitored by GC-MS, the mixture was diluted with 30 mL diethyl ether and filtered through a pad of silica gel eluted by diethyl ether. Then the solvent was evaporated using a rotary evaporator. 0.287 g **8** was isolated by column chromatography with silica gel; the yield was 43%.

Synthesis of siloxane **9**^[4]: compound **8** (59.4 mg, 0.2 mmol) was dissolved in 5 mL dichloromethane, then *meta*-chloroperoxybenzoic acid (77% purity, 180 mg) was added to the above mixture, followed by reaction at room temperature for 12 hours. The mixture was diluted with diethyl ether and filtered through a pad of silica gel eluted by diethyl ether. The solvent was evaporated using a rotary evaporator, 54.5 mg product **9** was isolated by preparation thin-layer chromatography with silica gel; the yield was 88%.

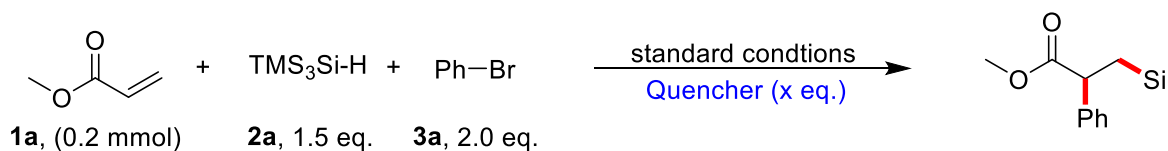
5. Mechanistic study

5.1. Control experiments



Scheme S4 Control experiment to exclude α -arylation **4'a**.

Procedure: In a glovebox, Ni(COD)₂ (2.8 mg, 0.01 mmol, 5 mol%) and 4,4'-di-tert-butyl-2,2'-dipyridyl (3.2 mg, 0.012 mmol, 6 mol%) were added to a dry vial with a magnetic stir, then 1, 4-dioxane (2.0 mL) was added to the above vial through a syringe, which was stirred for 10 minutes until no solid remained and the solution became dark purple. To another vial with a magnetic stir, Na₂CO₃ (21.2 mg, 0.20 mmol, 2.0 equiv) and [Ir(*d*F(Me)ppy)₂(dtbbpy)]PF₆ (0.5 mg, 0.0005 mmol, 0.5 mol%) were added in a glovebox. Compound **5a**^[5] (0.1 mmol) was dissolved in 1.0 ml 1, 4-dioxane in a glovebox in a vial. Then 1.0 ml Ni (0) complex solution and 1.0 ml solution of compound **5a** was added to the vial containing base and photoredox catalyst. After that, phenyl bromide **3a** (0.2 mmol, 2.0 equiv) was added and the vial was capped and took out from the glovebox. Electrical tape was used to further seal the cap to make sure no air will get inside of the vial. The vial was irradiated with two blue LEDs in the distance of 5 cm on a reactor with a small table fan to cool down the temperature. After 12 hours, the reaction was stopped and quenched by 5.0 mL of ethyl acetate. The solution was analyzed by GC-MS-FID with dodecane as internal standard. Only **5a** and **3a** observed in GC-MS.



Quencher = TEMPO,	x = 0.20, 57%; x = 0.80, 70%; x = 1.5, 0%.
Quencher = 1, 1-diphenylethene,	x = 0.20, 71%; x = 0.80, 51%; x = 1.5, 43%.

Scheme S5. Radical scavenger experiments

Procedure: the procedure is the same as the procedure for substrate scope, except that the addition of an appropriate amount of TEMPO or 1, 1-diphenylethene in the last step. After 12 hours, the reactions were quenched by ethyl acetate and analyzed by GC-MS-FID with dodecane as internal standard. The yields were determined by GC-FID analysis with dodecane as internal standard.

5.2. Light–dark interval experiments

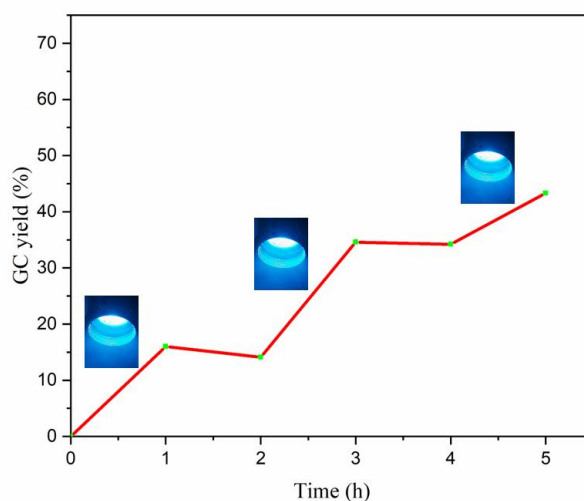


Figure S1. Light–dark interval experiments.

Procedure: The reaction was run similar with the standard procedure, except that 20 μL dodecane was added in the beginning. During the first hour, the reaction was irradiated with light. After one hour, 5 μL of the reaction mixture was extracted by micro syringe through the rubber on the cap. The sample was analyzed by GC-MS-FID. Then the vial was covered with aluminium foil on a normal reactor without light. After one hour, 5 μL reaction mixture was extracted by micro syringe again and analyzed by GC-MS-FID. During the third hour, the reaction was exposed to light, and 5 μL reaction mixture was extracted for analysis. During the fourth hour, the reaction was stirred under dark, and 5 μL reaction mixture was extracted for analysis again. During the fifth hour, the reaction was stirred under light, and the mixture was analyzed with GC-MS-FID. **Discussion:** The light–dark interval experiments cannot exclude the chain process totally, but from the above figure, we can see the light is essential to the generation of product. If there is some chain propagation after stopping of irradiation, its contribution to the product should be small.

5.3. Quantum yield measurement

For this experiment, the light is from Kessil Company (Kessil blue LED, A160 WE, 40 W). The incident photo flux was measured using a calibrated photodiode from Thorlabs (S120VC), assuming the wavelength of all photons from the light are 465 nm to simplify calculation.⁶

The reaction conditions was carried out with PC1 and irradiated with one blue LED in the distance of 10 cm. The reaction time was 120 min. The other conditions are the same as the standard reaction. We chose PC1 so that some parameters from ref 6 could be applied. The light power in the distance of 10 cm away is 119 mW (area: 3.14 cm²). After 120 min, the GC yield is 1.00%.

Calculation: According to the process showed in ref. 6, the quantum yield is 0.93.

Photo energy at 465 nm wavelength: $E = h \cdot c / \lambda = 6.626 \cdot 10^{-34} \cdot 2.998 \cdot 10^8 / (465 \cdot 10^{-9}) = 4.27 \cdot 10^{-19}$ J, in which h is Planck constant, c is the velocity of light and λ is the wavelength of LED.

Power density = light intensity measured/photodiode area = $0.119 / (3.14 \cdot 1^2) = 3.790 \cdot 10^{-2}$ J*s⁻¹*cm⁻²;

Photon density = power density/photon energy of 465 nm wavelength = $3.790 \cdot 10^{-2} / (4.27 \cdot 10^{-19}) = 8.88 \cdot 10^{16}$;

$\Phi = (\text{mol products}) / (\text{mol incident photos}) = (\text{mol products}) / (\text{photo density} \cdot t \cdot \text{area} / N_A) = 2.018 \cdot 10^{-3} \cdot 6.022 \cdot 10^{23} / (8.88 \cdot 10^{16} \cdot 2 \cdot 3600 \cdot 0.9999 \cdot 1.7 \cdot 1.2) = 0.93$

5.4. Fluorescence quenching experiments

Procedure: Fluorescence quenching experiments were conducted on a Varian Cary Eclipse machine. All solutions and samples were prepared in an N₂-filled glovebox, then analyzed immediately. Stock solution of [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ (4.1 mg in volumetric flask of 20.0 mL with 1, 4-dioxane, 2.0 × 10⁻⁴ M). Stock solution of TMS₃SiH (197.5 μL in 8.0 mL 1, 4-dioxane solution), phenyl bromide (67.4 μL in 8.0 mL 1, 4-dioxane solution) and methyl acrylate (57.6 μL in 8.0 mL 1, 4-dioxane solution) were all 0.08M. (dtbbpy)PhNiBr solution (1.0 × 10⁻² M) was prepared by mixing 0.1 mmol Ni(COD)₂ with 0.1 mmol dtbbpy for 10 minutes in 5.0 mL 1, 4-dioxane. 0.1 mmol phenyl bromide was then added. After 10 minutes, the mixture was transferred to a volumetric flask of 10.0 mL. Then 0.400 mL of the above (dtbbpy)PhNiBr solution (1.0 × 10⁻² M) was diluted in a 20 mL volumetric flask to give a solution of 2.0 × 10⁻⁴ M solution. 0.400 mL Bu₄NBr (32.2 mg, 0.1 mmol in 10 mL 1, 4-dioxane solution) was diluted to 20.0 mL to give a 2.0 × 10⁻⁴ M solution.

With the above stock solutions, the samples for analysis were prepared as following.

TMS₃SiH: To four volumetric flasks of 5.0 mL were added 0.25 mL, 1.0 mL, 1.75 mL and 2.5 mL TMS₃SiH stock solution, followed by addition of 0.5 mL [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ (2.0 × 10⁻⁴ M) to each flask. The final concentration of [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ was 2.0 × 10⁻⁵ M, and the concentrations of TMS₃SiH were 0.0040 M, 0.016 M, 0.028 M or 0.040 M.

Phenyl bromide: The process is the same as above. The final concentration of [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ was 2.0 × 10⁻⁵ M. The concentrations of phenyl bromide were 0.0040 M, 0.016 M, 0.028 M or 0.040 M.

Methyl acrylate: The process is the same as above. The final concentration for analysis of [Ir(dF(Me)ppy)₂(dtbbpy)]PF₆ was 2.0 × 10⁻⁵ M. The concentrations of methyl acrylate were 0.0040 M, 0.016 M, 0.028 M and 0.040 M.

(dtbbpy)PhNiBr: To five volumetric flasks of 5.0 mL were added 0.25 mL, 0.5 mL, 1.0 mL, 1.5 and 2.0 mL (dtbbpy)PhNiBr solution (2.0×10^{-4} M). 0.5 mL $[\text{Ir}(\text{dF}(\text{Me})\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (2.0×10^{-4} M) was added to each flask. The final concentration of $[\text{Ir}(\text{dF}(\text{Me})\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ was 2.0×10^{-5} M. The concentrations of (dtbbpy)PhNiBr were 1.0×10^{-5} M, 2.0×10^{-5} M, 4.0×10^{-5} M, 6.0×10^{-5} M or 8.0×10^{-5} M.

Bu₄NBr: The process is the same as for (dtbbpy)PhNiBr. The final concentration of $[\text{Ir}(\text{dF}(\text{Me})\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ was 2×10^{-5} M. The concentrations of Bu₄NBr were 1.0×10^{-5} M, 2.0×10^{-5} M, 4.0×10^{-5} M, 6.0×10^{-5} M or 8.0×10^{-5} M.

The above solutions were transferred to cuvettes and sealed with parafilm in a glovebox before being taken out for analysis. The solution was excited at 400 nm and the emission intensity was recorded at 495 nm.

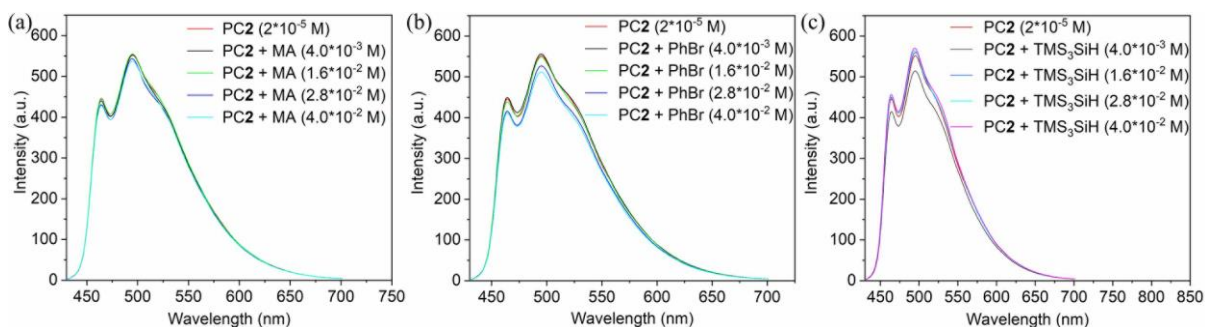


Figure S2. Quenching of excited Ir*(III) complex (PC2) with methyl acrylate (MA, Figure S2a), phenyl bromide (PhBr, Figure S2b) and TMS₃SiH (Figure S2c) at different concentrations.

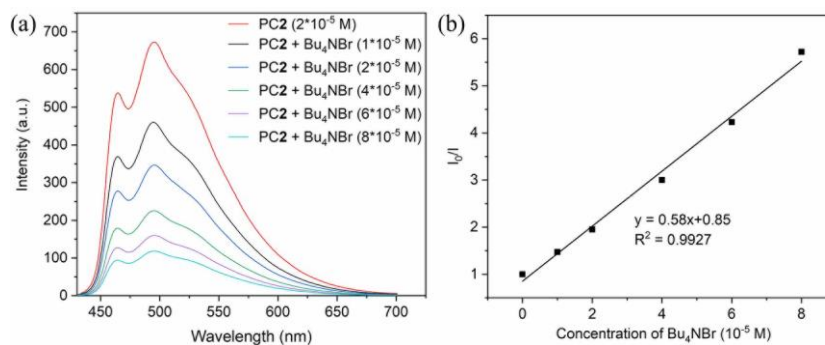


Figure S3. Quenching of excited Ir*(III) complex (PC2) with Bu₄NBr at different concentrations (Figure S2a) and the corresponding Stern-Volmer linear fitting (Figure S2b).

6. Single crystal X-ray diffraction

Experimental. Single clear pale colourless plate crystals of **4p** were obtained by recrystallization from diethyl ether and hexane. Details of growth of single crystals of **4p**: a minimum amount of diethyl ether was used to dissolve **4p**, then the solution was filtered with a 0.22 μm pore size filter to a new 5 mL vial. An equal amount of filtered hexane was put carefully on the top of diethyl ether. Then, the cap was closed, but not very tightly. The vial was put in a stable table for two days. Clear needle-shaped crystals were formed. A suitable crystal with dimensions $0.82 \times 0.68 \times 0.42 \text{ mm}^3$ was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady $T = 140.00(10) \text{ K}$ during data collection. The structure was solved with the **ShelXT**^[7] 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Mercury 4.1.3 (CCDC, 2019)^[8] as the graphical interface. The model was refined with **ShelXL-2018/3** (Sheldrick, 2018)^[9] using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{20}\text{H}_{40}\text{O}_4\text{SSi}_4$, $M_r = 488.94$, monoclinic, $P2_1/c$ (No. 14), $a = 22.0893(4) \text{ \AA}$, $b = 9.47947(15) \text{ \AA}$, $c = 14.2315(3) \text{ \AA}$, $\beta = 107.915(2)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 2835.53(10) \text{ \AA}^3$, $T = 140.00(10) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{Cu } K\alpha) = 2.806$, 19497 reflections measured, 5533 unique ($R_{int} = 0.0400$) which were used in all calculations. The final wR_2 was 0.1139 (all data) and R_1 was 0.0414 ($I > 2(I)$).

CCDC-1959278 contains the supplementary crystallographic data for **4p**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound	4p
Formula	$\text{C}_{20}\text{H}_{40}\text{O}_4\text{SSi}_4$
$D_{calc.}/\text{g cm}^{-3}$	1.145
μ/mm^{-1}	2.806
Formula Weight	488.94
Colour	clear pale colourless
Shape	plate
Size/ mm^3	$0.82 \times 0.68 \times 0.42$
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
$a/\text{\AA}$	22.0893(4)
$b/\text{\AA}$	9.47947(15)
$c/\text{\AA}$	14.2315(3)
α°	90
β°	107.915(2)
γ°	90
$V/\text{\AA}^3$	2835.53(10)
Z	4
Z'	1
Wavelength/ \AA	1.54184
Radiation type	$\text{Cu } K\alpha$
$\theta_{min}/^\circ$	4.207
$\theta_{max}/^\circ$	72.466
Measured Refl's.	19497
Ind't Refl's	5533
Refl's with $I > 2(I)$	5290
R_{int}	0.0400
Parameters	274
Restraints	0
Largest Peak/ $e \text{ \AA}^{-3}$	0.498
Deepest Hole/ $e \text{ \AA}^{-3}$	-0.431
GooF	1.047
wR_2 (all data)	0.1139
wR_2	0.1124
R_1 (all data)	0.0428
R_1	0.0414

Structure Quality Indicators

Reflections:	$d_{\text{min}}(\text{Cu})$ CIF	0.81	I/σ CIF	31.6	R_{int} CIF	4.00%	complete	100%
Refinement:	Shift CIF	0.001	Max Peak CIF	0.5	Min Peak CIF	-0.4	Goof CIF	1.047

A clear pale colourless plate-shaped crystal with dimensions $0.82 \times 0.68 \times 0.42 \text{ mm}^3$ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, Atlas diffractometer operating at $T = 140.00(10) \text{ K}$.

Data were measured using ω scans using Cu K_{α} radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.53, 2019). The maximum resolution that was achieved was $\theta = 72.466^{\circ}$ (0.81 \AA).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program **CrysAlisPro** (Rigaku, V1.171.40.53, 2019)^[10]. The unit cell was refined using **CrysAlisPro** (Rigaku, V1.171.40.53, 2019) on 11230 reflections, 58% of the observed reflections.

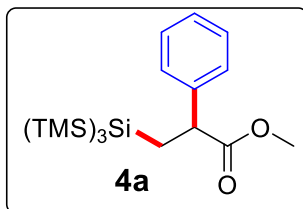
Data reduction, scaling and absorption corrections were performed using **CrysAlisPro** (Rigaku, V1.171.40.53, 2019). The final completeness is 100.00 % out to 72.466° in θ . A Gaussian absorption correction was performed using CrysAlisPro 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK. The absorption coefficient μ of this material is 2.806 mm^{-1} at this wavelength ($\lambda = 1.54184 \text{ \AA}$) and the minimum and maximum transmissions are 0.068 and 0.997.

The structure was solved and the space group $P2_1/c$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL-2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

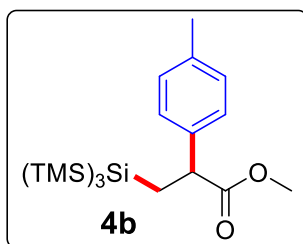
7. Spectral data

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-Phenylpropanoate (4a)



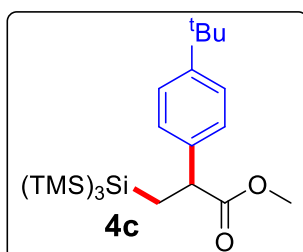
Yield: 64.5 mg, 80%, colorless oil; $R_f = 0.31$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.34-7.29 (m, 4H), 7.28-7.22 (m, 1H), 3.68 (dd, $J = 8.9, 5.3$ Hz, 1H), 3.63 (s, 3H), 1.82 (dd, $J = 14.6, 8.9$ Hz, 1H), 1.26 (dd, $J = 14.6, 5.3$ Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.1, 142.2, 128.9, 127.7, 127.4, 52.1, 50.7, 12.9, 1.3.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ 29Si NMR (79 MHz, CDCl_3) δ -12.5, -81.2.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{38}\text{NaO}_2\text{Si}_4^+ = 433.1841$, found 433.1843.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(p-Tolyl)Propanoate (4b)



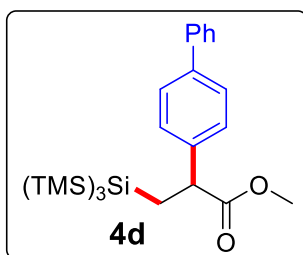
Yield: 60.8 mg, 72%, colorless oil; $R_f = 0.31$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.20 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 3.64 (dd, $J = 9.2, 5.0$ Hz, 1H), 3.62 (s, 3H), 2.32 (s, 3H), 1.81 (dd, $J = 14.6, 9.2$ Hz, 1H), 1.22 (dd, $J = 14.6, 5.0$ Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.2, 139.4, 137.0, 129.5, 127.5, 52.1, 50.3, 21.2, 13.0, 1.3.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.6, -81.3; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{40}\text{NaO}_2\text{Si}_4^+ = 447.1998$, found 447.1992.

Methyl 2-(4-(Tert-Butyl)Phenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4c)



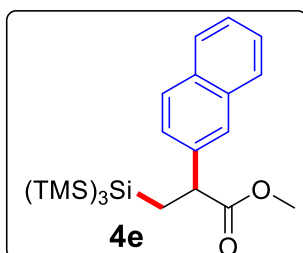
Yield: 66.6 mg, 71%, colorless oil; $R_f = 0.28$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.34-7.31 (m, 2H), 7.25-7.21 (m, 2H), 3.65 (dd, $J = 8.6, 6.0$ Hz, 1H), 3.62 (s, 3H), 1.77 (dd, $J = 14.6, 8.5$ Hz, 1H), 1.32-1.27 (m, 10H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.4, 150.2, 138.9, 127.3, 125.8, 52.1, 50.2, 34.6, 31.5, 13.0, 1.3.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.6, -81.5.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{46}\text{NaO}_2\text{Si}_4^+ = 489.2467$, found 489.2479.

Methyl 2-([1,1'-Biphenyl]-4-Yl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4d)



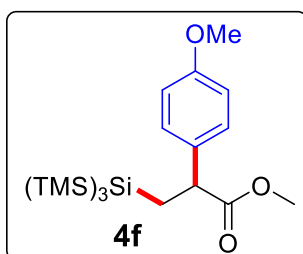
Yield: 80.5 mg, 83%, colorless oil; $R_f=0.26$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.58-7.54 (m, 4H), 7.45-7.32 (m, 5H), 3.76 – 3.69 (m, 1H), 3.65 (s, 3H), 1.85 (dd, $J = 14.4$, 9.0 Hz, 1H), 1.30 (dd, $J = 15.3$, 5.7 Hz, 1H), 0.17 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.1, 141.2, 140.9, 140.4, 128.9, 128.1, 127.6, 127.4, 127.2, 52.2, 50.4, 13.0, 1.3; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.5, -81.2. ; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{42}\text{NaO}_2\text{Si}_4^+$ = 509.2154, found 509.2156.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(Naphthalen-2-Yl)Propanoate (4e)



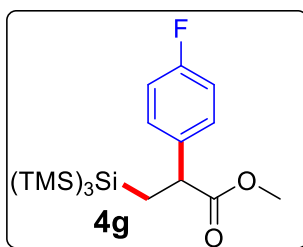
Yield: 64.5 mg, 73%, colorless oil; $R_f= 0.26$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.83-7.81 (m, 3H), 7.75 (s, 1H), 7.51-7.44 (m, 3H), 3.87 (dd, $J = 9.2$, 4.9 Hz, 1H), 3.64 (s, 3H), 1.95 (dd, $J = 14.6$, 9.2 Hz, 1H), 1.34 (dd, $J = 14.6$, 4.9 Hz, 1H), 0.18 (27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.0, 139.8, 133.6, 132.8, 128.7, 128.0, 127.8, 126.3, 126.2, 125.9, 125.8, 52.2, 50.9, 13.0, 1.3.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.5, -81.1.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{23}\text{H}_{40}\text{NaO}_2\text{Si}_4^+$ = 483.1998, found 483.2001.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(4-Methoxyphenyl)Propanoate (4f)



Yield: 55.3 mg, 63%, colorless oil; $R_f= 0.25$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.24-7.21 (m, 2H), 6.87-6.83 (m, 2H), 3.79 (s, 3H), 3.64-3.61 (m, 4H), 1.78 (dd, $J = 14.6$, 8.8 Hz, 1H), 1.23 (dd, $J = 14.6$, 5.5 Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.4, 158.9, 134.4, 128.7, 114.2, 55.4, 52.1, 49.8, 12.9, 1.3.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.6, -81.5.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{20}\text{H}_{40}\text{NaO}_3\text{Si}_4^+$ = 463.1947, found 463.1945.

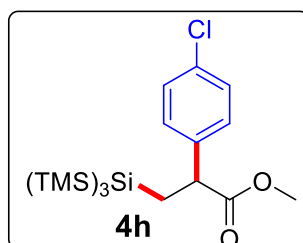
Methyl 2-(4-Fluorophenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4g)



Yield: 58.3 mg, 68%, colorless oil; R_f = 0.28 (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.33-7.28 (m, 2H), 7.05-6.99 (m, 2H), 3.68 (dd, J = 8.8, 5.5 Hz, 1H), 3.65 (s, 3H), 1.82 (dd, J = 14.6, 8.8 Hz, 1H), 1.23 (dd, J = 14.6, 5.5 Hz, 1H), 0.17 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.0, 162.19 (d, J = 245.8 Hz), 137.91 (d, J = 3.1 Hz), 129.22 (d, J = 8.1 Hz), 115.69 (d, J = 21.3 Hz), 52.2, 50.0, 13.0, 1.3.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -115.5.

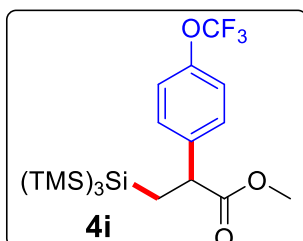
$^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.3.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{37}\text{FNaO}_2\text{Si}_4^+$ = 451.1747, found 451.1737.

Methyl 2-(4-Chlorophenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4h)



Yield: 61.7 mg, 69%, colorless oil; R_f = 0.28 (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.32-7.26 (m, 4H), 3.68-3.65 (m, 4H), 1.82 (dd, J = 14.7, 9.1 Hz, 1H), 1.21 (dd, J = 14.6, 5.1 Hz, 1H), 0.17 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 140.8, 133.2, 129.0, 129.0, 52.3, 50.1, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.1; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{37}\text{ClNaO}_2\text{Si}_4^+$ = 467.1451, found 467.1450.

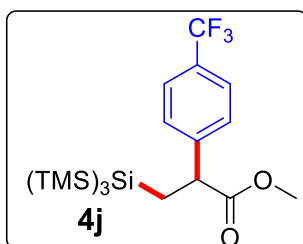
Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-(4-(Trifluoromethoxy)Phenyl)Propanoate (4i)



Yield: 69.6 mg, 70%, colorless oil; R_f = 0.28 (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.35-7.32 (m, 2H), 7.17-7.15 (m, 2H), 3.68 (dd, J = 8.7, 5.5 Hz, 1H), 3.63 (s, 3H), 1.80 (dd, J = 14.6, 8.7 Hz, 1H), 1.23 (dd, J = 14.6, 5.6 Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.8, 148.5 (q, J = 1.6 Hz), 140.8, 129.1, 121.4, 120.6 (q, J = 257.1 Hz), 52.3, 50.1, 13.1, 1.3.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -57.9. $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -

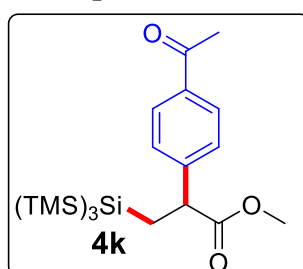
81.2; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{37}\text{F}_3\text{NaO}_3\text{Si}_4^+$ = 517.1664, found 517.1647.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-(4-(Trifluoromethyl)Phenyl)Propanoate (4j)



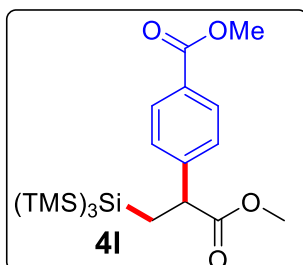
Yield: 57.7 mg, 60%, colorless oil; R_f = 0.28 (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.58 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 3.73 (dd, J = 9.4, 4.7 Hz, 1H), 3.64 (s, 3H), 1.85 (dd, J = 14.6, 9.4 Hz, 1H), 1.20 (dd, J = 14.6, 4.8 Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.3, 146.3, 129.7 (q, J = 32.5 Hz), 128.0, 125.9 (q, J = 3.8 Hz), 124.2 (q, J = 272.0 Hz), 52.4, 50.7, 13.1, 1.3.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.5.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.6, -80.9.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{37}\text{F}_3\text{NaO}_2\text{Si}_4^+$ = 501.1715, found 501.1691.

Methyl 2-(4-Acetylphenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4k)



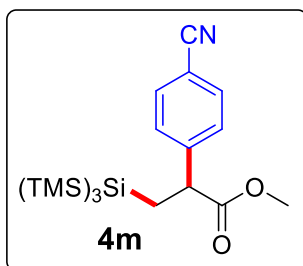
Yield: 61.6 mg, 68%, colorless oil; R_f = 0.44 (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.91 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 3.72 (dd, J = 9.3, 4.7 Hz, 1H), 3.63 (s, 3H), 2.58 (s, 3H), 1.84 (dd, J = 14.6, 9.3 Hz, 1H), 1.19 (dd, J = 14.6, 4.7 Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 197.7, 174.3, 147.7, 136.3, 129.0, 127.9, 52.4, 50.8, 26.8, 13.0, 1.3.; $^{29}\text{Si NMR}$ (CDCl_3 , 79 MHz) δ -12.6, -80.8.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{41}\text{O}_3\text{Si}_4^+$ = 453.2127, found 453.2116.

Methyl 4-(3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-1-Methoxy-1-Oxopropan-2-yl)Benzoate (4l)



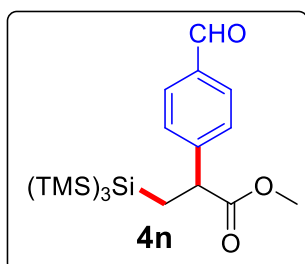
Yield: 69.4 mg, 74%, colorless oil; R_f = 0.56 (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.98 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 3.89 (s, 3H), 3.72 (dd, J = 9.2, 4.9 Hz, 1H), 3.62 (s, 3H), 1.83 (dd, J = 14.6, 9.2 Hz, 1H), 1.20 (dd, J = 14.6, 4.9 Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.4, 166.9, 147.4, 130.2, 129.3, 127.7, 52.3, 52.2, 50.8, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.9.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{40}\text{NaO}_4\text{Si}_4^+$ = 491.1896, found 491.1882.

Methyl 2-(4-Cyanophenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4m)



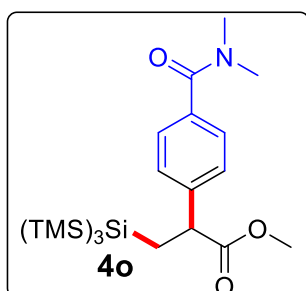
Yield: 54.9 mg, 63%, colorless oil; $R_f=0.56$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.62-7.60 (m, 2H), 7.42-7.40 (m, 2H), 3.70 (dd, $J = 9.3, 4.7$ Hz, 1H), 3.63 (s, 3H), 1.82 (dd, $J = 14.6, 9.3$ Hz, 1H), 1.15 (dd, $J = 14.6, 4.8$ Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.9, 147.5, 132.8, 128.5, 118.8, 111.4, 52.5, 50.9, 13.0, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.7.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{20}\text{H}_{37}\text{NNaO}_2\text{Si}_4^+ = 458.1794$, found 458.1772.

Methyl 2-(4-Formylphenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4n)



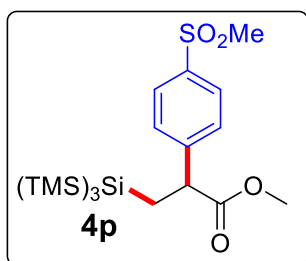
Yield: 62.3 mg, 71%, colorless oil; $R_f = 0.51$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 9.99 (s, 1H), 7.84 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 3.74 (dd, $J = 9.3, 4.8$ Hz, 1H), 3.63 (s, 3H), 1.85 (dd, $J = 14.7, 9.3$ Hz, 1H), 1.20 (dd, $J = 14.6, 4.8$ Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 191.9, 174.2, 149.1, 135.6, 130.4, 128.4, 52.4, 51.0, 13.0, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.7.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{20}\text{H}_{39}\text{O}_3\text{Si}_4^+ = 439.1971$, found 439.1955.

Methyl 2-(4-(Dimethylcarbamoyl)Phenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4o)



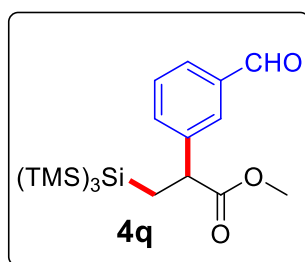
Yield: 57.7 mg, 60%, colorless oil; $R_f = 0.33$ (hexane : ethyl acetate : TEA = 5 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.35-7.31 (m, 4H), 3.67 (dd, $J = 8.5, 4.9$ Hz, 1H), 3.61 (s, 3H), 3.04 (brs, 6H), 1.80 (dd, $J = 14.3, 9.5$ Hz, 1H), 1.20 (dd, $J = 14.7, 4.2$ Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.5, 171.3, 143.6, 135.3, 127.6, 127.6, 52.1, 50.5, 39.5 (brs, very low), 35.6 (brs, very low), 12.7, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.2.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{22}\text{H}_{44}\text{NO}_3\text{Si}_4^+ = 482.2393$, found 482.2379.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-(4-(Methylsulfonyl)Phenyl)Propanoate (4p)



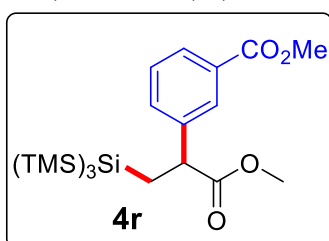
Yield: 55.9 mg, 57%, white solid; $R_f = 0.31$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.88 (d, $J = 7.5$ Hz, 2H), 7.50 (d, $J = 7.5$ Hz, 2H), 3.79 – 3.72 (m, 1H), 3.63 (s, 3H), 3.03 (s, 3H), 1.89-1.81 (m, 1H), 1.17 (dd, $J = 14.6, 4.1$ Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.9, 148.5, 139.6, 128.6, 128.1, 52.4, 50.7, 44.6, 13.1, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.7.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{20}\text{H}_{40}\text{NaSO}_2\text{Si}_4^+ = 511.1617$, found 511.1598.

Methyl 2-(3-Formylphenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4q)



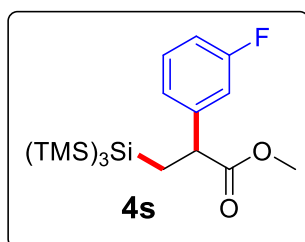
Yield: 42.9 mg, 49%, colorless oil; $R_f = 0.55$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 0.98 (s, 1H), 7.82-7.82 (m, 1H), 7.77 (dt, $J = 7.5, 1.4$ Hz, 1H), 7.59 (dt, $J = 7.7, 1.6$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 3.76 (dd, $J = 9.0, 5.2$ Hz, 1H), 3.63 (s, 3H), 1.85 (dd, $J = 14.6, 9.0$ Hz, 1H), 1.24 (dd, $J = 14.7, 5.1$ Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 192.2, 174.5, 143.4, 137.0, 133.8, 129.6, 128.9, 128.8, 52.3, 50.5, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.0.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{20}\text{H}_{38}\text{NaO}_3\text{Si}_4^+ = 461.1790$, found 461.1787.

Methyl 3-(3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-1-Methoxy-1-Oxopropan-2-Yl)Benzoate (4r)



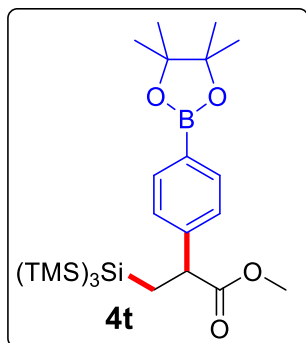
Yield: 51.7 mg, 55%, colorless oil; $R_f = 0.62$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.97-7.97 (m, 1H), 7.93 (dt, $J = 7.7, 1.4$ Hz, 1H), 7.51 (dt, $J = 7.7, 1.6$ Hz, 1H), 7.39 (t, $J = 7.7$ Hz, 1H), 3.92 (s, 3H), 3.72 (dd, $J = 8.8, 5.4$ Hz, 1H), 3.62 (m, 3H), 1.83 (dd, $J = 14.6, 8.9$ Hz, 1H), 1.24 (dd, $J = 14.6, 5.4$ Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 167.0, 142.5, 132.3, 130.8, 129.0, 128.9, 128.7, 52.3, 52.3, 50.6, 12.8, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.1.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{21}\text{H}_{40}\text{NaO}_4\text{Si}_4^+ = 491.1896$, found 491.1889.

Methyl 2-(3-Fluorophenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4s)



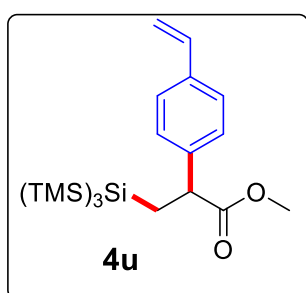
Yield: 60.5 mg, 71%, colorless oil; $R_f = 0.45$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.32-7.27 (m, 1H), 7.10 (dt, $J = 7.7, 1.3$ Hz, 1H), 7.05 (dt, $J = 9.9, 2.1$ Hz, 1H), 6.96 (tdd, $J = 8.4, 2.6, 1.0$ Hz, 1H), 3.70-3.67 (m, 1H), 3.66 (s, 3H), 1.82 (dd, $J = 14.6, 9.0$ Hz, 1H), 1.24 (dd, $J = 14.6, 5.2$ Hz, 1H), 0.17 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.6, 163.11 (d, $J = 246.4$ Hz), 144.61 (d, $J = 7.1$ Hz), 130.28 (d, $J = 8.4$ Hz), 123.45 (d, $J = 2.9$ Hz), 114.63 (d, $J = 21.8$ Hz), 114.33 (d, $J = 21.1$ Hz), 52.3, 50.48 (d, $J = 1.8$ Hz), 12.9, 1.3.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -112.6.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.1.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{19}\text{H}_{37}\text{FNaO}_2\text{Si}_4^+ = 451.1747$, found 451.1745.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(4-(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)Phenyl)Propanoate (4t)



Yield: 79.8 mg, 74%, colorless oil; $R_f = 0.61$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.77 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 3.69 (dd, $J = 9.8, 4.2$ Hz, 1H), 3.61 (s, 3H), 1.86 (dd, $J = 14.6, 9.8$ Hz, 1H), 1.33 (s, 12H), 1.18 (dd, $J = 14.6, 4.2$ Hz, 1H), 0.16 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 145.7, 135.4, 126.9, 83.9, 52.1, 51.0, 25.0, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.0.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{25}\text{H}_{49}\text{BNaO}_4\text{Si}_4^+ = 559.2693$, found 559.2676.

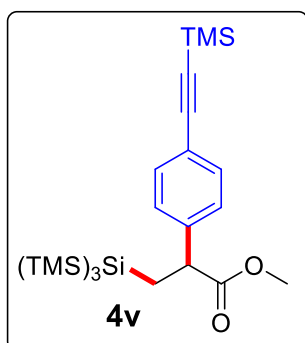
Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-(4-Vinylphenyl)Propanoate (4u)



Yield: 22.2 mg, 25%, colorless oil; $R_f = 0.41$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.36 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 8.2$ Hz, 2H), 6.69 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.72 (dd, $J = 17.6, 0.9$ Hz, 1H), 5.22 (dd, $J = 10.9, 0.9$ Hz, 1H), 3.66 (dd, $J = 9.2, 5.0$ Hz, 1H), 3.62 (s, 3H), 1.82 (dd, $J = 14.6, 9.2$ Hz, 1H), 1.22 (dd, $J = 14.6, 5.0$ Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.0, 141.9, 136.8, 136.5, 127.8, 126.7, 113.9, 52.2, 50.5, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.2.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{21}\text{H}_{40}\text{NaO}_2\text{Si}_4^+ = 459.1998$, found

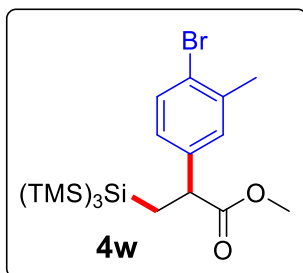
459.1993.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-(4-((Trimethylsilyl)Ethynyl)Phenyl)Propanoate (4v)



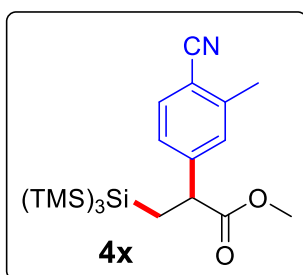
Yield: 17.6 mg, 17%, colorless oil; $R_f = 0.49$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.40 (d, $J = 7.6$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 2H), 3.64 (dd, $J = 8.6, 5.6$ Hz, 1H), 3.61 (s, 3H), 1.79 (dd, $J = 14.0, 9.6$ Hz, 1H), 1.18 (dd, $J = 14.6, 3.6$ Hz, 1H), 0.24 (s, 9H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 142.7, 132.5, 127.6, 122.3, 104.9, 94.5, 52.2, 50.7, 12.7, 1.3, 0.1.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -17.8, -81.0.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{24}\text{H}_{47}\text{O}_2\text{Si}_5^+ = 507.2417$, found 507.2412.

Methyl 2-(4-Bromo-3-Methylphenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4w)



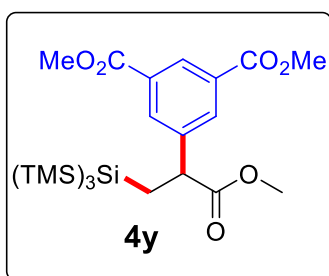
Yield: 52.2 mg, 52%, colorless oil; R_f = 0.56 (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.46 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 2.3 Hz, 1H), 6.99 (dd, J = 8.2, 2.3 Hz, 1H), 3.62 (s, 3H), 3.59 (dd, J = 9.1, 5.1 Hz, 1H), 2.38 (s, 3H), 1.78 (dd, J = 14.6, 9.1 Hz, 1H), 1.18 (dd, J = 14.6, 5.2 Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 141.5, 138.3, 132.7, 130.0, 126.7, 123.7, 52.2, 50.2, 23.1, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.2.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{39}\text{BrNaO}_2\text{Si}_4^+$ = 525.1103, found 525.1097.

Methyl 2-(4-Cyano-3-Methylphenyl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)Propanoate (4x)



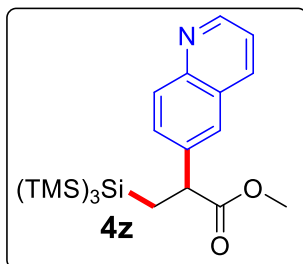
Yield: 45.2 mg, 50%, colorless oil; R_f = 0.63 (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.54 (d, J = 7.9 Hz, 1H), 7.23 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H), 3.69-3.60 (m, 4H), 2.53 (s, 3H), 1.80 (dd, J = 14.2, 9.6 Hz, 1H), 1.15 (dd, J = 14.5, 3.7 Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.0, 147.2, 142.6, 133.1, 129.4, 125.7, 118.1, 111.8, 52.4, 50.8, 20.7, 12.9, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.8.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{39}\text{NNaO}_2\text{Si}_4^+$ = 472.1950, found 472.1945.

Dimethyl 5-(3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-1-Methoxy-1-Oxopropan-2-Yl)Isophthalate (4y)



Yield: 62.8 mg, 60%, white solid; R_f = 0.57 (hexane : ethyl acetate = 5 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.57 (s, 1H), 8.16 (d, J = 1.7 Hz, 2H), 3.94 (s, 6H), 3.78 (dd, J = 9.0, 5.3 Hz, 1H), 3.62 (s, 3H), 1.87 (dd, J = 14.6, 9.0 Hz, 1H), 1.22 (dd, J = 14.6, 5.3 Hz, 1H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.2, 166.2, 143.2, 133.1, 131.2, 129.9, 52.5, 52.4, 50.5, 12.8, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.8.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{42}\text{NaO}_6\text{Si}_4^+$ = 549.1951, found 549.1966.

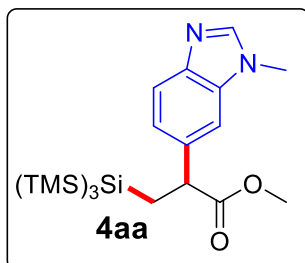
Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(Quinolin-6-Yl)Propanoate (4z)



Yield: 58.8 mg, 64%, colorless oil; R_f = 0.58 (hexane : ethyl acetate : TEA = 5 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.90 – 8.80 (m, 1H), 8.32 – 8.11 (m, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.39 (dd, J = 8.3, 4.2 Hz, 1H), 3.86 (dd, J = 9.2, 4.9 Hz, 1H), 3.63 (s, 3H), 1.92 (dd, J = 14.6, 9.2 Hz, 1H), 1.31 (dd, J = 14.6, 4.9 Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 150.4, 147.7, 140.6, 136.1, 130.1, 129.6, 128.4, 126.0, 121.5, 52.3, 50.7,

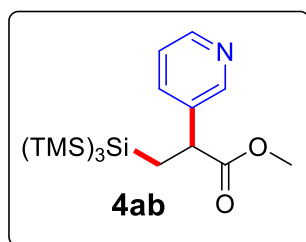
13.1, 1.3.; ^{29}Si NMR (79 MHz, CDCl_3) δ -12.5, -81.0.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{22}\text{H}_{40}\text{NO}_2\text{Si}_4^+ = 462.2131$, found 462.2134.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(1-Methyl-1H-Benzo[d]Imidazol-6-Yl)Propanoate (4aa)



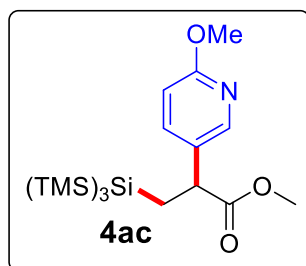
Yield: 42.5 mg, 46%, colorless oil; $R_f = 0.23$ (hexane : ethyl acetate : TEA = 5 : 1 : 1); ^1H NMR (CDCl_3 , 400 MHz) δ 7.86 (s, 1H), 7.67 (d, $J = 8.9$ Hz, 1H), 7.55 (s, 1H), 7.28 (d, $J = 7.9$ Hz, 1H), 4.22 (s, 3H), 3.75 (td, $J = 6.4, 5.6, 3.2$ Hz, 1H), 3.64 (s, 3H), 1.87 (ddd, $J = 14.3, 9.5, 1.9$ Hz, 1H), 1.41 – 1.14 (m, 1H), 0.16 (s, 27H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 175.3, 148.6, 135.5, 126.5, 123.7, 122.3, 118.1, 117.9, 52.1, 50.7, 40.5, 12.8, 1.3.; ^{29}Si NMR (79 MHz, CDCl_3) δ -12.6, -81.3.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{21}\text{H}_{41}\text{N}_2\text{O}_2\text{Si}_4^+ = 465.2240$, found 465.2244.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(Pyridin-3-Yl)Propanoate (4ab)



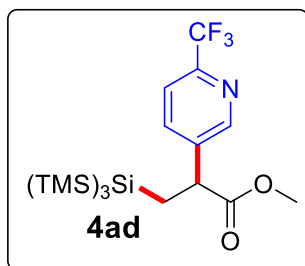
Yield: 40.4 mg, 49%, colorless oil; $R_f = 0.67$ (hexane : ethyl acetate : TEA = 5 : 1 : 1); ^1H NMR (CDCl_3 , 400 MHz) δ 8.56 (d, $J = 2.3$ Hz, 1H), 8.52 (dd, $J = 4.9, 1.6$ Hz, 1H), 7.68 (dt, $J = 7.9, 2.0$ Hz, 1H), 7.40 – 7.22 (m, 1H), 3.69 (dd, $J = 8.9, 5.3$ Hz, 1H), 3.65 (s, 3H), 1.84 (dd, $J = 14.6, 8.9$ Hz, 1H), 1.22 (dd, $J = 14.6, 5.3$ Hz, 1H), 0.16 (s, 27H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.3, 149.3, 148.7, 137.8, 134.9, 123.9, 52.4, 48.2, 12.9, 1.3.; ^{29}Si NMR (79 MHz, CDCl_3) δ -12.6, -80.9.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{18}\text{H}_{38}\text{NO}_2\text{Si}_4^+ = 412.1974$, found 412.1980.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(6-Methoxypyridin-3-Yl)Propanoate (4ac)



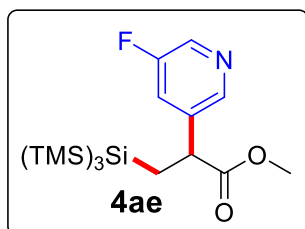
Yield: 36.1 mg, 41%, colorless oil; $R_f = 0.74$ (hexane : ethyl acetate : TEA = 10 : 1 : 1); ^1H NMR (CDCl_3 , 400 MHz) δ 8.06 (s, 1H), 7.56 (d, $J = 8.6$ Hz, 1H), 6.71 (d, $J = 8.6$ Hz, 1H), 3.91 (s, 3H), 3.66 – 3.53 (m, 4H), 1.78 (dd, $J = 14.2, 8.8$ Hz, 1H), 1.17 (dd, $J = 14.8, 4.3$ Hz, 1H), 0.13 (s, 27H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.9, 163.7, 145.9, 137.7, 130.5, 111.3, 53.6, 52.2, 47.3, 12.9, 1.3.; ^{29}Si NMR (79 MHz, CDCl_3) δ -12.6, -81.2.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for calcd for $\text{C}_{19}\text{H}_{40}\text{NO}_3\text{Si}_4^+ = 442.2080$, found 442.2084.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(6-(Trifluoromethyl)Pyridin-3-Yl)Propanoate (4ad)



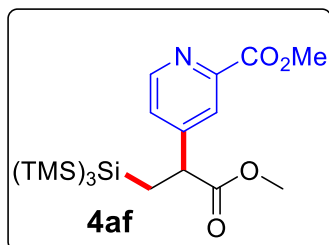
Yield: 56.2 mg, 59%, colorless oil; R_f = 0.74 (hexane : ethyl acetate : TEA = 10 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.64 (s, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 3.76 (dd, J = 8.7, 3.9 Hz, 1H), 3.65 (s, 3H), 1.87 (dd, J = 14.2, 9.8 Hz, 1H), 1.16 (dd, J = 14.4, 3.3 Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.6, 149.5, 147.3 (q, J = 34.8 Hz), 141.2, 136.1, 121.6 (q, J = 273.9 Hz), 120.74 (q, J = 2.4 Hz), 52.6, 48.2, 13.2, 1.2.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.9; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.5; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{37}\text{F}_3\text{NO}_2\text{Si}_4^+$ = 480.1848, found 480.1853.

Methyl 2-(5-Fluoropyridin-3-yl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4ae)



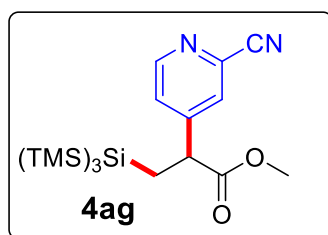
Yield: 28.1 mg, 33%, colorless oil; R_f = 0.71 (hexane : ethyl acetate : TEA = 10 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.36 (s, 2H), 7.41 (d, J = 9.0 Hz, 1H), 3.72 (dd, J = 8.7, 4.8 Hz, 1H), 3.65 (s, 3H), 1.82 (dd, J = 14.5, 9.3 Hz, 1H), 1.16 (dd, J = 14.3, 4.2 Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.8, 159.8 (d, J = 258.4 Hz), 144.9 (d, J = 3.8 Hz); 139.7, 137.1 (d, J = 23.3 Hz), 121.8 (d, J = 18.3 Hz), 52.5, 47.7, 13.1, 1.2.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -125.9.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.7.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{37}\text{FO}_2\text{Si}_4^+$ = 430.1880, found 430.1879.

Methyl 4-(3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-1-Methoxy-1-Oxopropan-2-yl)Picolinate (4af)



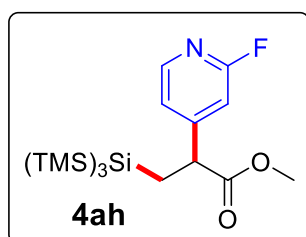
Yield: 55.3 mg, 59%, white solid; R_f = 0.48 (hexane : ethyl acetate : TEA = 5 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.65 (d, J = 4.6 Hz, 1H), 8.04 (s, 1H), 7.46 – 7.30 (m, 1H), 3.98 (s, 3H), 3.70 (dd, J = 9.4, 3.4 Hz, 1H), 3.62 (s, 3H), 1.83 (dd, J = 14.1, 10.1 Hz, 1H), 1.13 (dd, J = 14.5, 3.0 Hz, 1H), 0.13 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.1, 165.6, 152.4, 150.3, 148.5, 125.9, 124.3, 53.0, 52.5, 50.3, 12.6, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.4.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{40}\text{NO}_4\text{Si}_4^+$ = 470.2029, found 470.2031.

Methyl 2-(2-Cyanopyridin-4-yl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4ag)



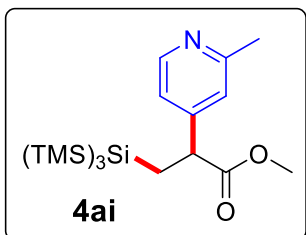
Yield: 31.7 mg, 36%, white solid; $R_f = 0.50$ (hexane : ethyl acetate : TEA = 10 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.64 (d, $J = 5.0$ Hz, 1H), 7.63 (s, 1H), 7.44 (d, $J = 4.3$ Hz, 1H), 3.72 – 3.61 (m, 4H), 1.88 – 1.75 (m, 1H), 1.09 (dd, $J = 14.4, 3.5$ Hz, 1H), 0.16 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 172.7, 152.6, 151.5, 134.5, 127.6, 125.9, 117.2, 52.8, 50.1, 12.9, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.2.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{37}\text{N}_2\text{O}_2\text{Si}_4^+ = 437.1927$, found 437.1922.

Methyl 2-(2-Fluoropyridin-4-yl)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Propanoate (4ah)



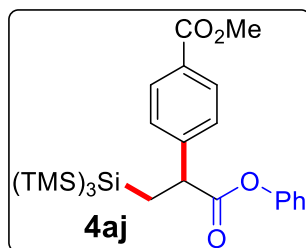
Yield: 53.6 mg, 62%, colorless oil; $R_f = 0.68$ (hexane : ethyl acetate : TEA = 10 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.14 (d, $J = 4.9$ Hz, 1H), 7.11 (d, $J = 4.1$ Hz, 1H), 6.85 (s, 1H), 3.73 – 3.60 (m, 4H), 1.80 (dd, $J = 14.3, 10.0$ Hz, 1H), 1.13 (dd, $J = 14.5, 3.2$ Hz, 1H), 0.15 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.1, 164.2 (d, $J = 239.3$ Hz), 156.7 (d, $J = 7.6$ Hz), 148.1 (d, $J = 15.3$ Hz), 120.6 (d, $J = 4.1$ Hz), 108.5 (d, $J = 37.8$ Hz), 52.6, 50.2 (d, $J = 2.7$ Hz), 12.7, 1.2.; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -67.5.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.5.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{37}\text{NFO}_2\text{Si}_4^+ = 430.1880$, found 430.1872.

Methyl 3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-(2-Methylpyridin-4-yl)Propanoate (4ai)



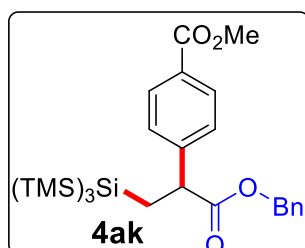
Yield: 64.9 mg, 76%, colorless oil; $R_f = 0.50$ (hexane : ethyl acetate : TEA = 10 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.44 – 8.32 (m, 1H), 7.05 (s, 1H), 7.01 (d, $J = 5.2$ Hz, 1H), 3.62 (s, 3H), 3.57 (dd, $J = 8.7, 4.5$ Hz, 1H), 2.52 (s, 3H), 1.82-1.69 (m, 1H), 1.14 (dd, $J = 14.6, 3.3$ Hz, 1H), 0.13 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.8, 158.9, 151.2, 149.5, 122.2, 120.0, 52.4, 50.2, 24.5, 12.5, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.8.; HRMS (ESI, m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{40}\text{NO}_2\text{Si}_4^+ = 426.2131$, found 426.2133.

Methyl 4-(3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-1-Oxo-1-Phenoxypropan-2-yl)Benzoate (4aj)



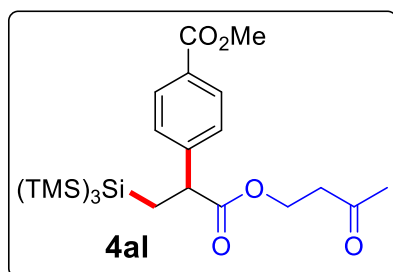
Yield: 77.9 mg, 73%, colorless oil; $R_f = 0.57$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.06 (dd, $J = 8.3, 2.1$ Hz, 2H), 7.55 – 7.44 (m, 2H), 7.38 – 7.26 (m, 2H), 7.17 (dd, $J = 8.5, 6.5$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 2H), 4.01 – 3.94 (m, 1H), 3.92 (s, 3H), 1.94 (dd, $J = 14.6, 8.7$ Hz, 1H), 1.32 (dd, $J = 14.7, 4.8$ Hz, 1H), 0.18 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 172.5, 166.9, 151.0, 146.8, 130.4, 129.5, 129.4, 127.9, 125.9, 121.3, 52.3, 51.1, 12.4, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.7.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{42}\text{NaO}_4\text{Si}_4^+ = 553.2052$, found 553.2055.

Methyl 4-(1-(Benzyloxy)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-1-Oxopropan-2-Yl)Benzoate (4ak)



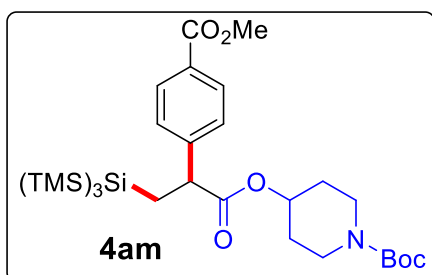
Yield: 81.0 mg, 74%, colorless oil; R_f = 0.60 (hexane : ethyl acetate = 5 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.02 – 7.97 (m, 2H), 7.45 – 7.36 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.14 (m, 2H), 5.20 – 5.00 (m, 2H), 3.94 (s, 3H), 3.85 – 3.75 (m, 1H), 1.88 (dd, J = 14.4, 8.7 Hz, 1H), 1.46 – 1.12 (m, 1H), 0.17 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.7, 166.9, 147.0, 135.7, 130.2, 129.3, 128.5, 128.2, 128.0, 127.8, 66.9, 52.2, 50.9, 12.6, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.8.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{44}\text{NaO}_4\text{Si}_4^+$ = 567.2209, found 567.2222.

Methyl 4-(3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-1-Oxo-1-(3-Oxobutoxy)Propan-2-Yl)Benzoate (4al)



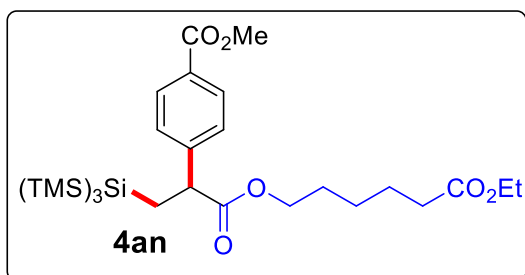
Yield: 70.2 mg, 67%, colorless oil; R_f = 0.34 (hexane : ethyl acetate = 5 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.97 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.28 (ddq, J = 17.8, 11.6, 6.4 Hz, 2H), 3.89 (s, 3H), 3.66 (dd, J = 8.6, 5.4 Hz, 1H), 2.58 (td, J = 6.4, 2.1 Hz, 2H), 1.99 (s, 3H), 1.78 (dd, J = 14.7, 8.6 Hz, 1H), 1.20 (dd, J = 14.7, 5.3 Hz, 1H), 0.12 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 205.3, 173.7, 166.9, 147.0, 130.2, 129.3, 127.7, 60.0, 52.2, 50.8, 42.0, 30.2, 12.5, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.9; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{44}\text{NaO}_5\text{Si}_4^+$ = 547.2158, found 547.2167.

Tert-Butyl 4-((3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-2-(4-(Methoxycarbonyl)Phenyl)Propanoyl)Oxy)Piperidine-1-Carboxylate (4am)



Yield: 85 mg, 67%, colorless oil; R_f = 0.60 (hexane : ethyl acetate : TEA = 10 : 1 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.97 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.87 (dt, J = 7.7, 3.9 Hz, 1H), 3.89 (s, 3H), 3.68 (dd, J = 8.8, 5.2 Hz, 1H), 3.57 – 3.37 (m, 1H), 3.24 (dt, J = 13.3, 4.0 Hz, 2H), 3.17 – 3.04 (m, 1H), 1.93 – 1.70 (m, 2H), 1.65 – 1.51 (m, 2H), 1.40 (s, 9H), 1.33 – 1.23 (m, 1H), 1.18 (dd, J = 14.7, 5.1 Hz, 1H), 0.12 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 173.1, 166.8, 154.7, 147.3, 130.2, 129.3, 127.6, 79.7, 70.0, 52.2, 51.0, 40.7 (brs), 30.5, 30.0, 28.5, 12.1, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.8.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{55}\text{NaNO}_6\text{Si}_4^+$ = 660.2999, found 660.2995.

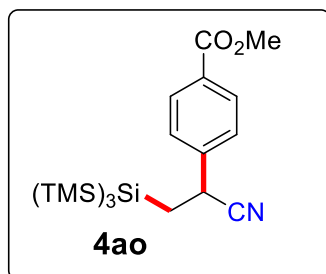
Methyl (S)-4-(1-((6-Ethoxy-6-Oxohexyl)Oxy)-3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-Yl)-1-Oxopropan-2-Yl)Benzoate (4an)



Yield: 84.5 mg, 71%, colorless oil; $R_f = 0.57$ (hexane : ethyl acetate = 5 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.97 (d, $J = 7.9$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.09 (q, $J = 7.2$ Hz, 2H), 4.05 – 3.95 (m, 2H), 3.89 (s, 3H), 3.68 (dd, $J = 8.9, 5.1$ Hz, 1H), 2.18 (t, $J = 7.5$ Hz, 2H), 1.81 (dd, $J = 14.6, 8.9$ Hz, 1H), 1.51 (dp, $J = 11.1, 6.9$ Hz, 4H), 1.29 – 1.14 (m, 6H), 0.12 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ

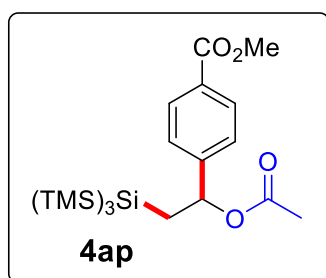
173.9, 173.5, 166.9, 147.4, 130.1, 129.2, 127.7, 64.8, 60.3, 52.2, 50.9, 34.2, 28.2, 25.4, 24.5, 14.3, 12.5, 1.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -80.9.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{28}\text{H}_{52}\text{NaO}_6\text{Si}_4^+ = 619.2733$, found 619.2749.

Methyl 4-(1-Cyano-2-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Ethyl)Benzoate (4ao)



Yield: 73.6 mg, 84%, colorless oil; $R_f = 0.54$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.05 (d, $J = 7.5$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 2H), 3.92 (s, 3H), 3.78 (d, $J = 11.5$ Hz, 1H), 1.60 (t, $J = 13.1$ Hz, 1H), 1.33 (d, $J = 14.6$ Hz, 1H), 0.24 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 166.5, 144.7, 130.7, 130.1, 126.8, 121.6, 52.4, 37.0, 17.6, 1.4.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.4, -80.9.; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{20}\text{H}_{37}\text{NaNO}_2\text{Si}_4^+ = 458.1794$, found 458.1794.

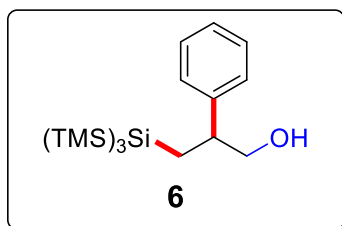
Methyl 4-(1-Acetoxy-2-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)Ethyl)Benzoate (4ap)



Yield: 13.2 mg, 14%, colorless oil; $R_f = 0.51$ (hexane : ethyl acetate = 10 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 5.70 (dd, $J = 9.7, 5.0$ Hz, 1H), 3.90 (s, 3H), 2.03 (s, 3H), 1.51 (dd, $J = 14.7, 9.8$ Hz, 1H), 1.33 (dd, $J = 14.7, 4.9$ Hz, 1H), 0.16 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 170.4, 166.9, 148.9, 130.2, 129.7, 126.1, 77.0, 52.3, 21.8, 17.4, 1.3.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.5, -84.1; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for calcd for $\text{C}_{21}\text{H}_{40}\text{NaO}_4\text{Si}_4^+ = 491.1896$, found

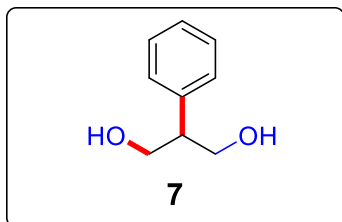
491.1896.

3-(1,1,1,3,3,3-Hexamethyl-2-(Trimethylsilyl)Trisilan-2-yl)-2-Phenylpropan-1-ol (6)



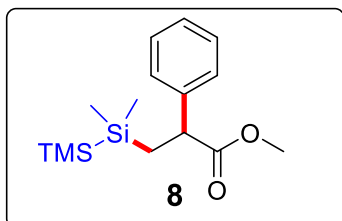
Yield: 46.2 mg, 95%, white solid; $R_f = 0.50$ (hexane : ethyl acetate = 5 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.38-7.34 (m, 2H), 7.28-7.24 (m, 3H), 3.75-3.70 (m, 1H), 3.60-3.55 (m, 1H), 2.89 (p, $J = 6.4$ Hz, 1H), 1.35 (s, 1H), 1.21 (d, $J = 6.8$ Hz, 2H), 0.14 (s, 27H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 144.2, 128.9, 128.2, 127.1, 70.2, 47.8, 10.8, 1.4; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -12.6, -81.9; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{38}\text{NaOSi}_4^+ = 405.1892$, found 405.1898.

2-phenylpropane-1,3-diol (7)^[6]



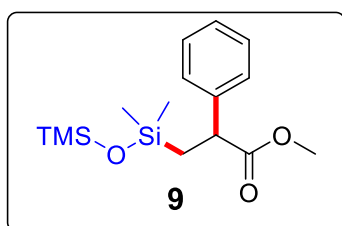
Yield: 26.6 mg, %, white solid; $R_f = 0.27$ (hexane : ethyl acetate = 1 : 4); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.37-7.33 (m, 2H), 7.29-7.27 (m, 1H), 7.24-7.22 (m, 2H), 4.00-3.90 (m, 4H), 3.11-3.05 (m, 1H), 2.88 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 139.5, 128.9, 128.1, 127.3, 66.0, 49.8. The spectrum is the same as that of commercial available compound **7**.

Methyl 3-(1,1,2,2,2-Pentamethyldisilaneyl)-2-Phenylpropanoate (8)



Yield: 287.0 mg, 43%, light yellow oil; $R_f = 0.27$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.37-7.31 (m, 4H), 7.28-7.25 (m, 1H), 3.70 (t, $J = 7.9$ Hz, 1H), 3.66 (s, 3H), 1.55 (dd, $J = 14.3, 8.3$ Hz, 1H), 1.21 (dd, $J = 14.2, 7.2$ Hz, 1H), 0.06 (s, 9H), 0.00 (s, 3H), -0.09 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.6, 141.5, 128.7, 127.9, 127.3, 52.2, 47.8, 19.6, -2.1, -4.1, -4.2.; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ -17.9, -19.6; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{26}\text{NaO}_2\text{Si}_2^+ = 317.1364$, found 317.1361.

Methyl 3-(1,1,3,3,3-Pentamethyldisiloxaneyl)-2-Phenylpropanoate (9)

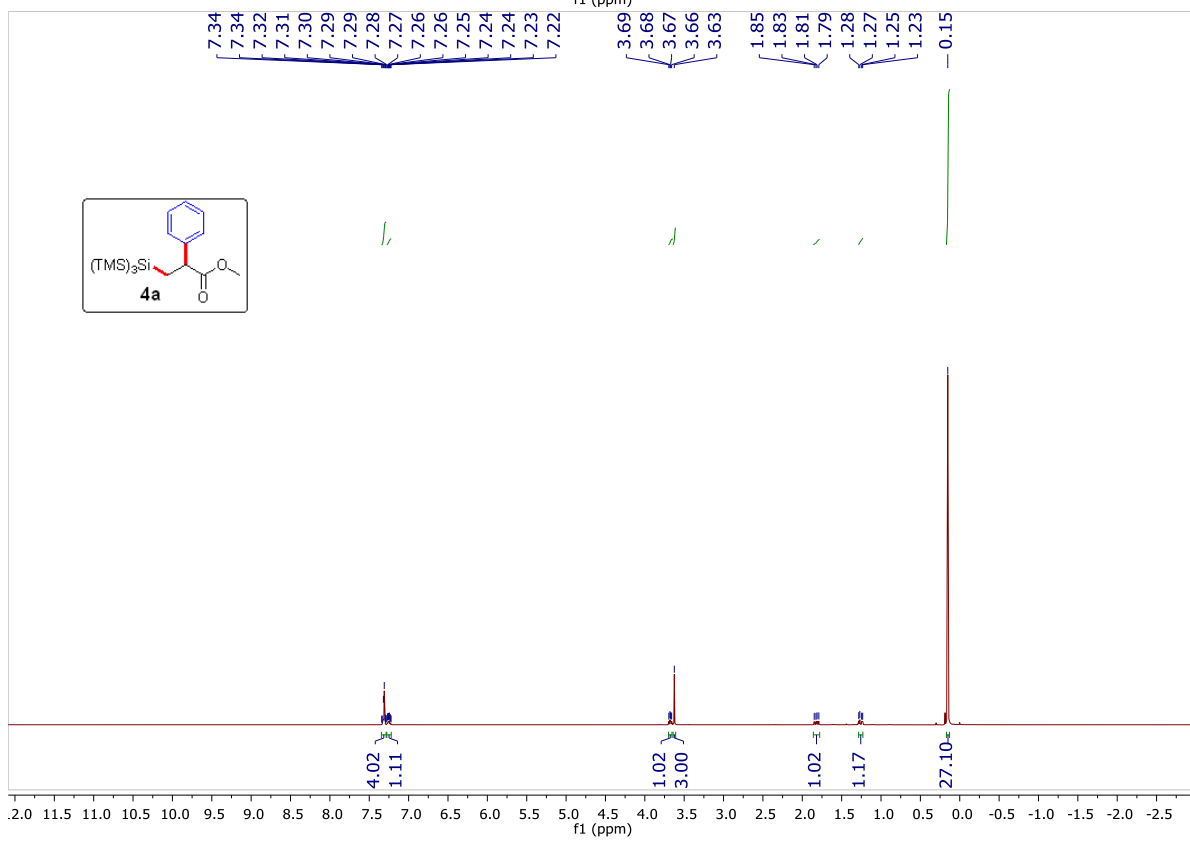
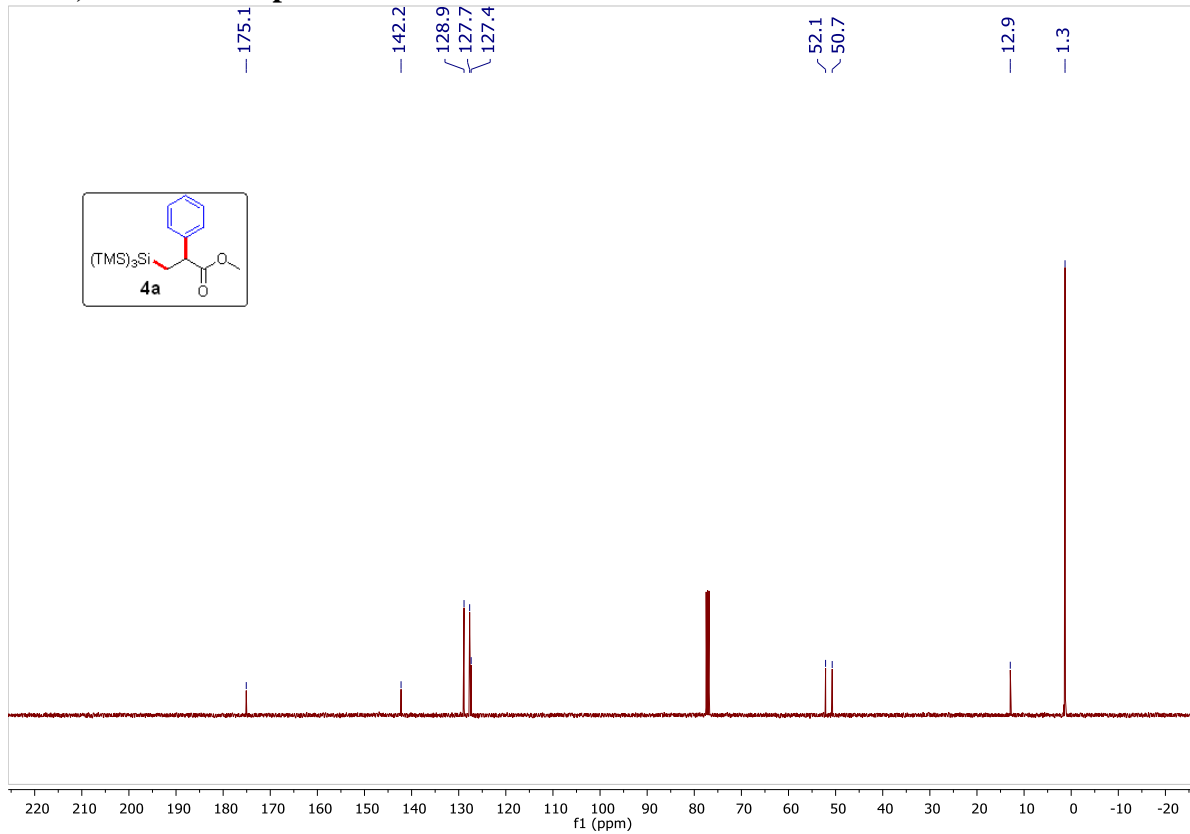


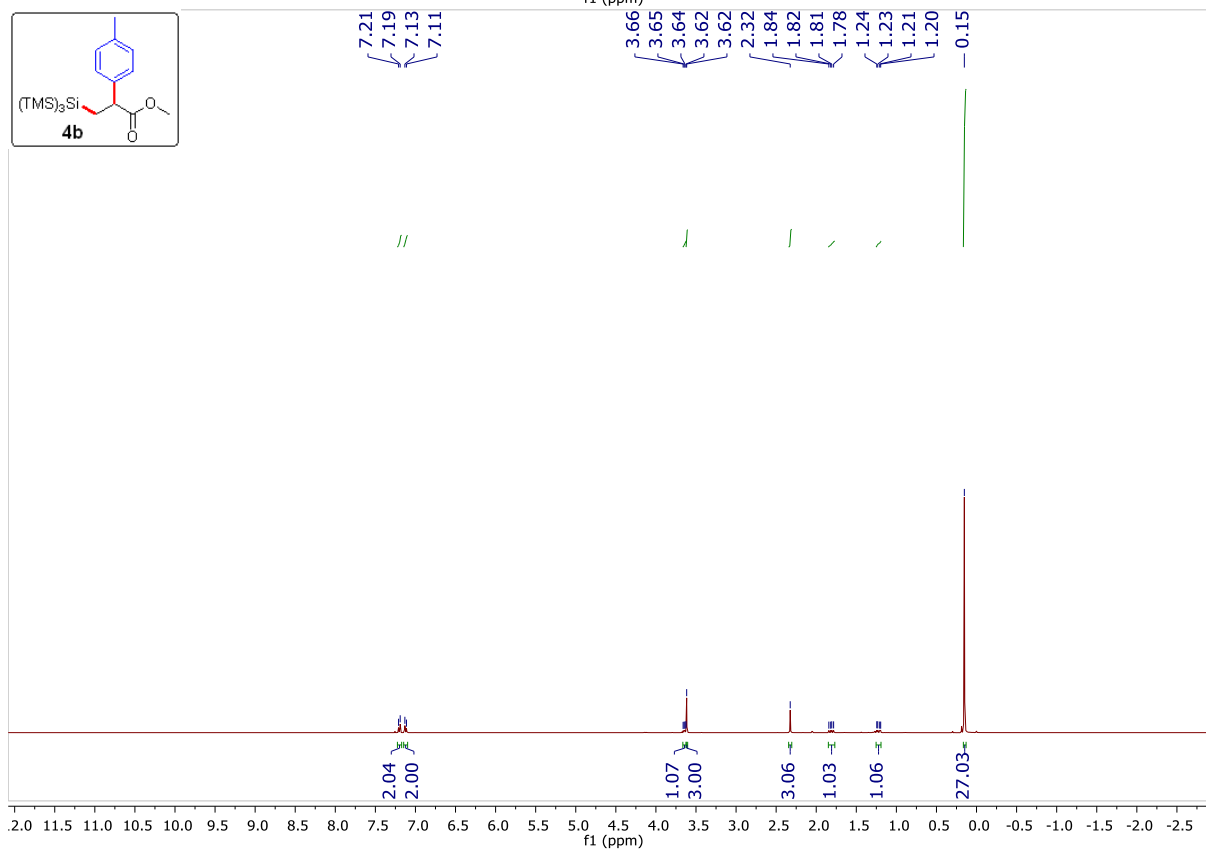
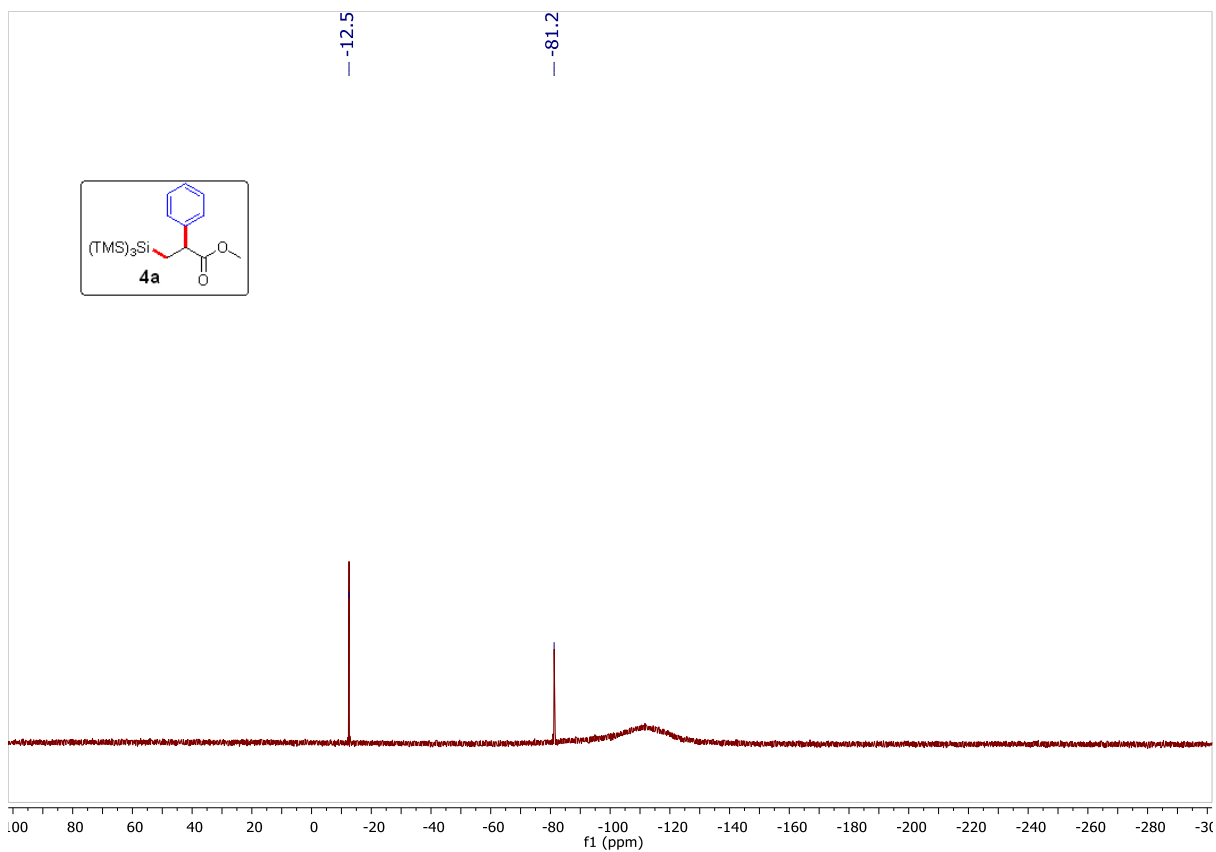
Yield: 54.5 mg, 88%, colorless oil; $R_f = 0.24$ (hexane : ethyl acetate = 30 : 1); $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.36-7.31 (m, 4H), 7.29-7.24 (m, 1H), 3.74 (t, $J = 7.7$ Hz, 1H), 3.66 (s, 3H), 1.48 (dd, $J = 14.8, 7.8$ Hz, 1H), 1.16 (dd, $J = 14.7, 7.7$ Hz, 1H), 0.08 (s, 9H), -0.01 (s, 3H), -0.06 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 175.5, 141.3, 128.7, 128.0, 127.2, 52.1, 46.8, 23.1, 2.0, 1.0, 0.8; $^{29}\text{Si NMR}$ (79 MHz, CDCl_3) δ 8.1, 6.1; HRMS (ESI, m/z): $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{26}\text{NaO}_3\text{Si}_2^+ = 333.1313$, found 333.1313.

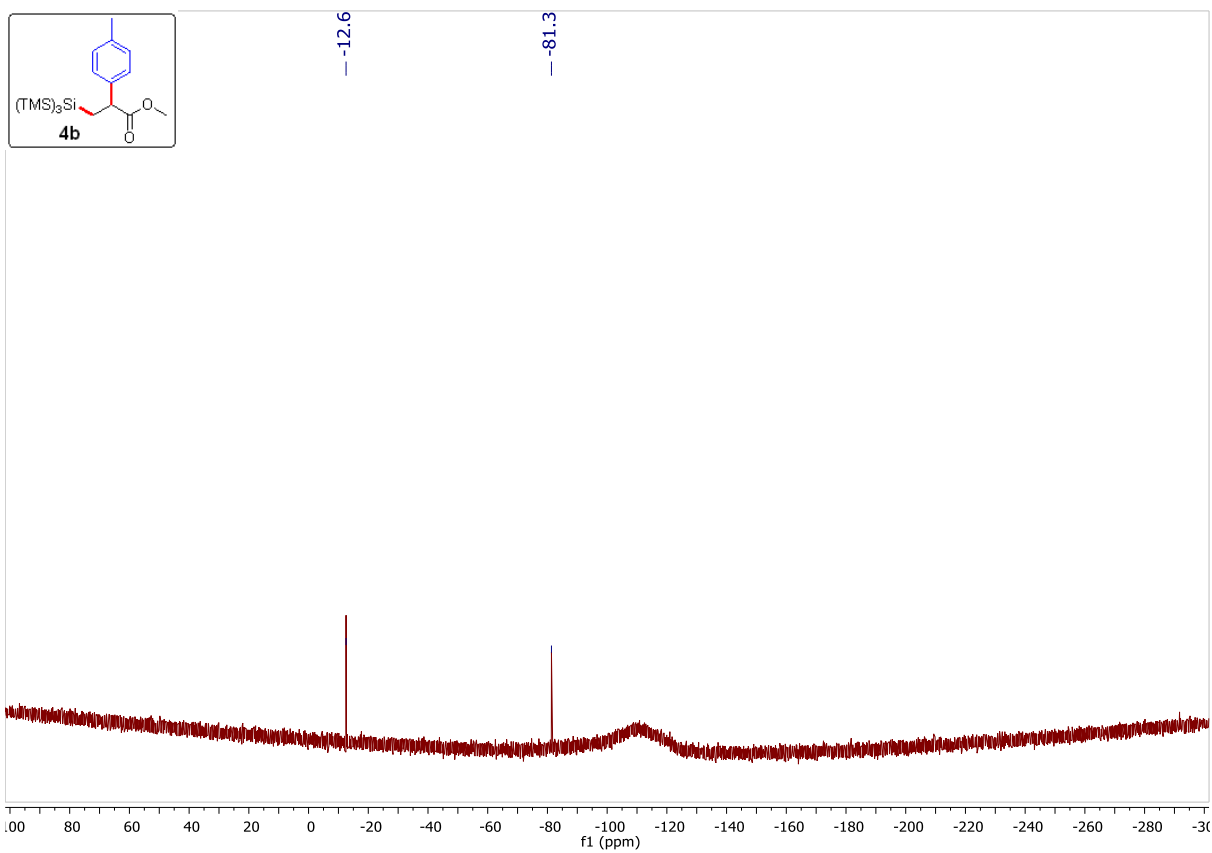
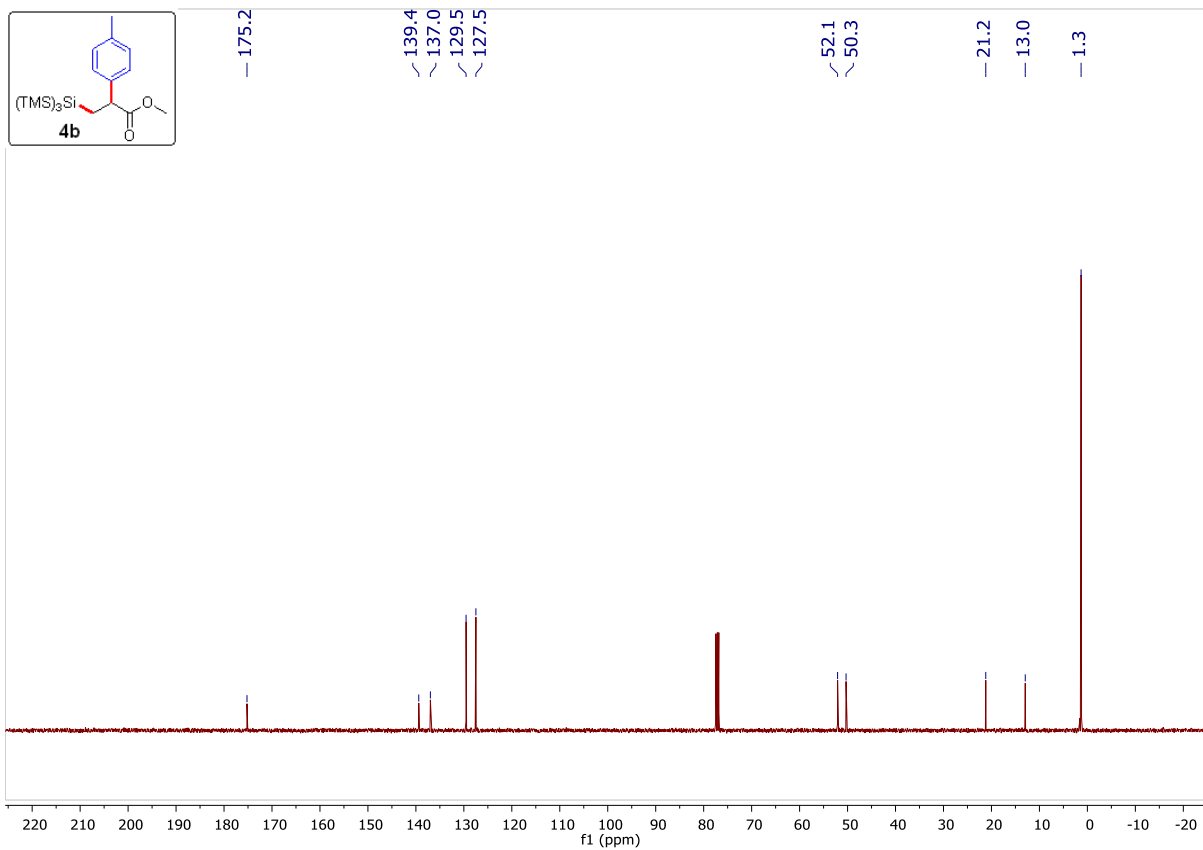
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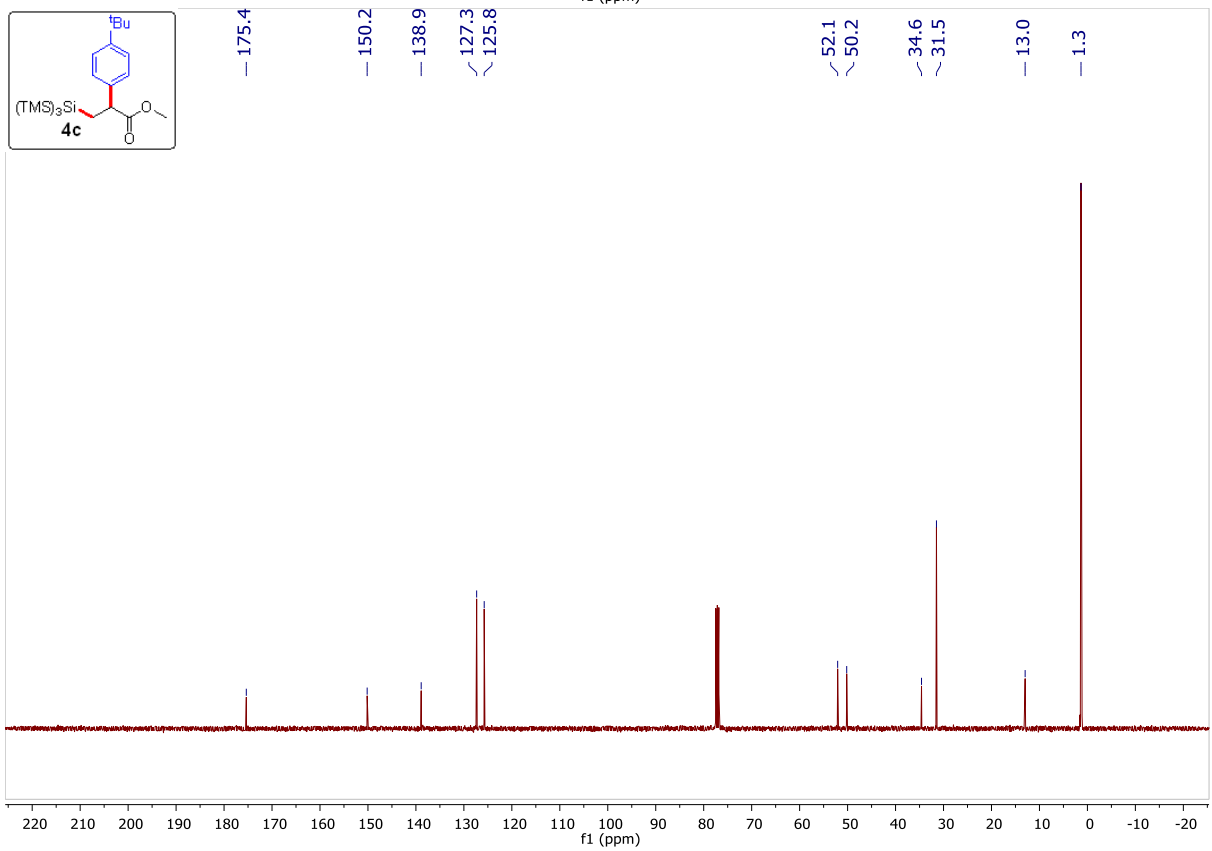
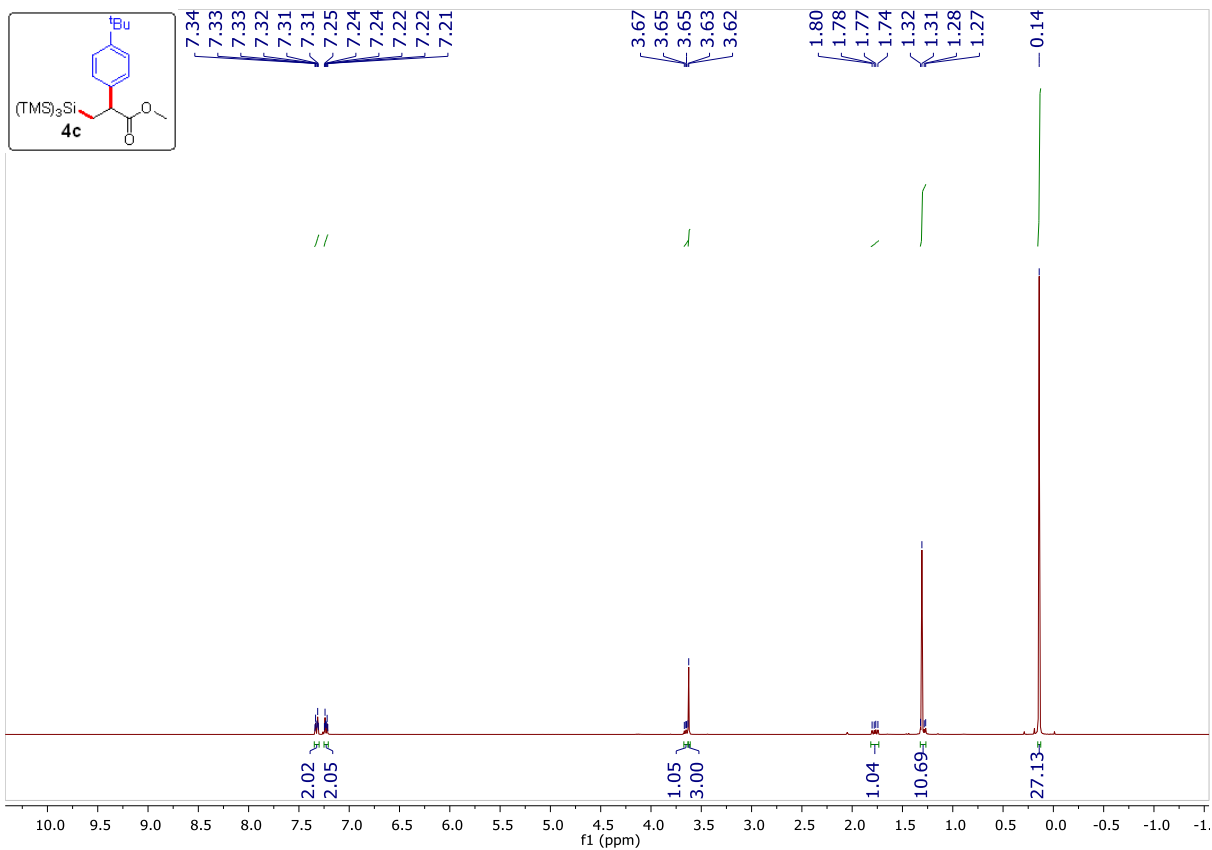
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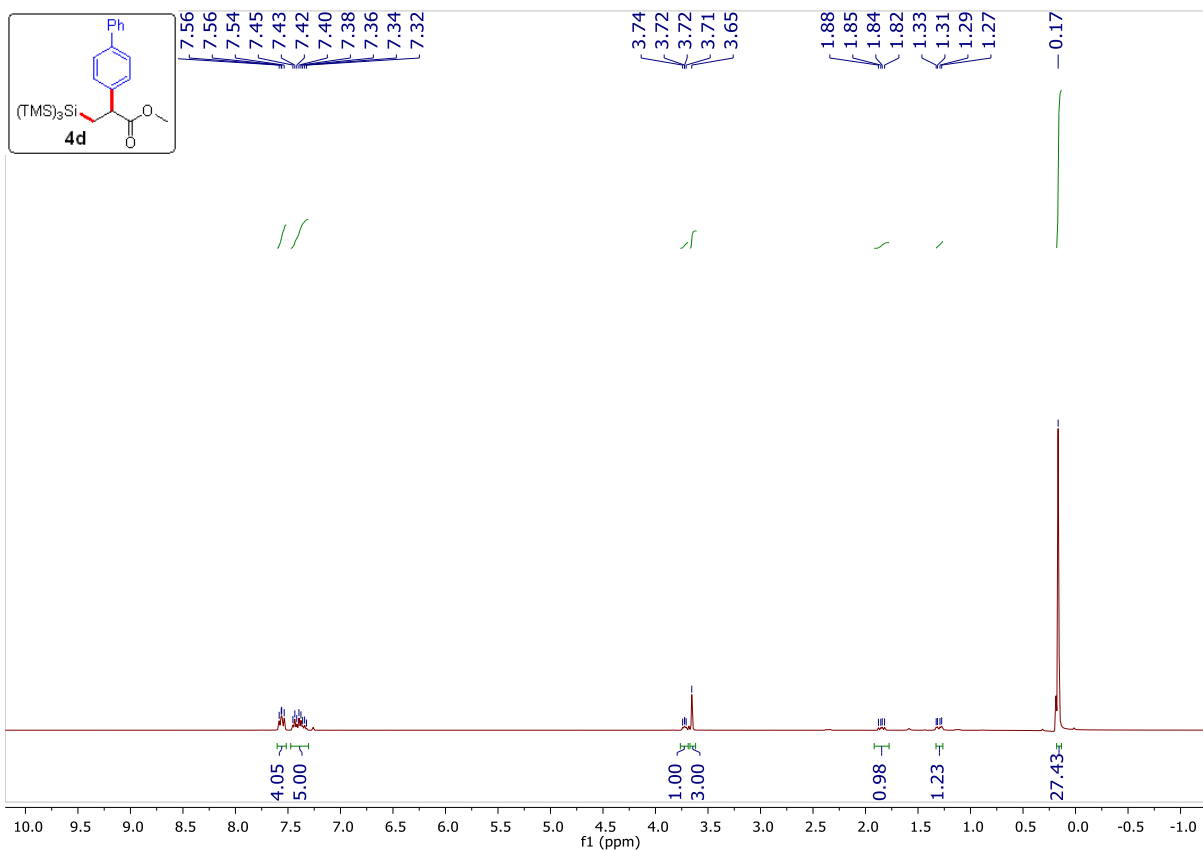
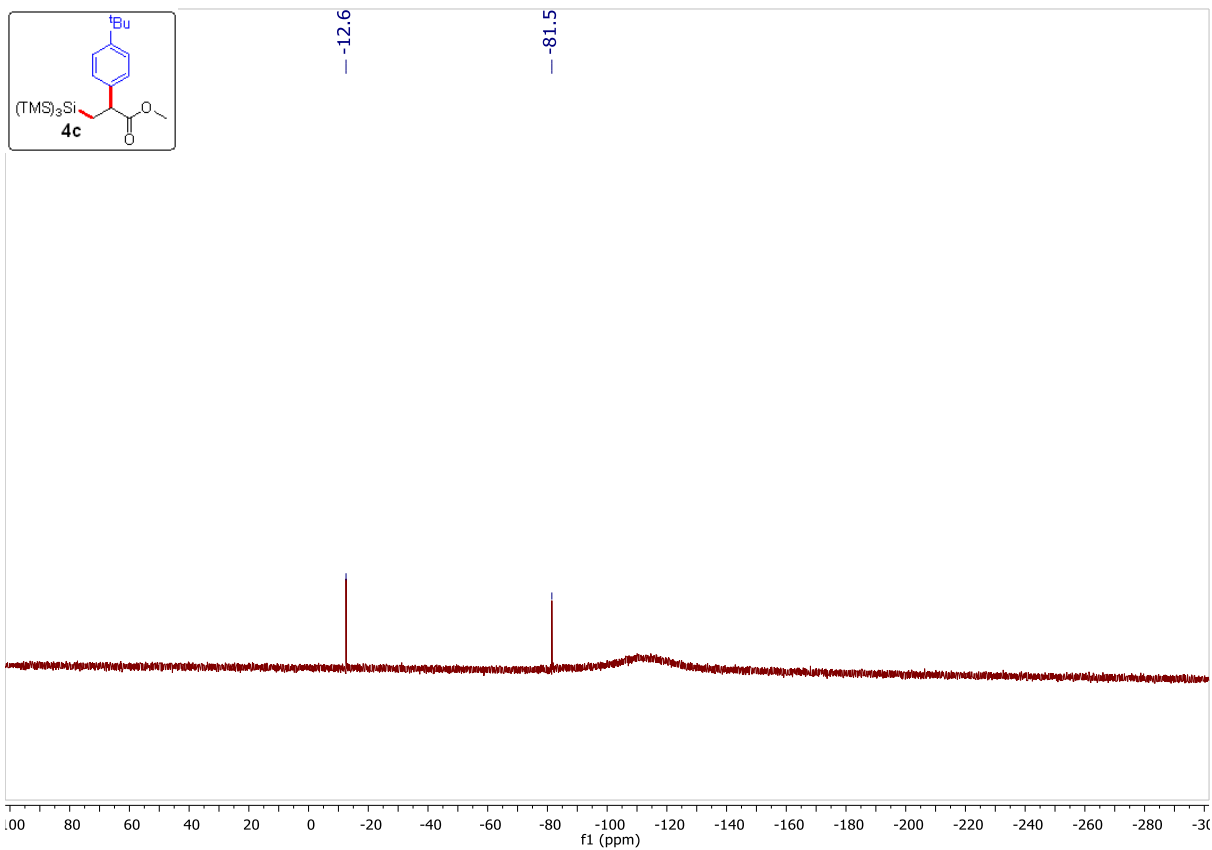
9. ^1H , ^{13}C and ^{29}Si spectra

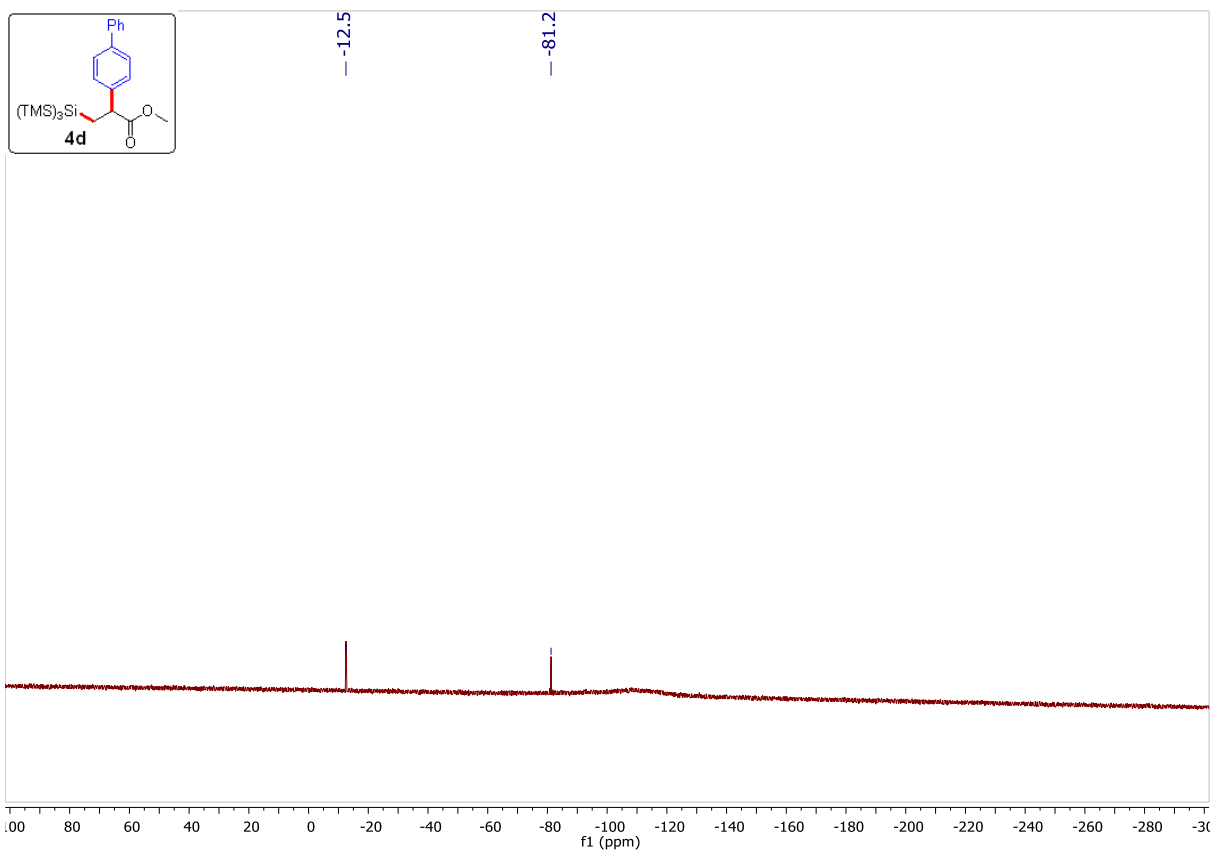
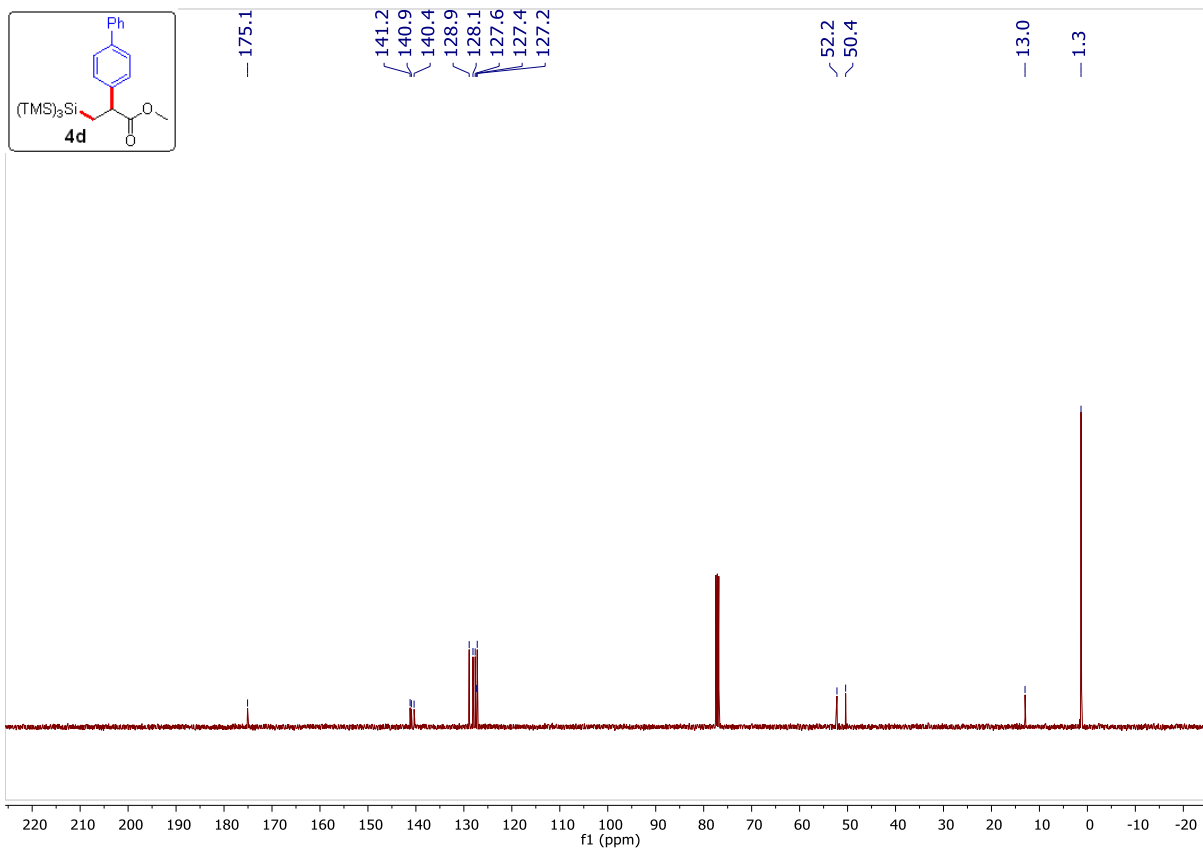




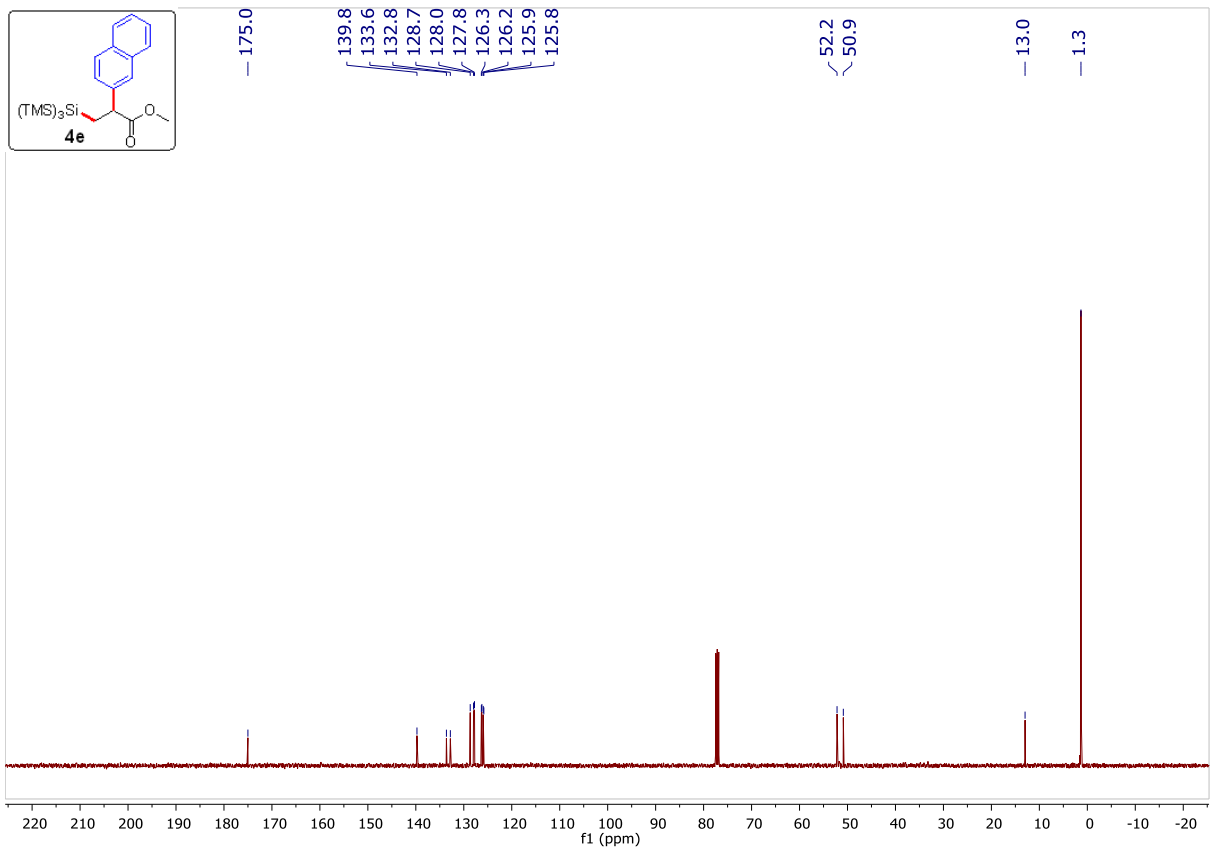
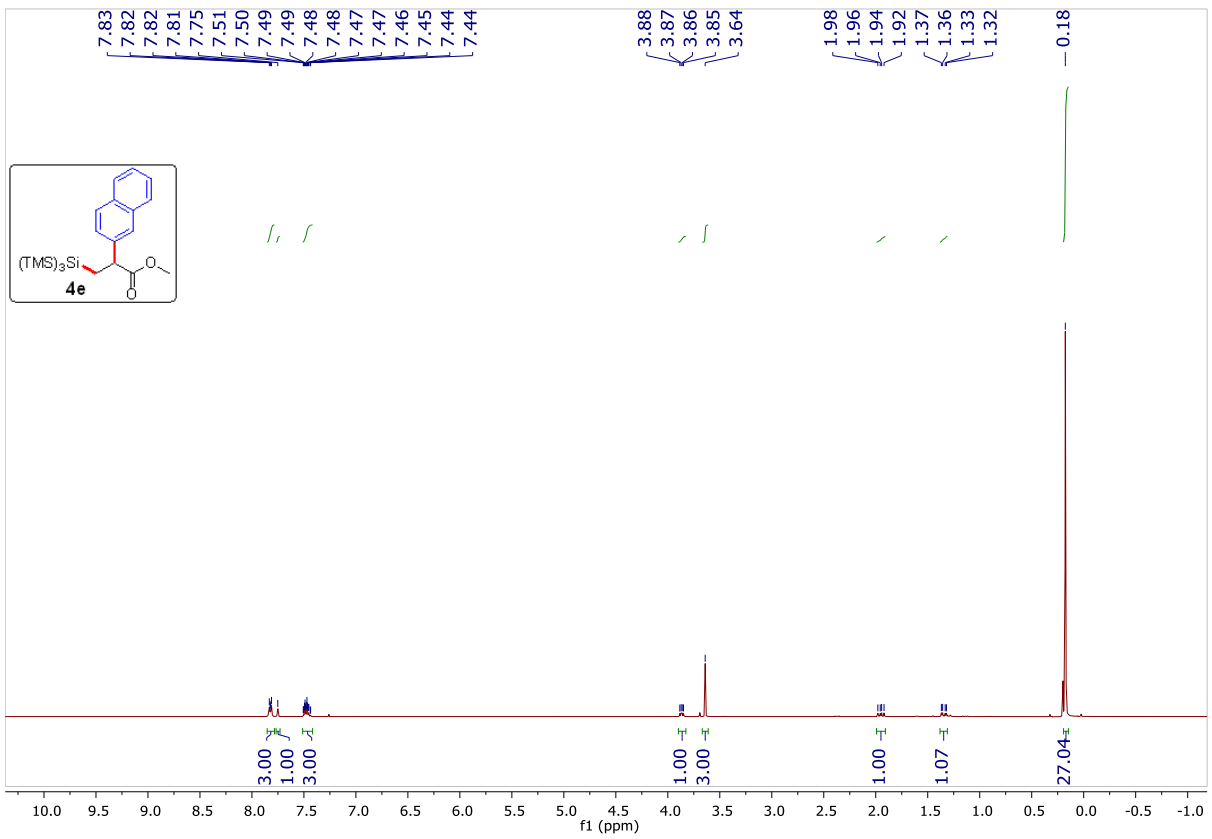


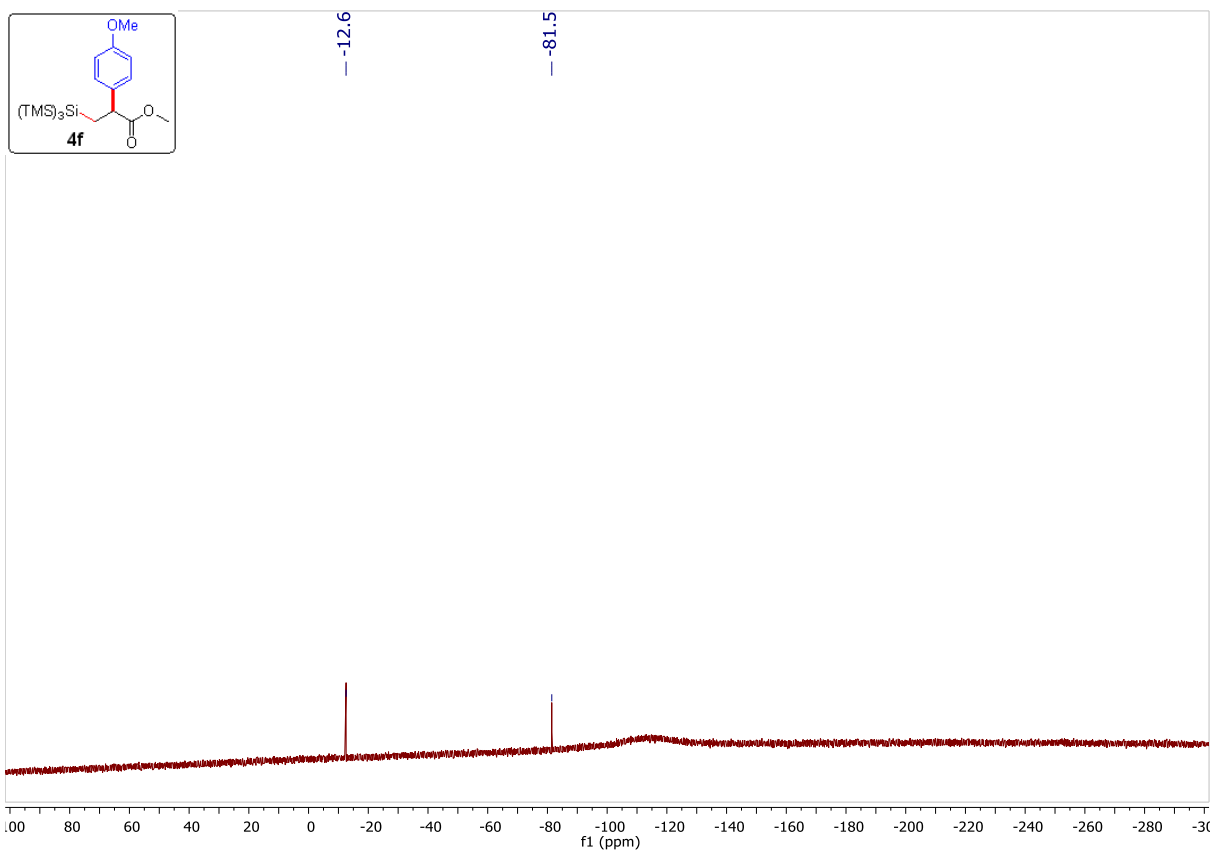
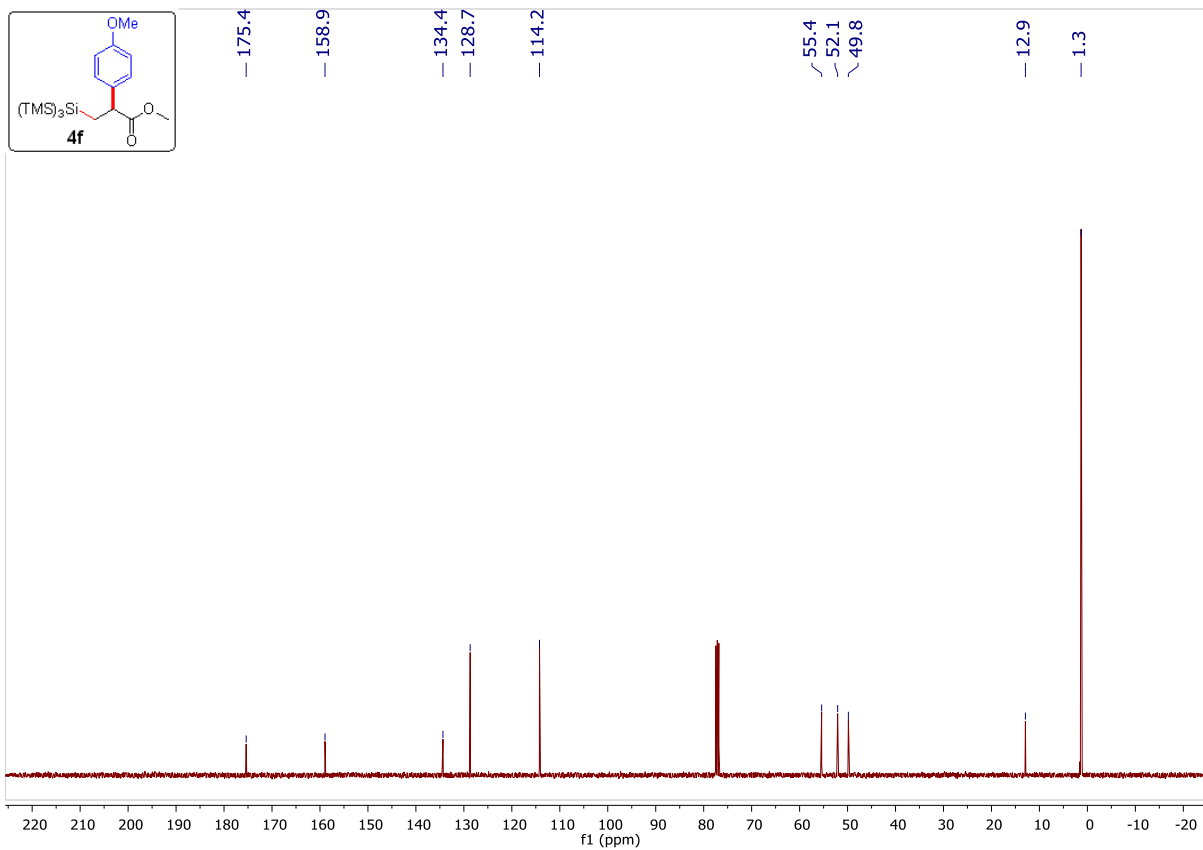




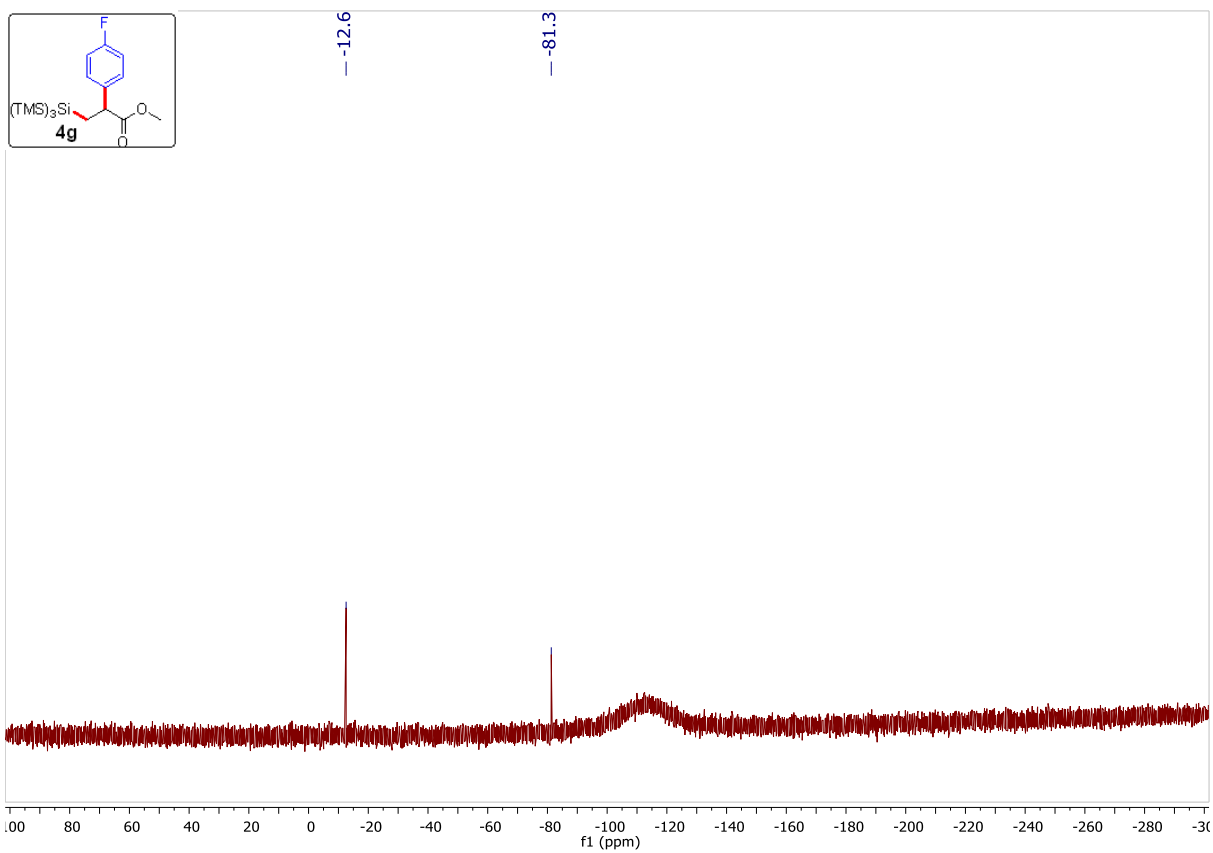
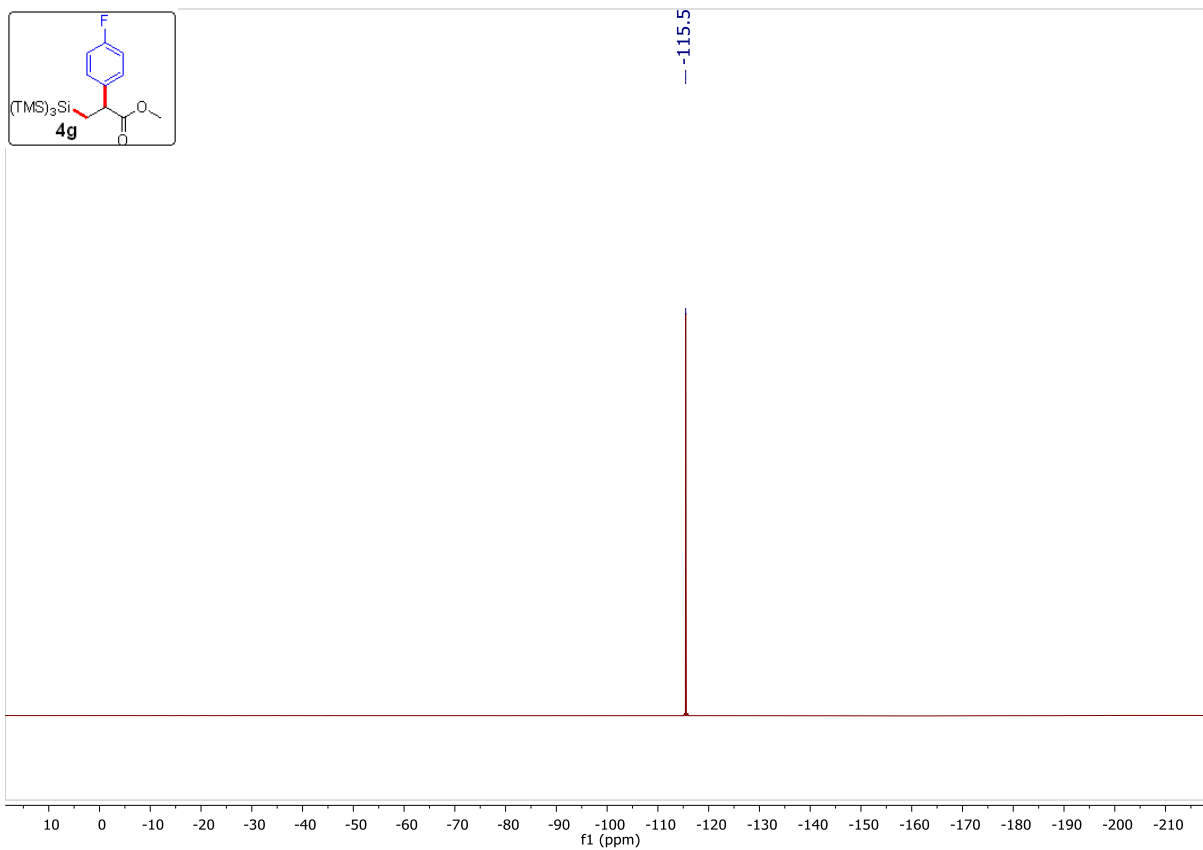


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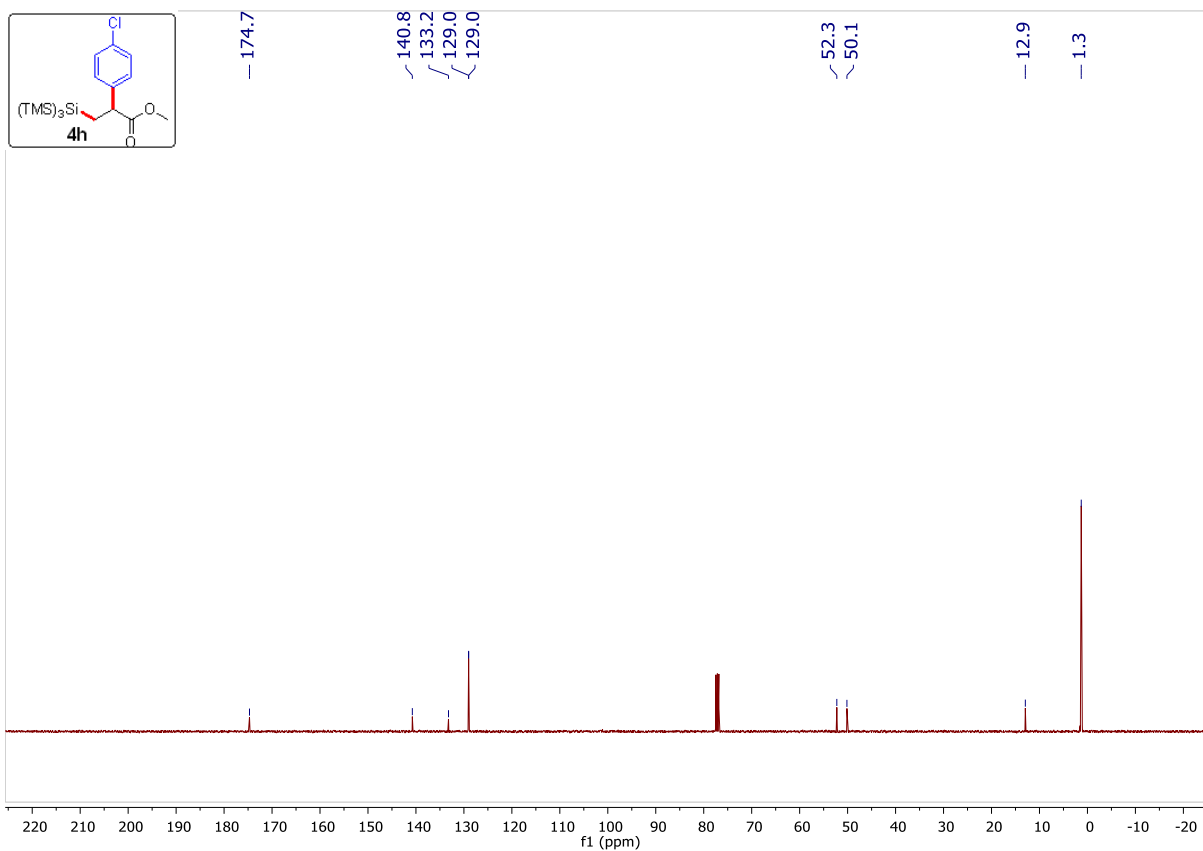
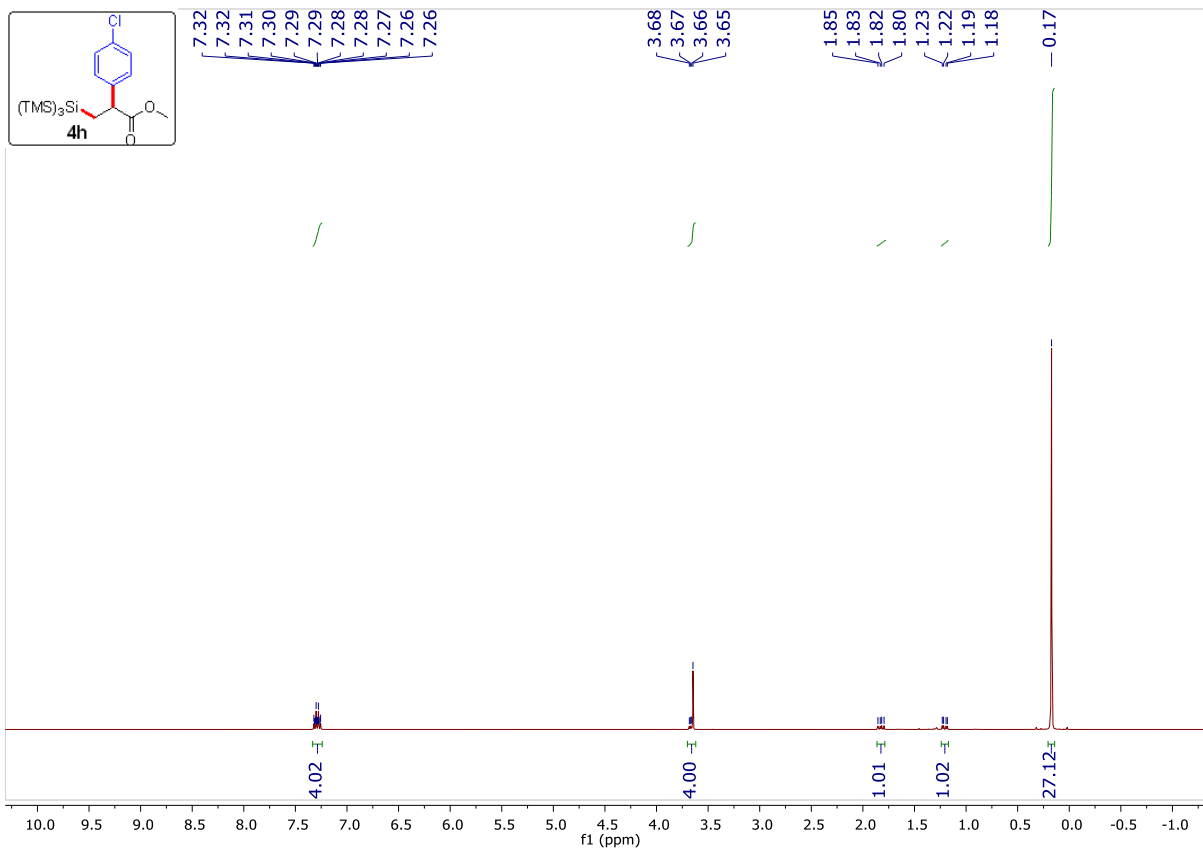




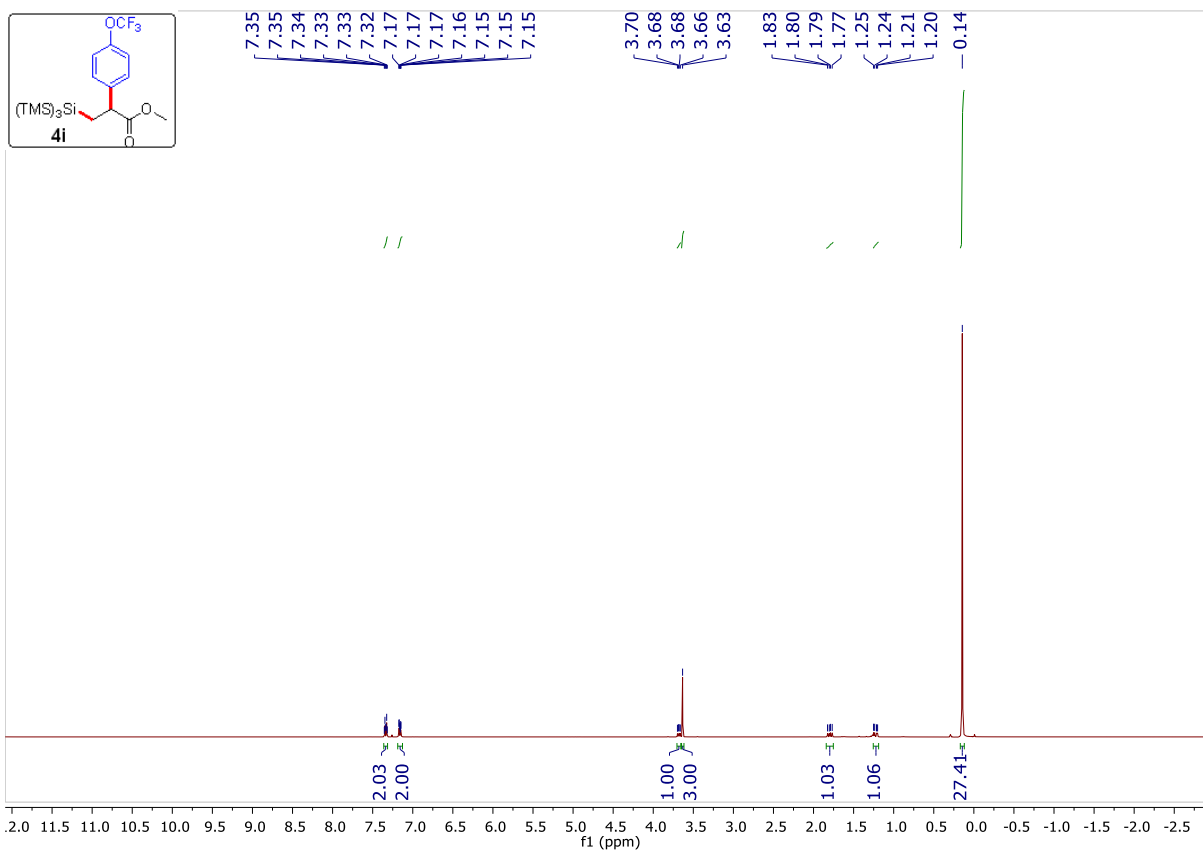
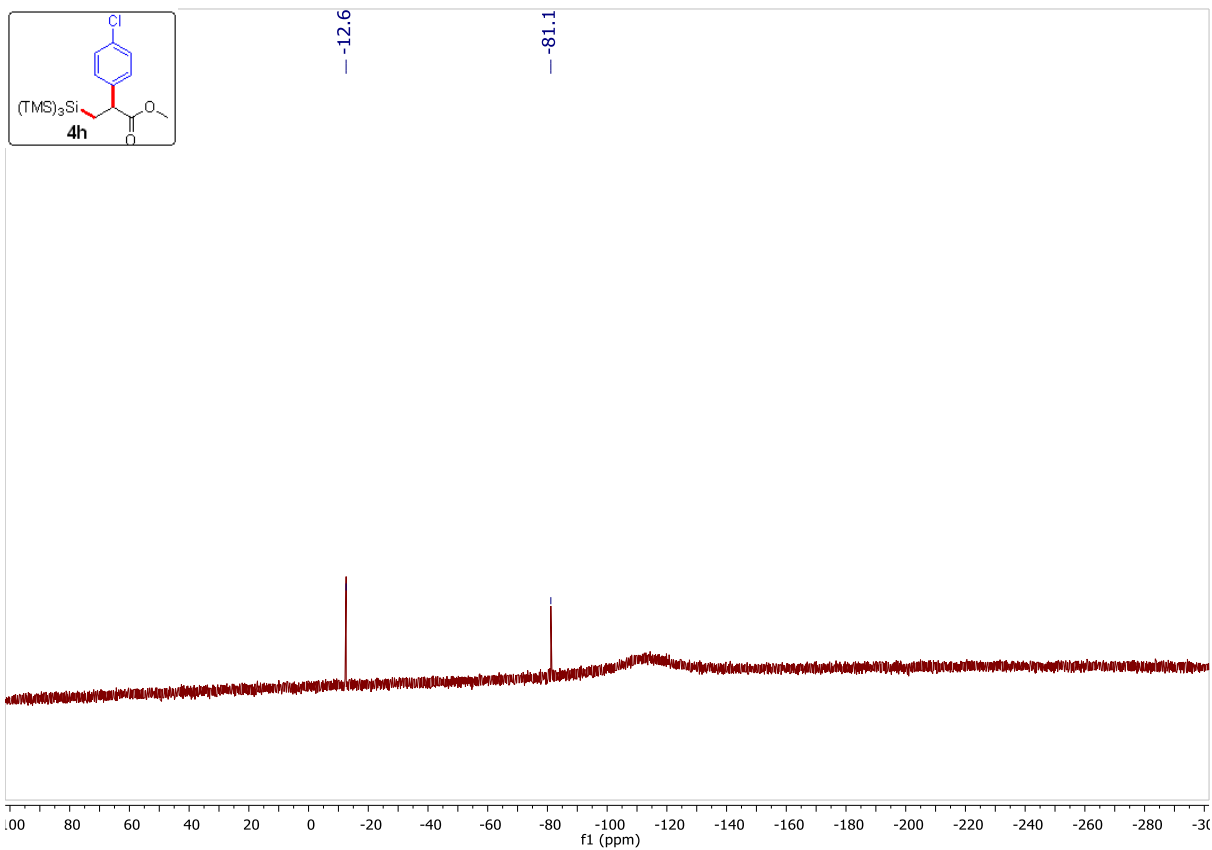
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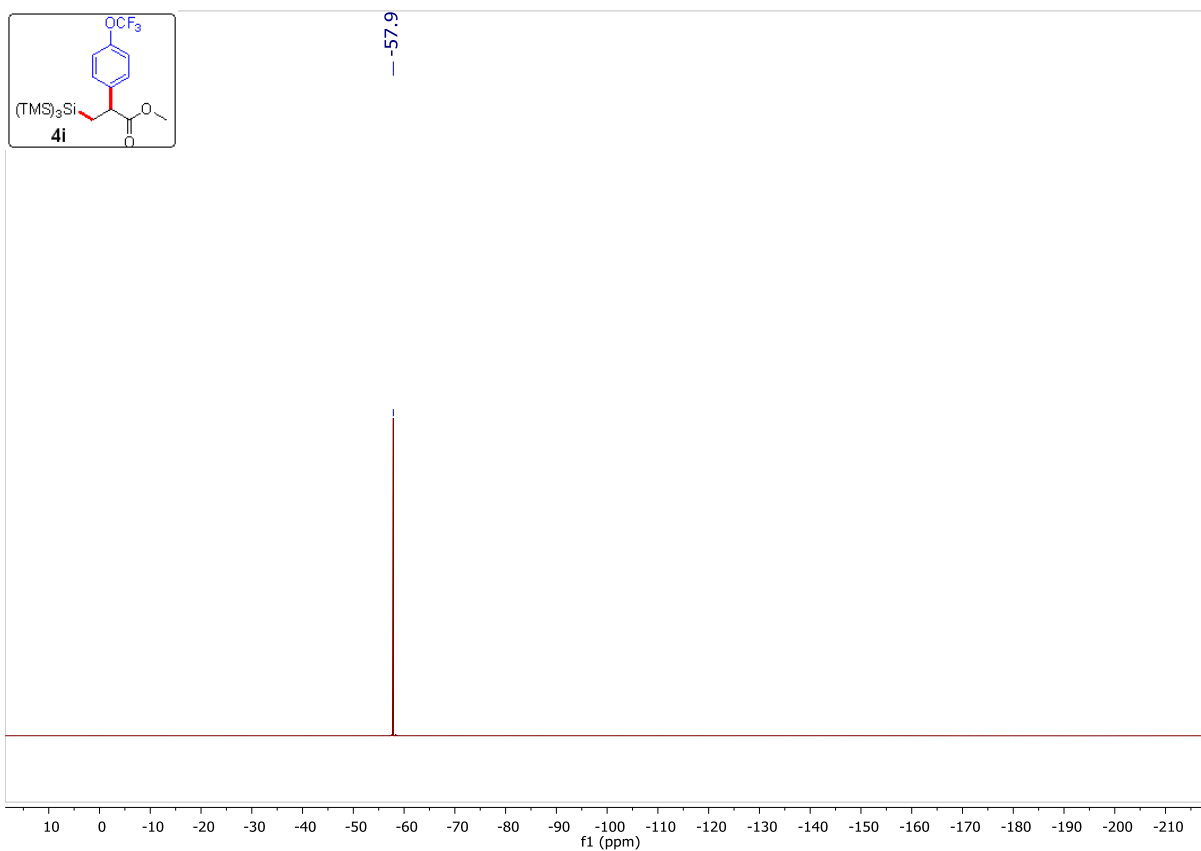
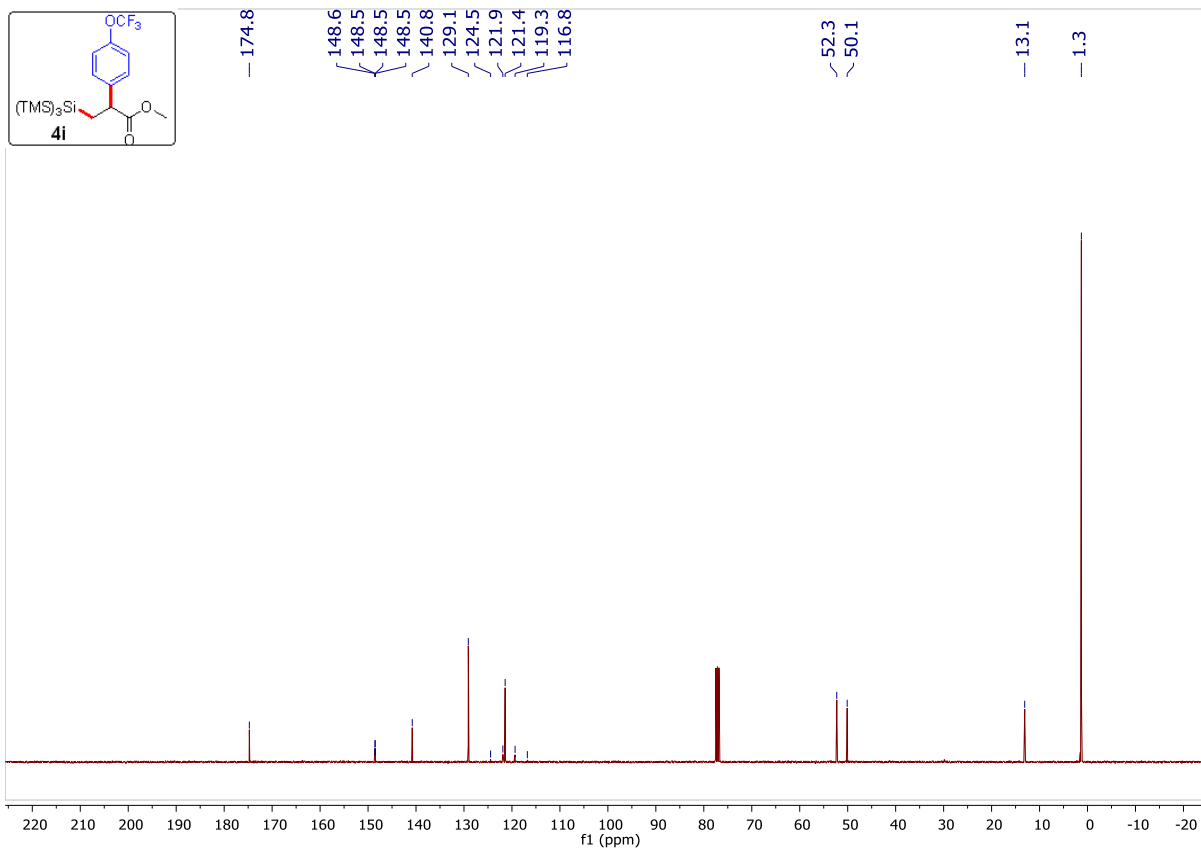


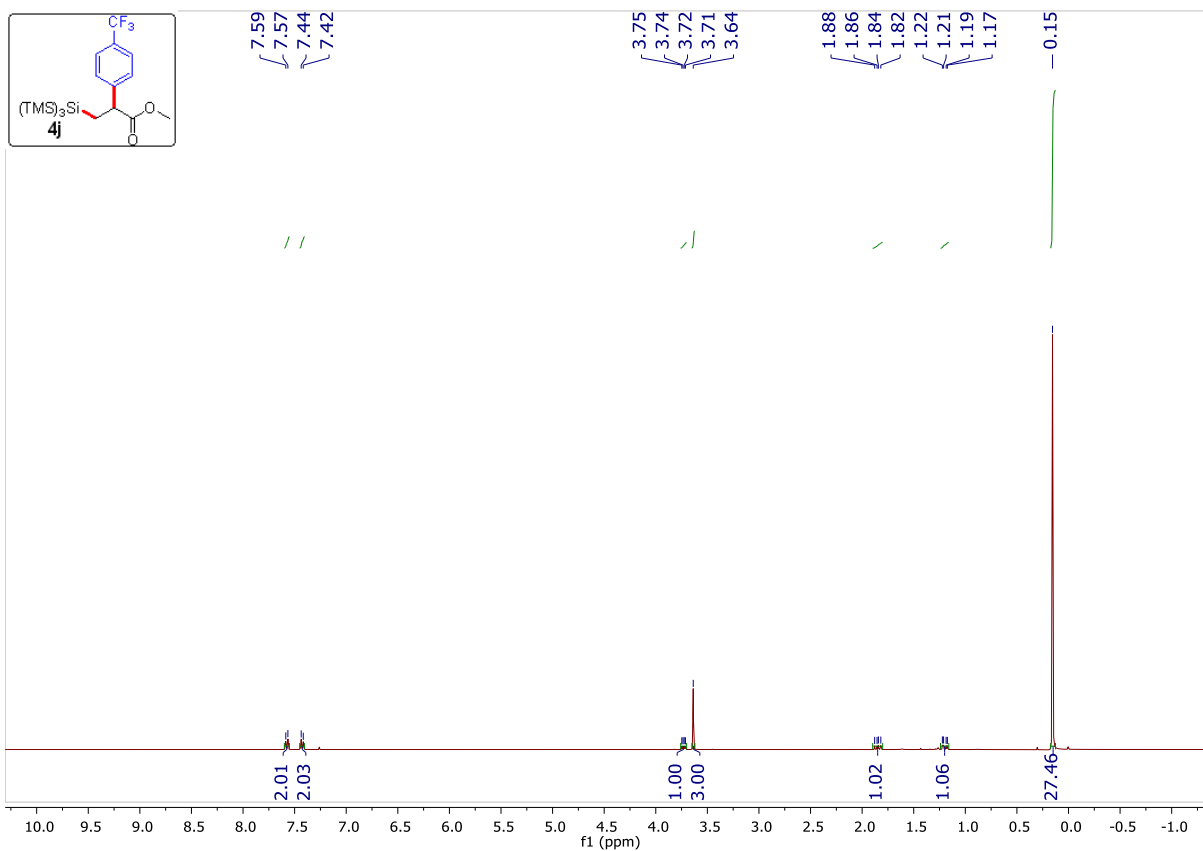
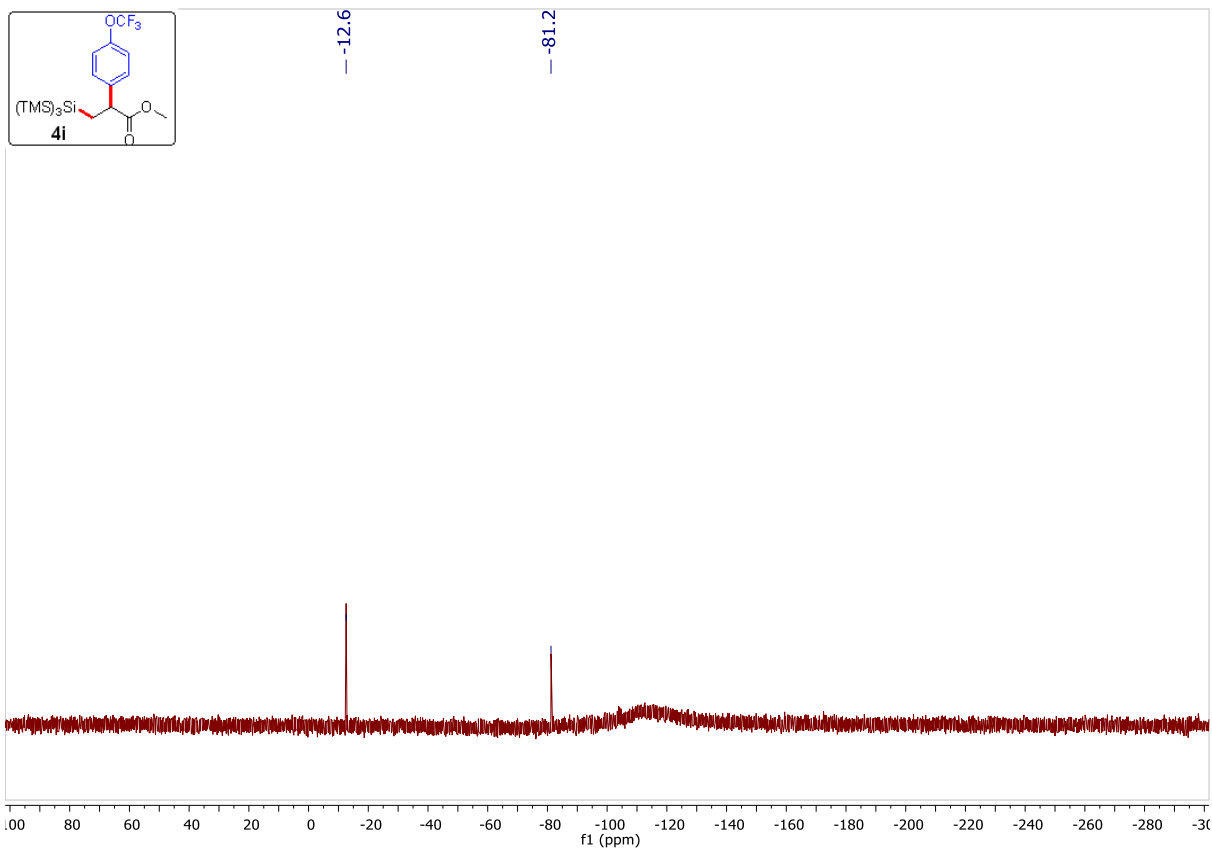
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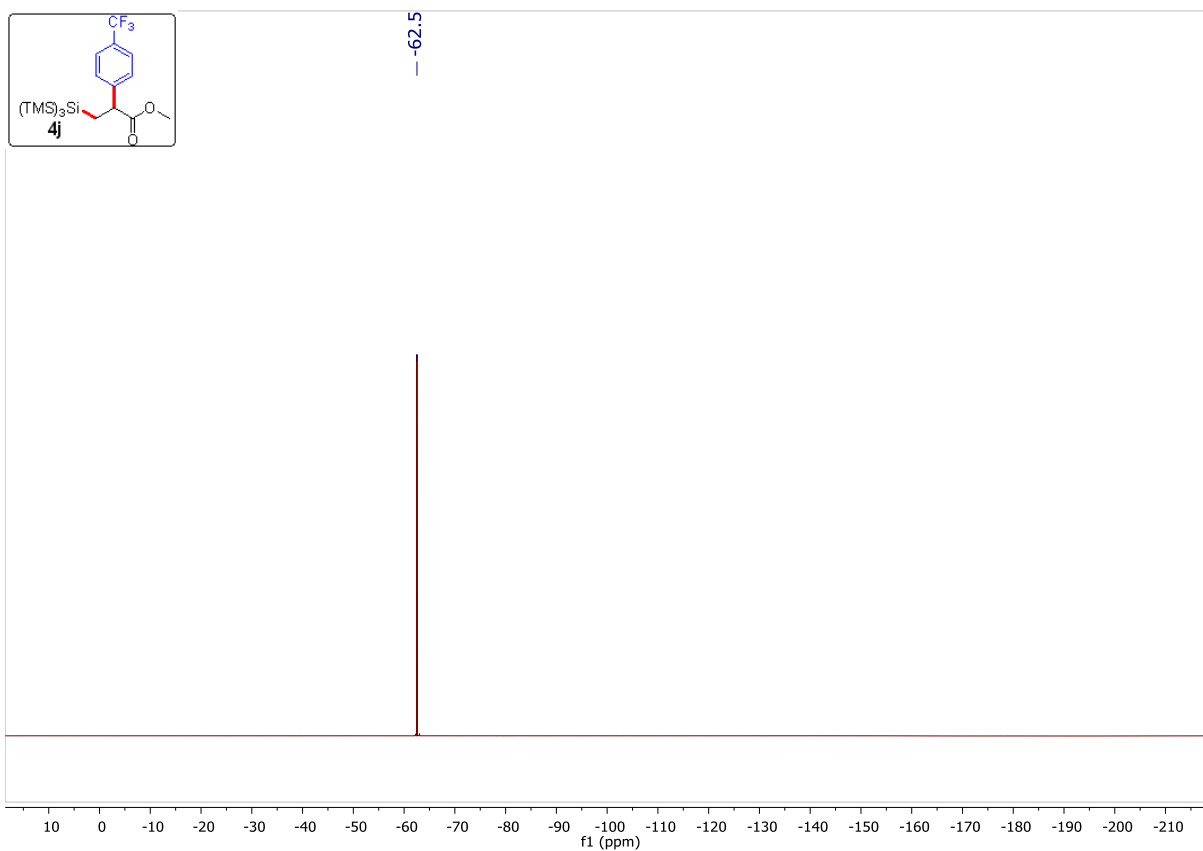
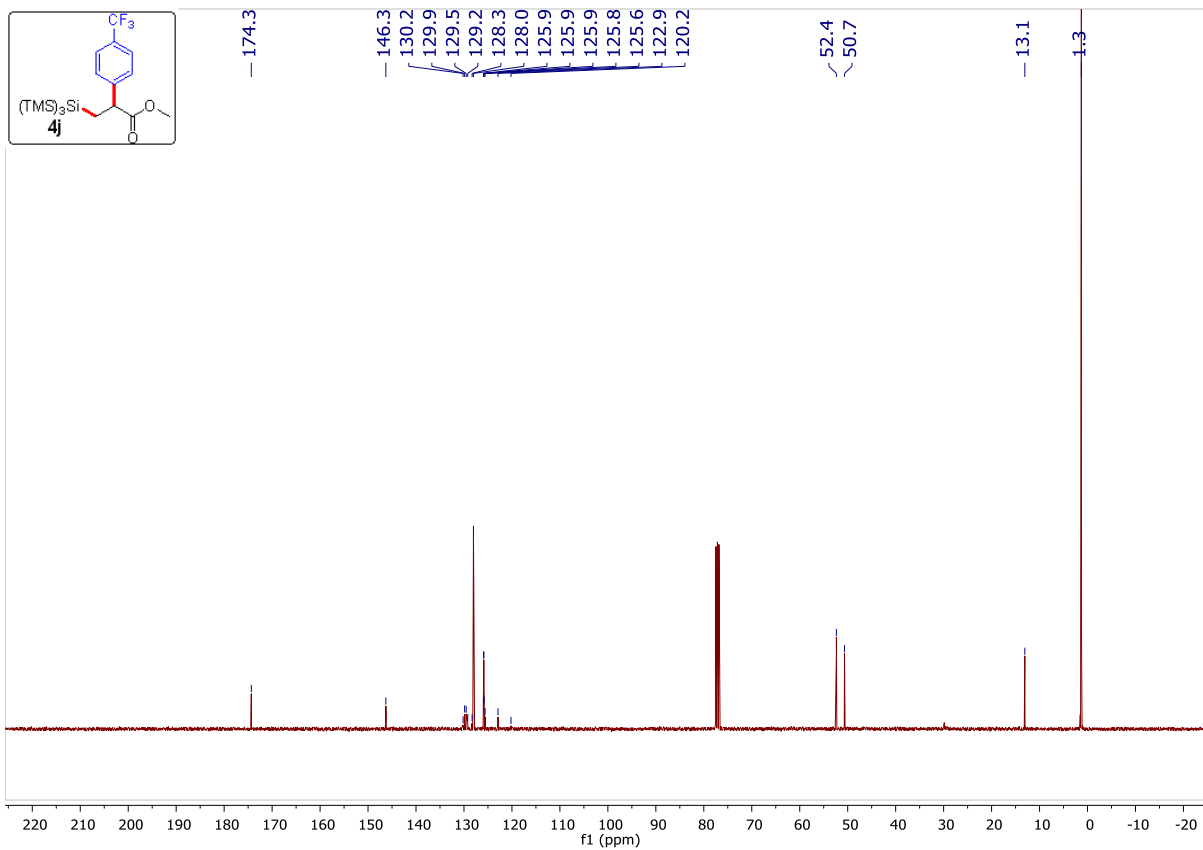


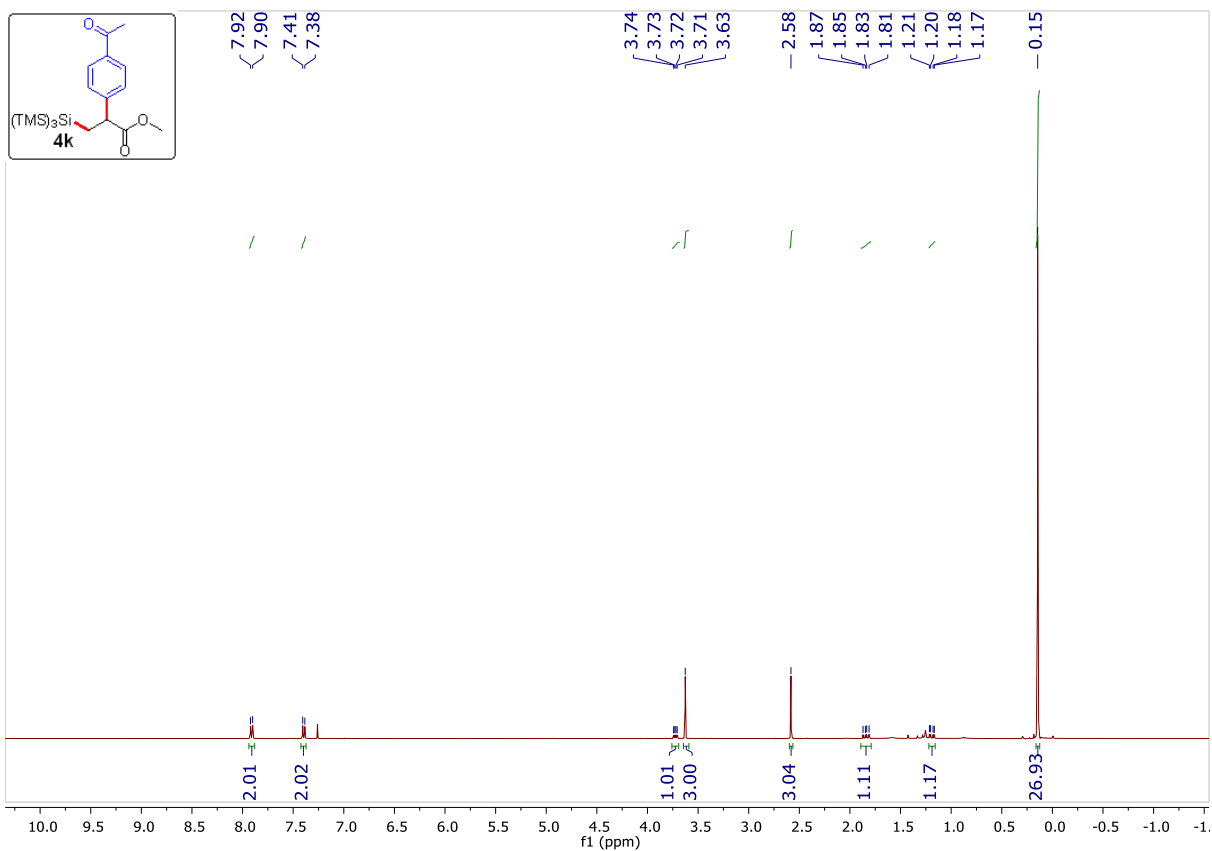
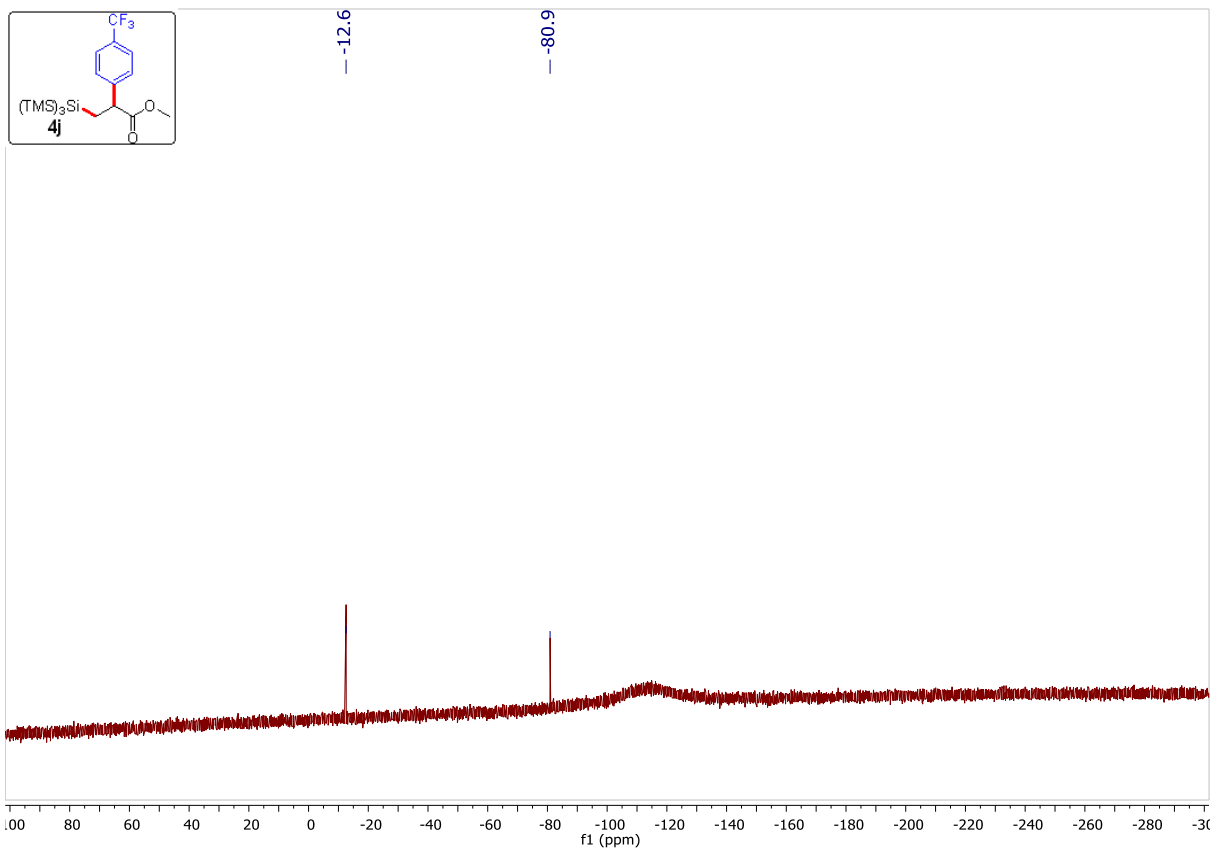
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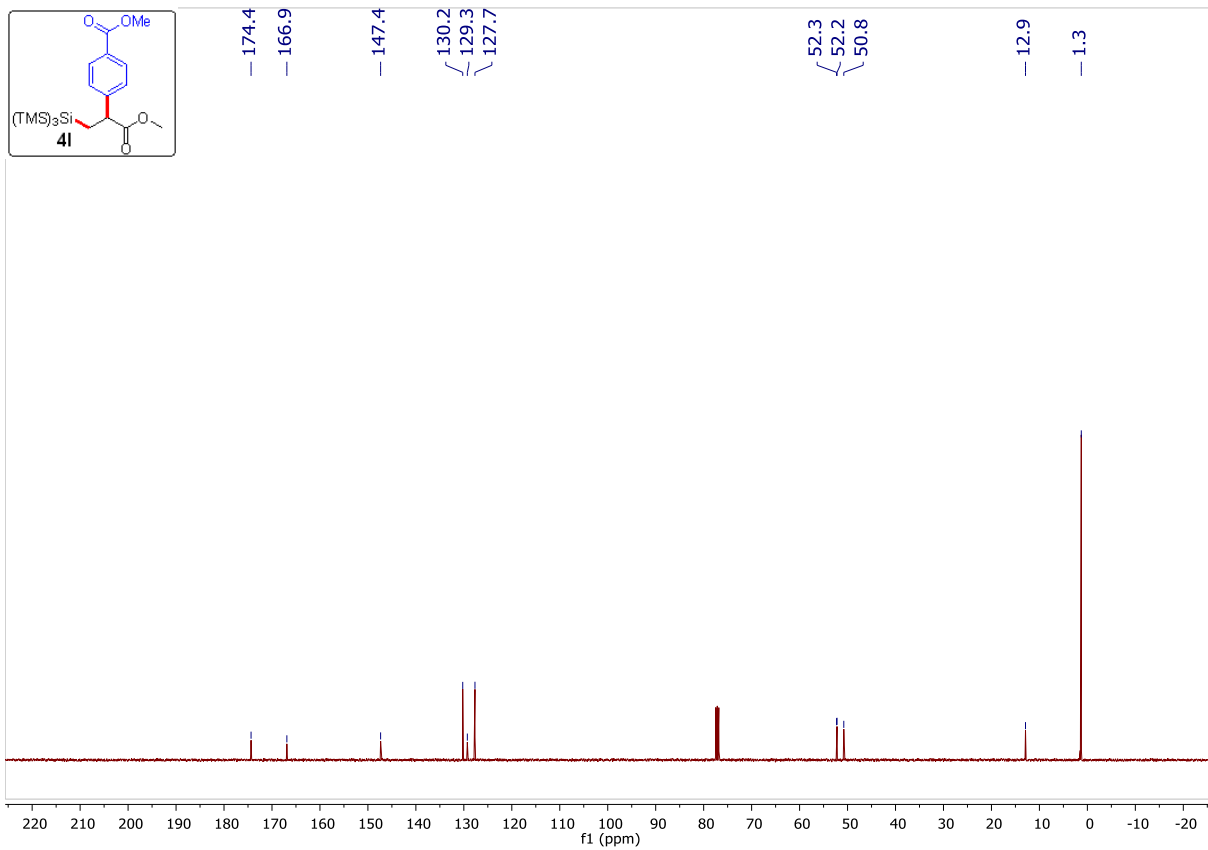
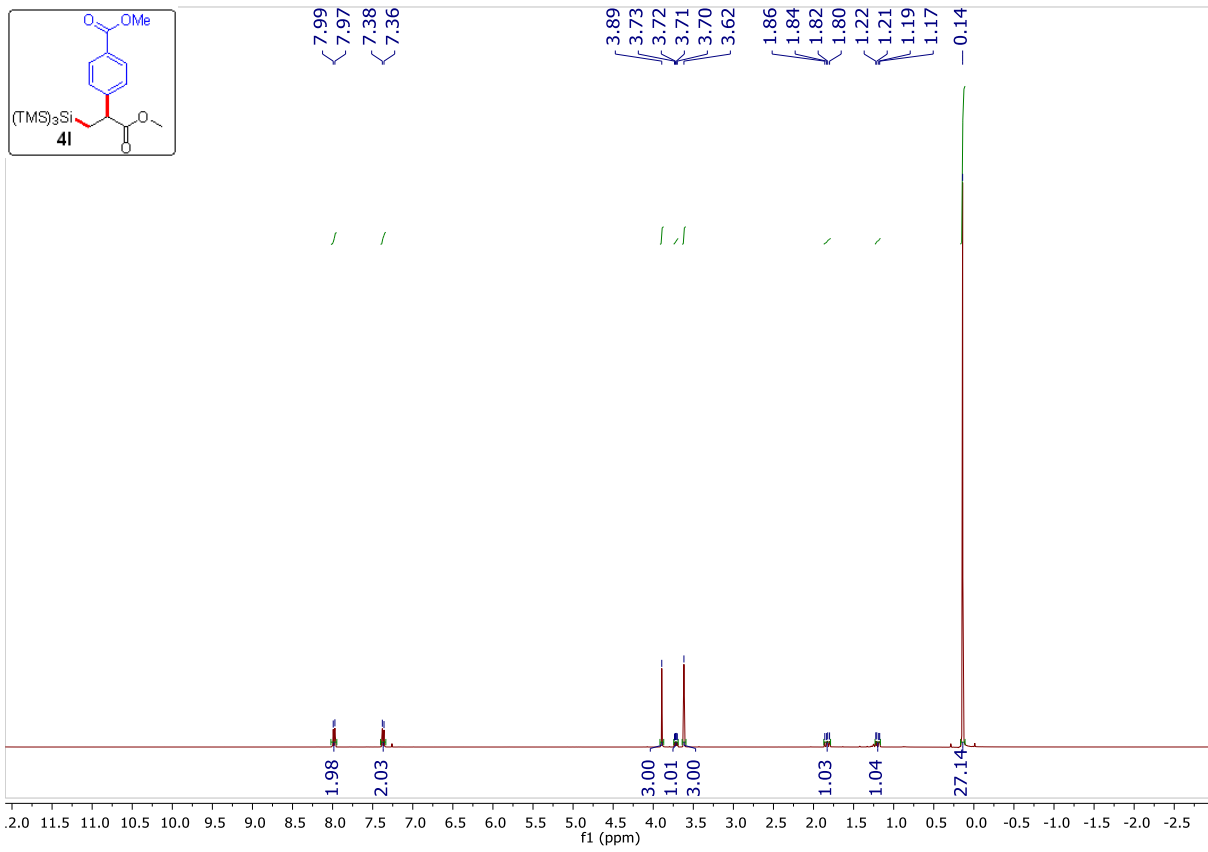


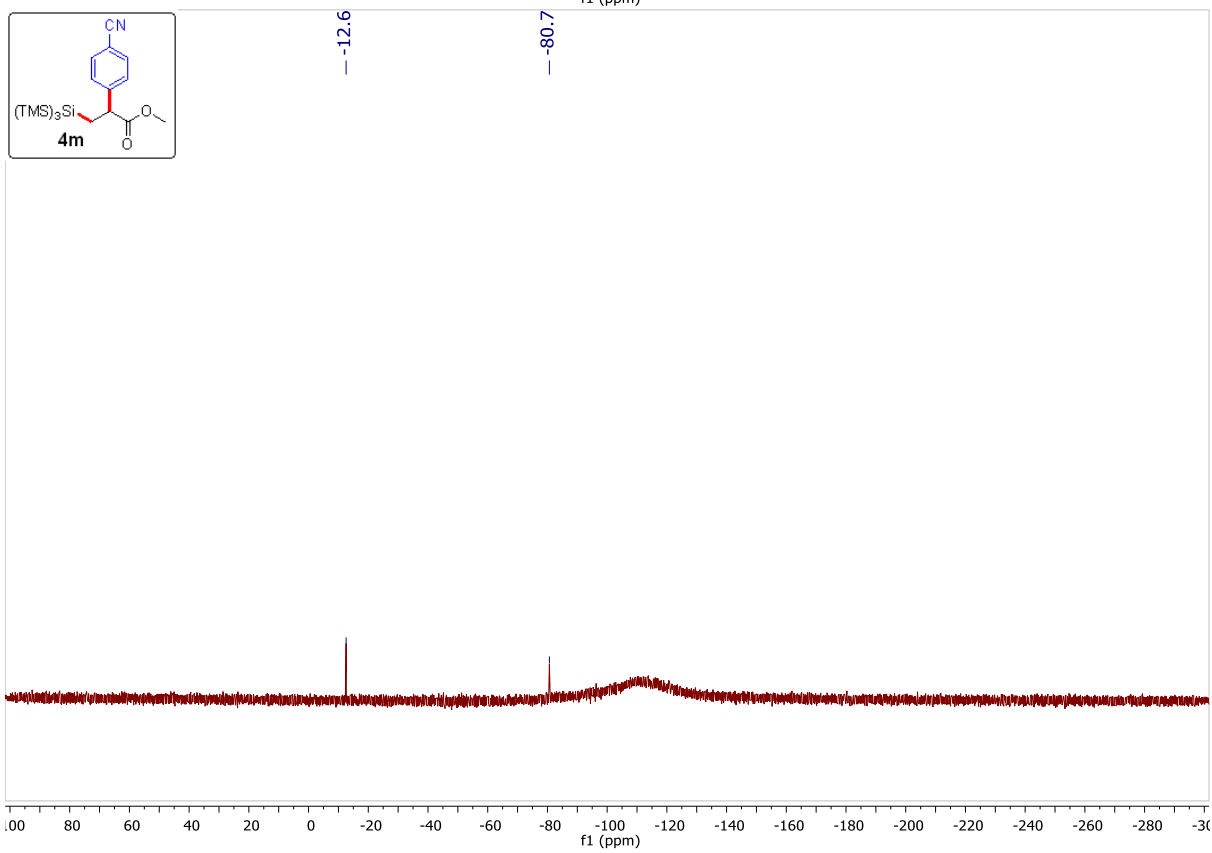
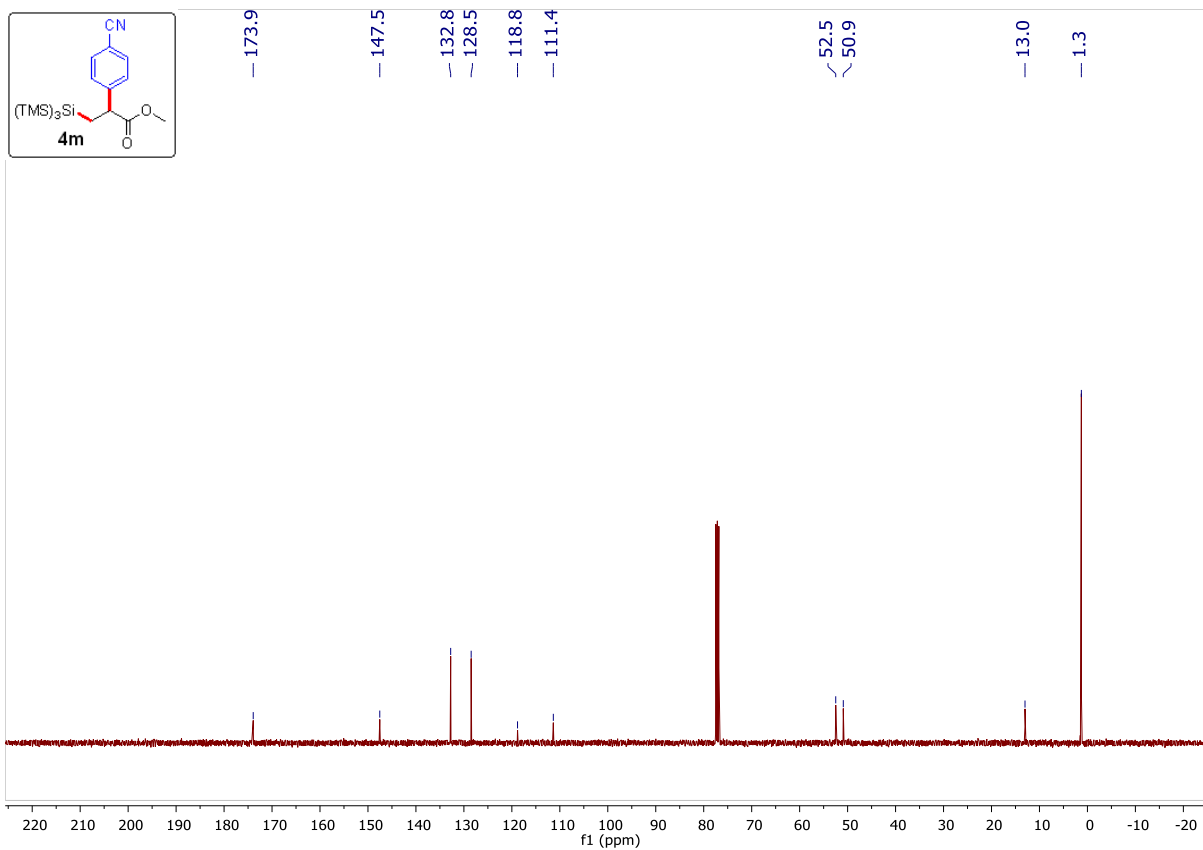


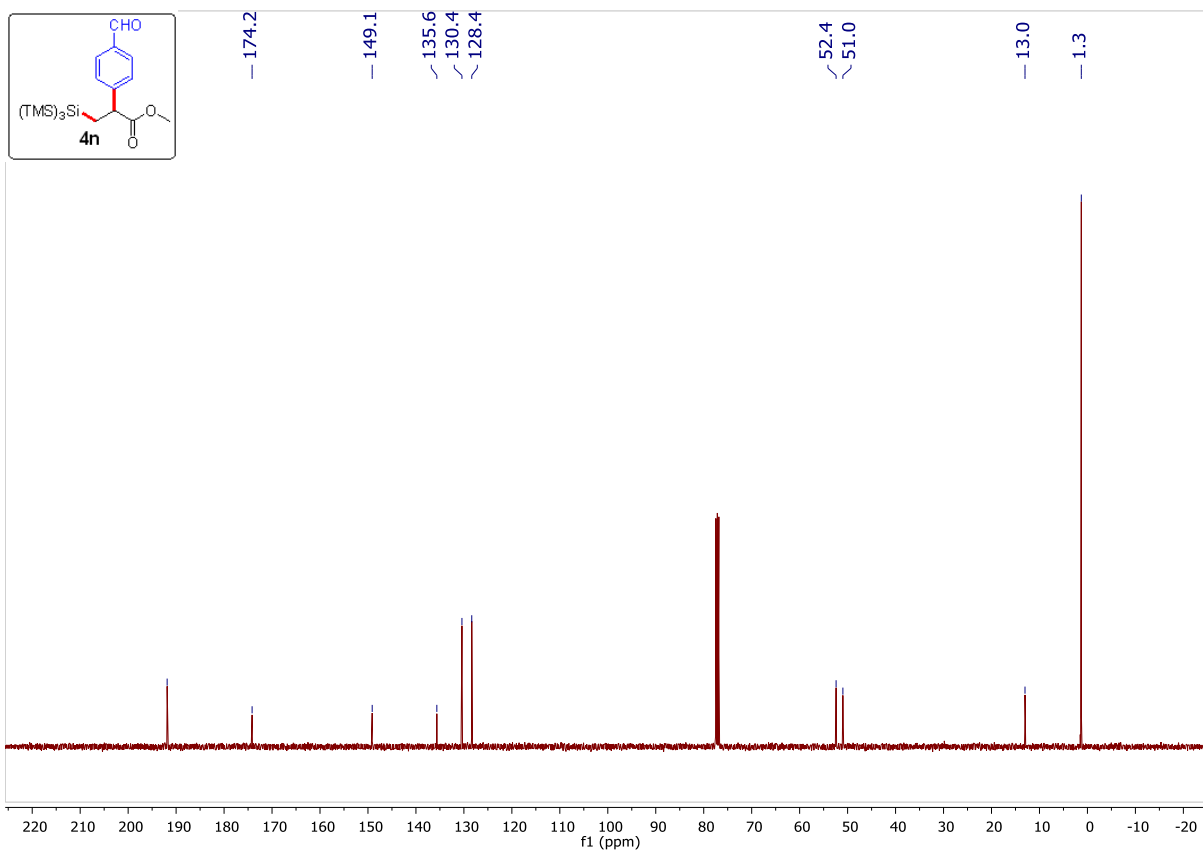
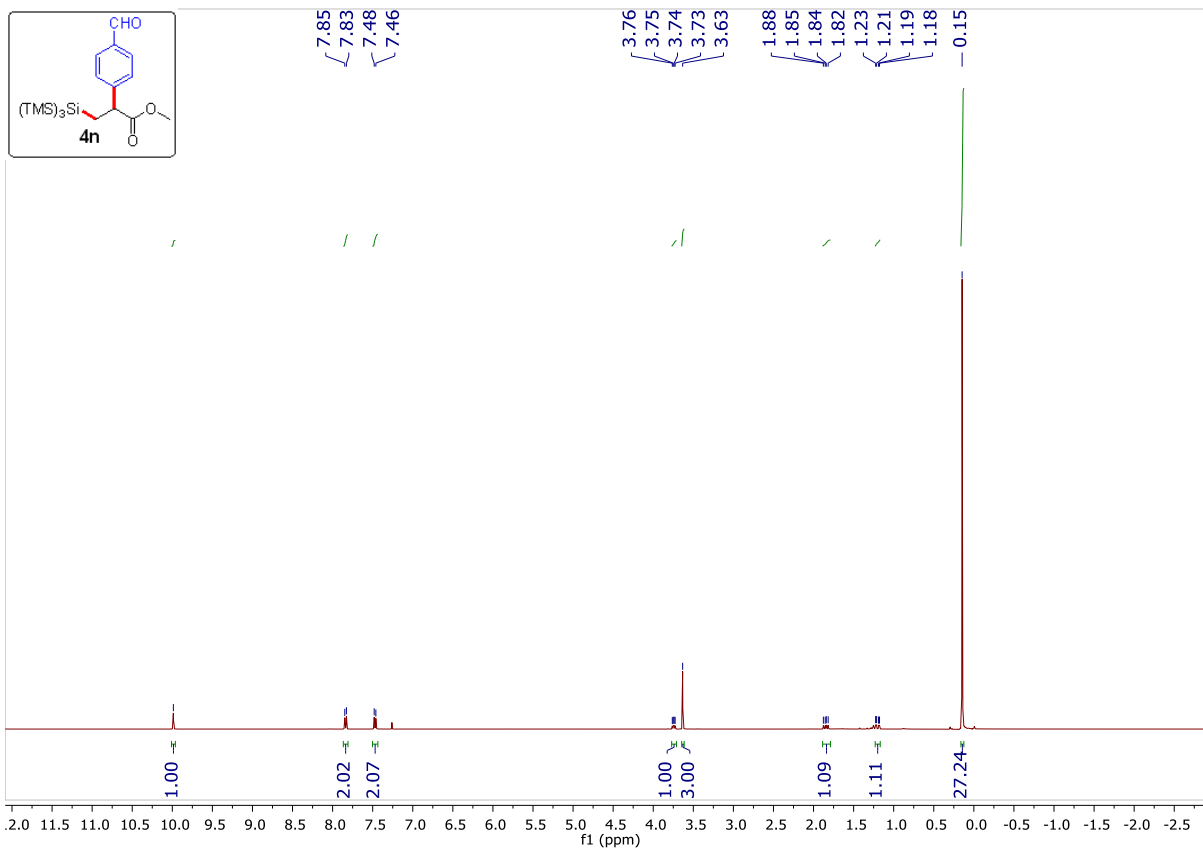




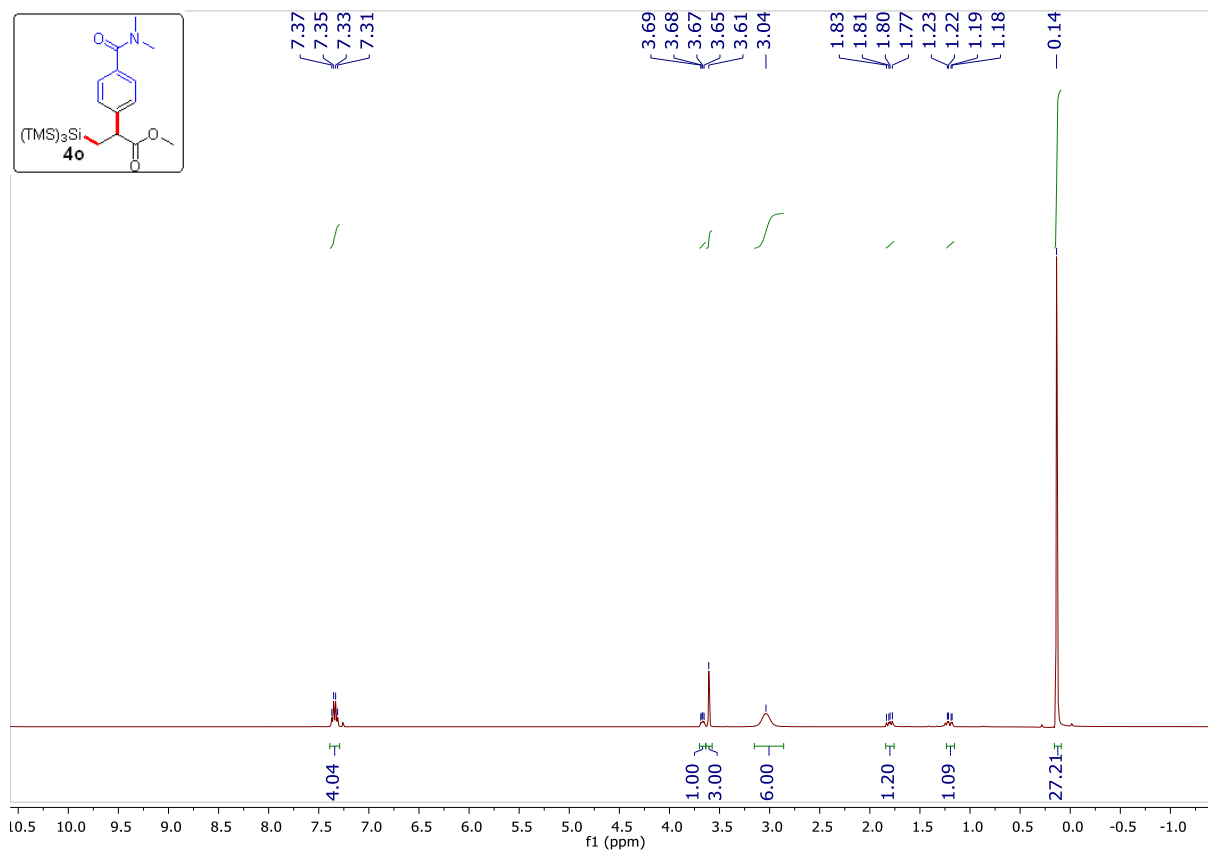
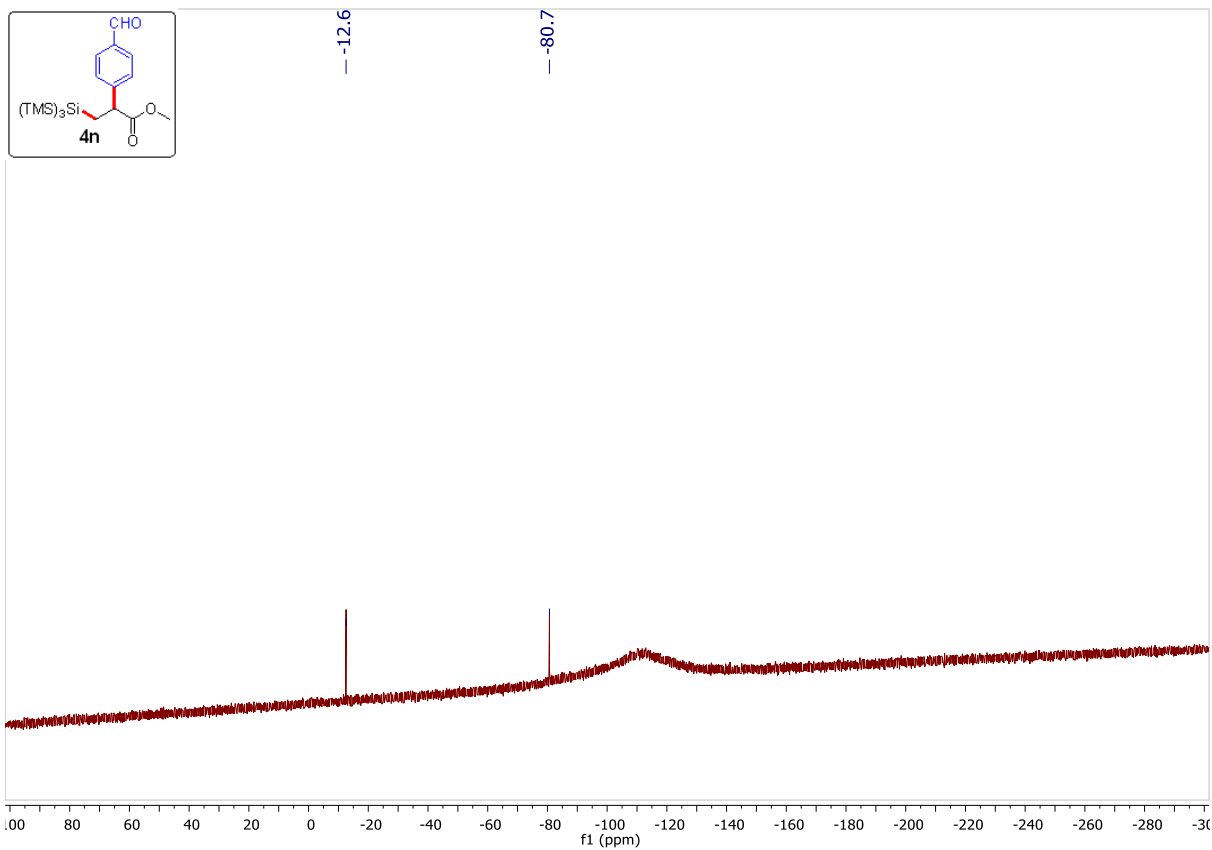




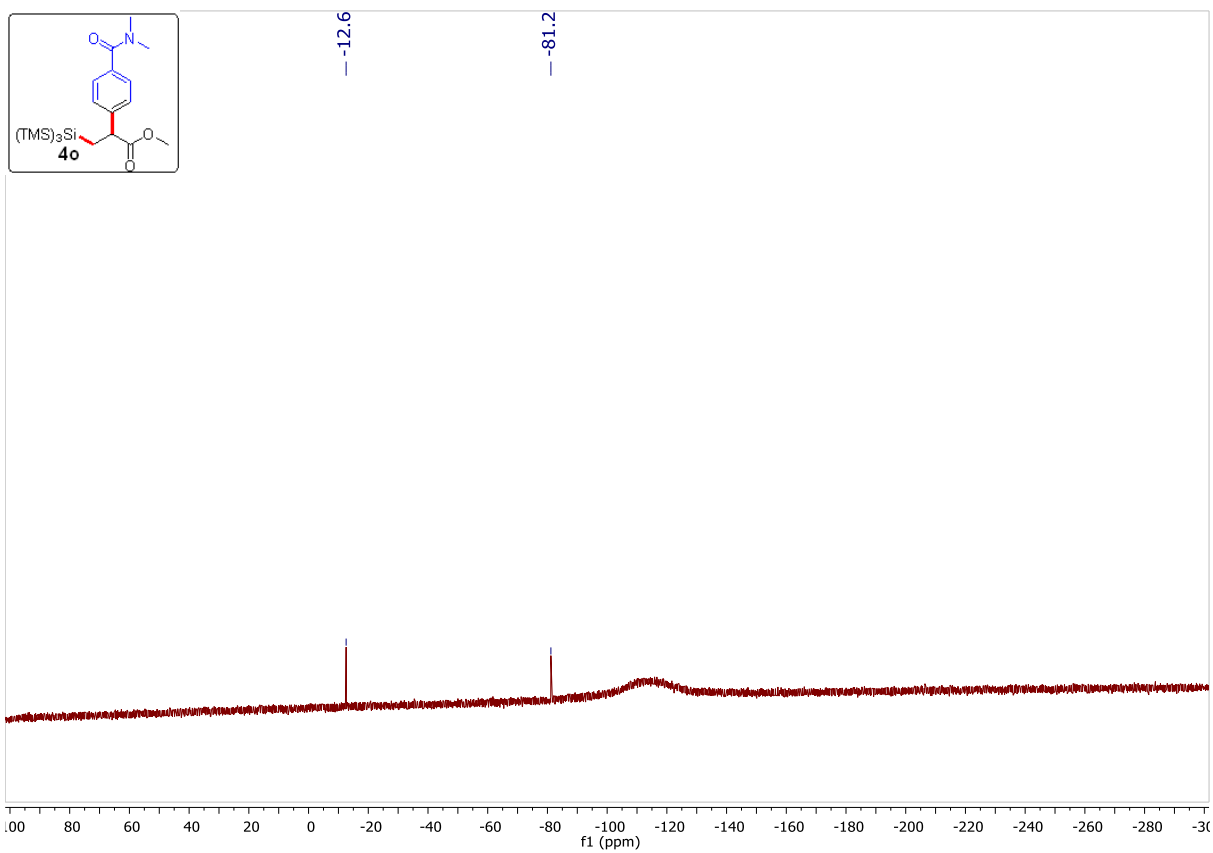
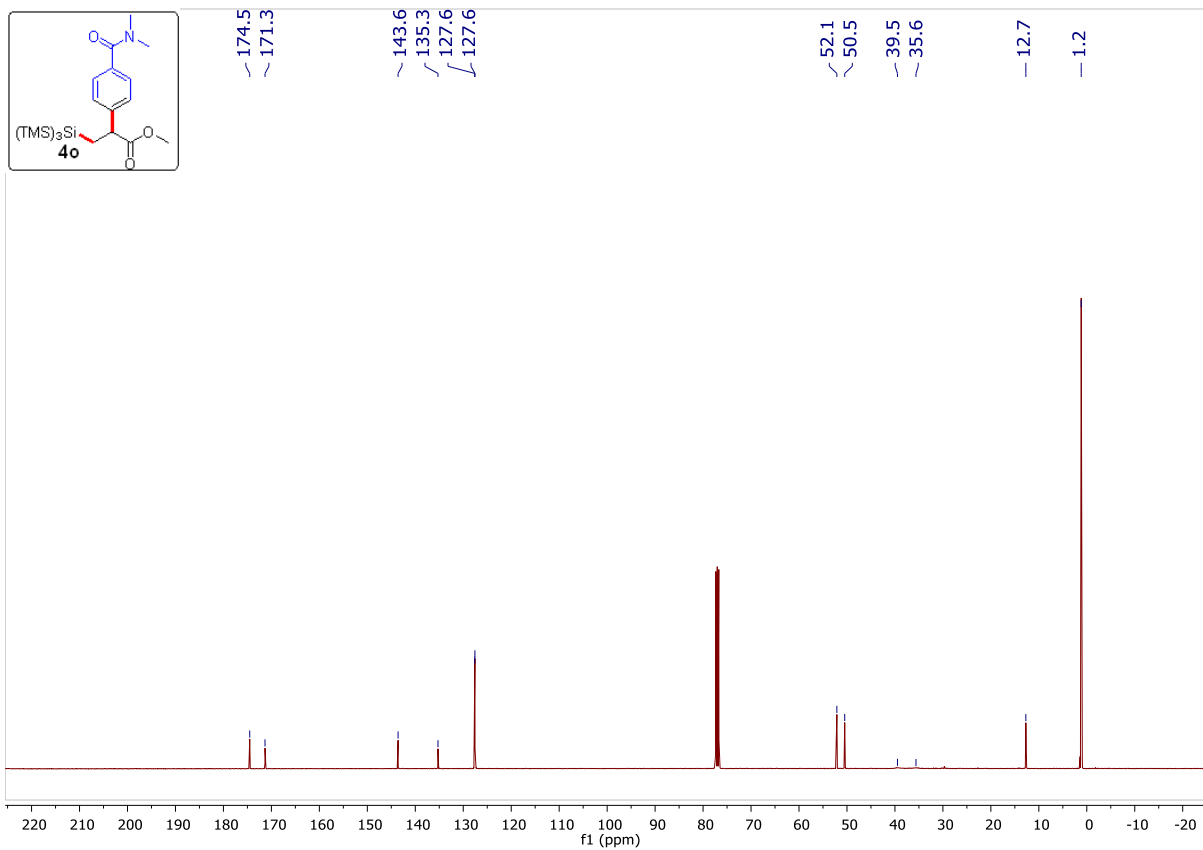




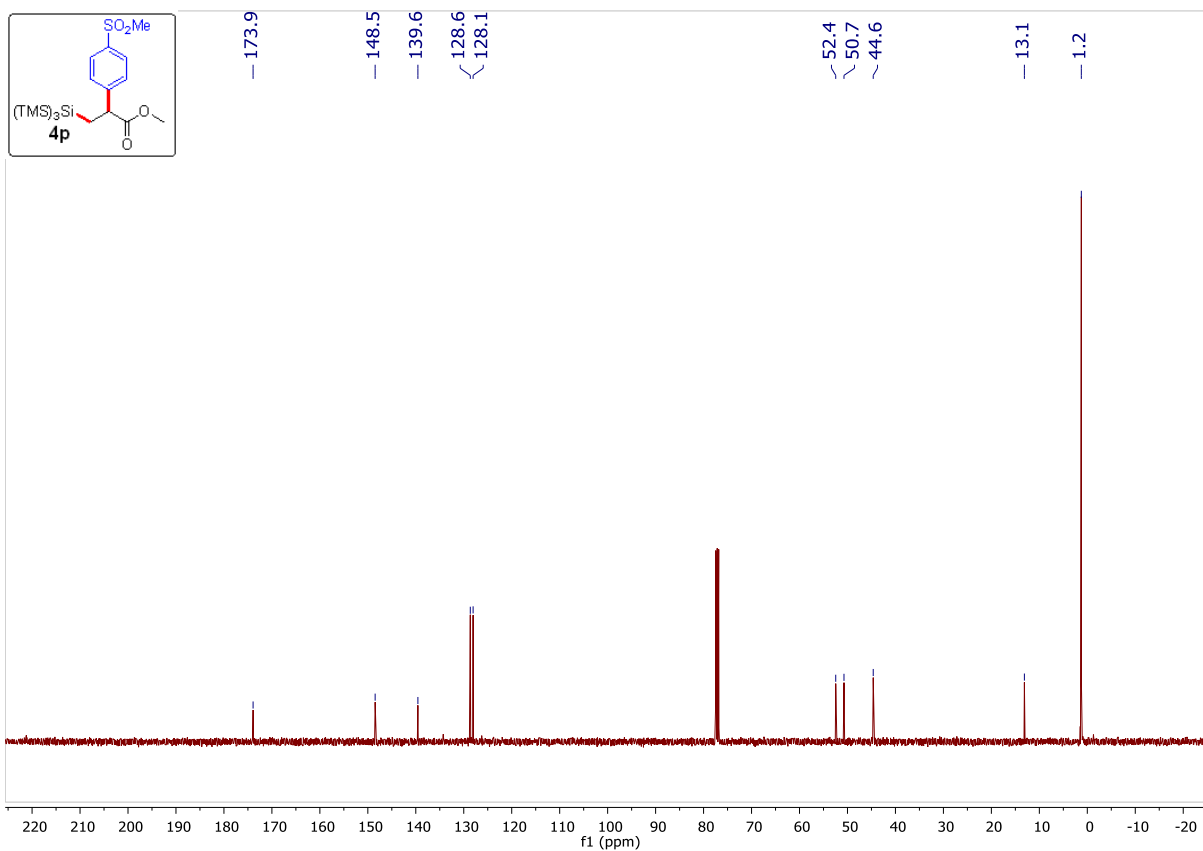
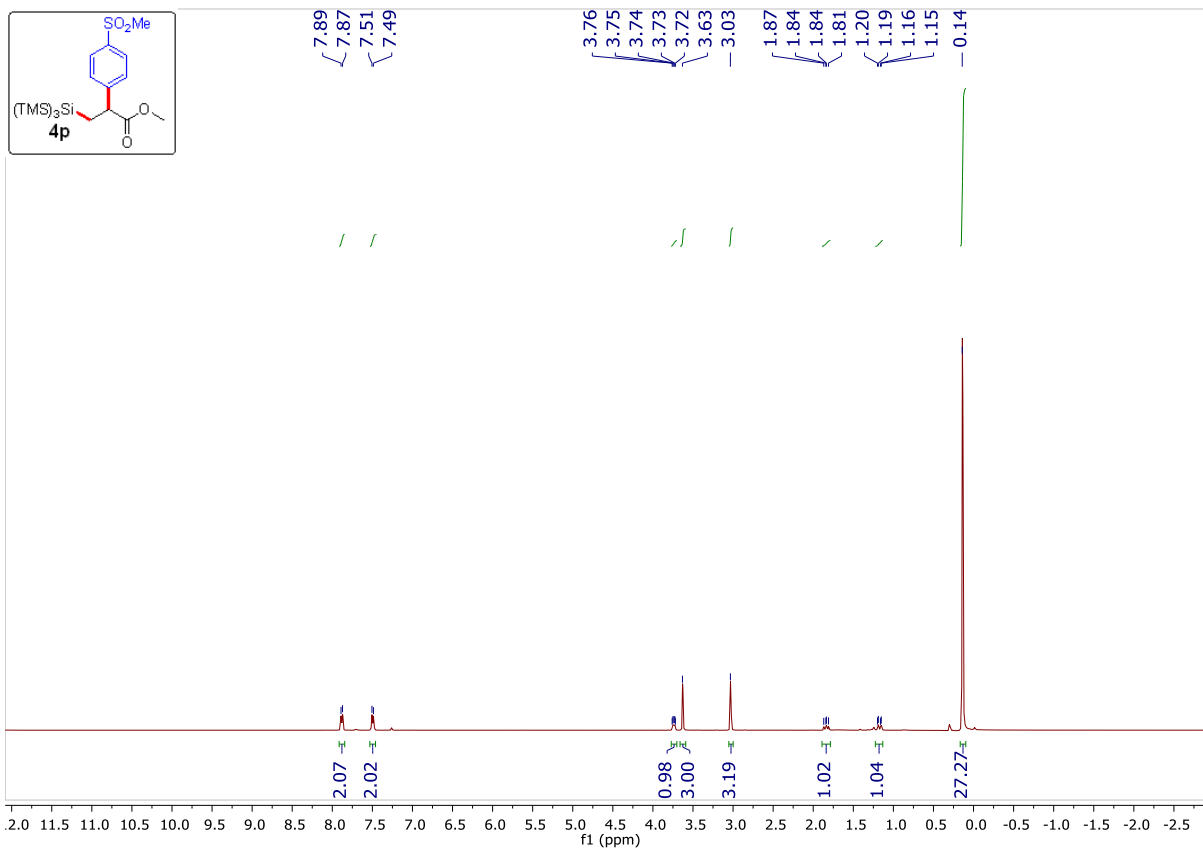
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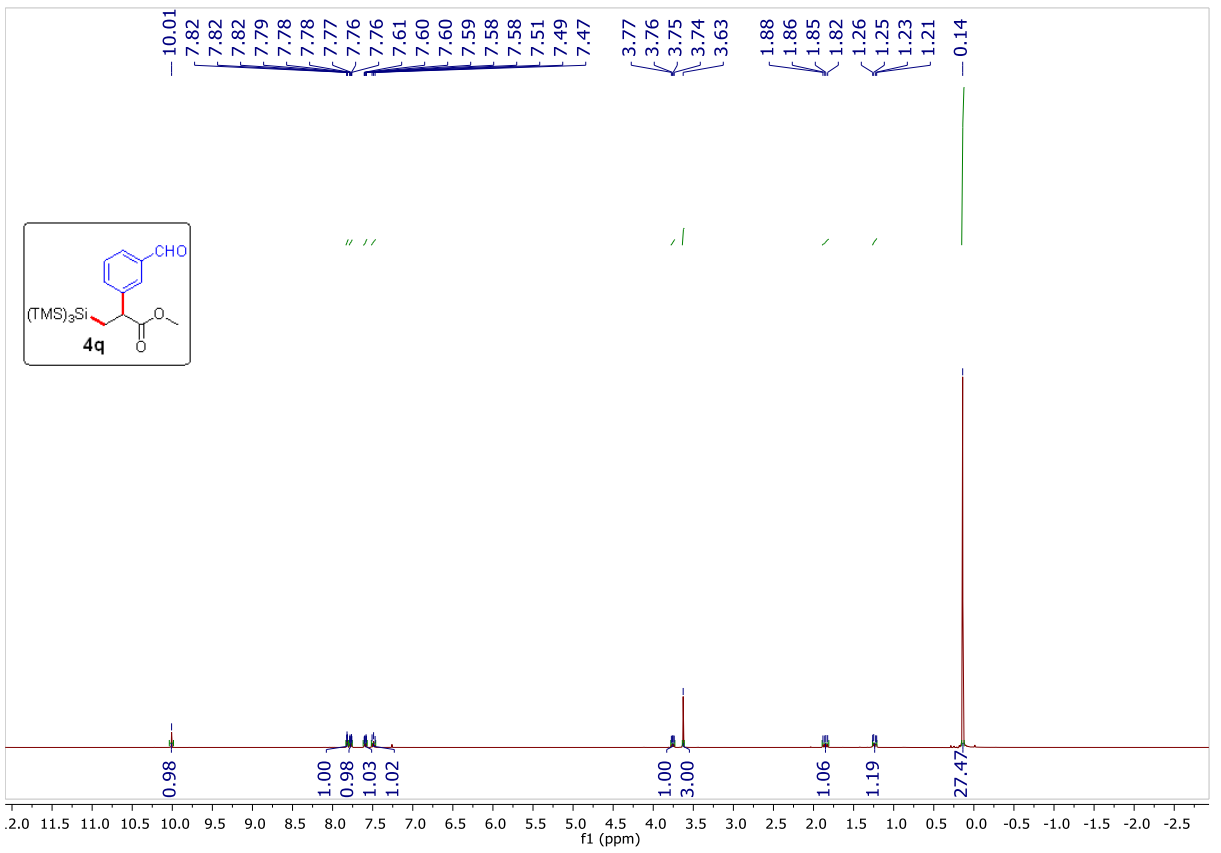
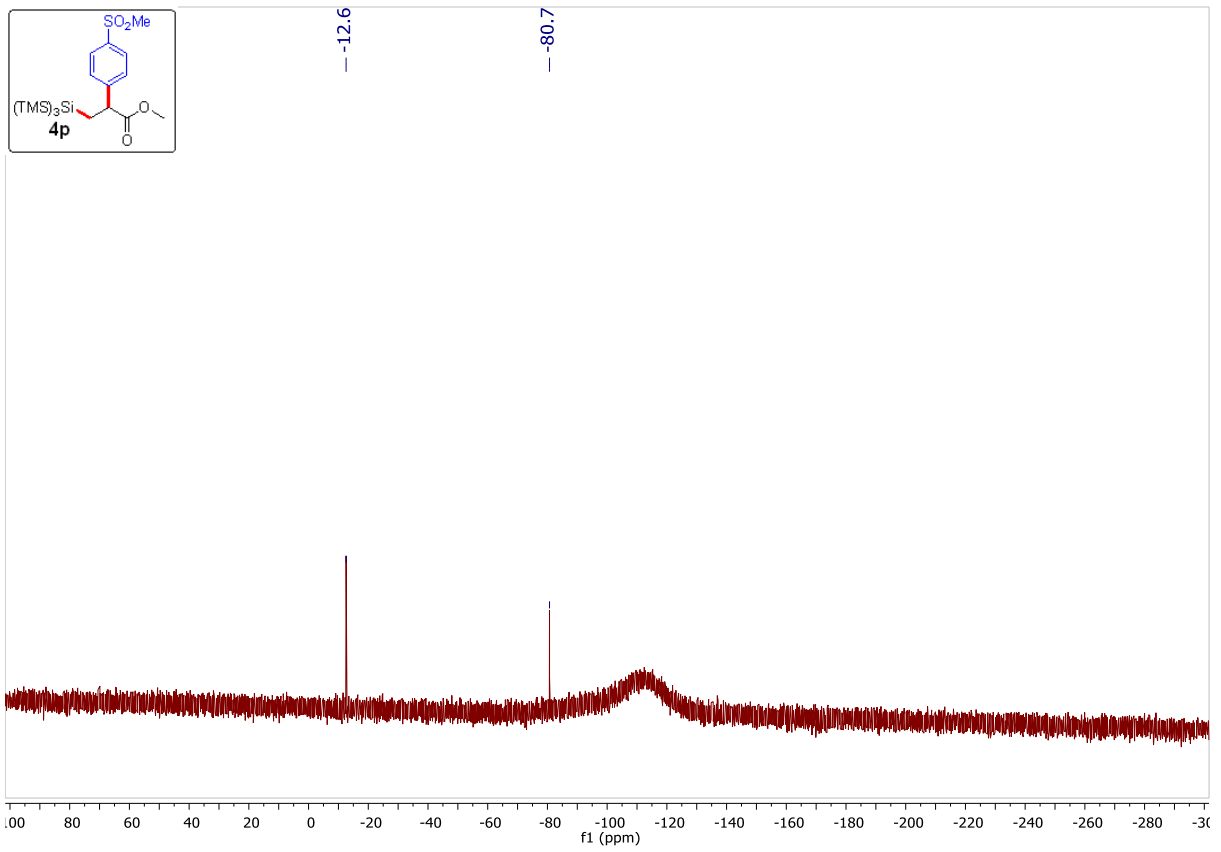


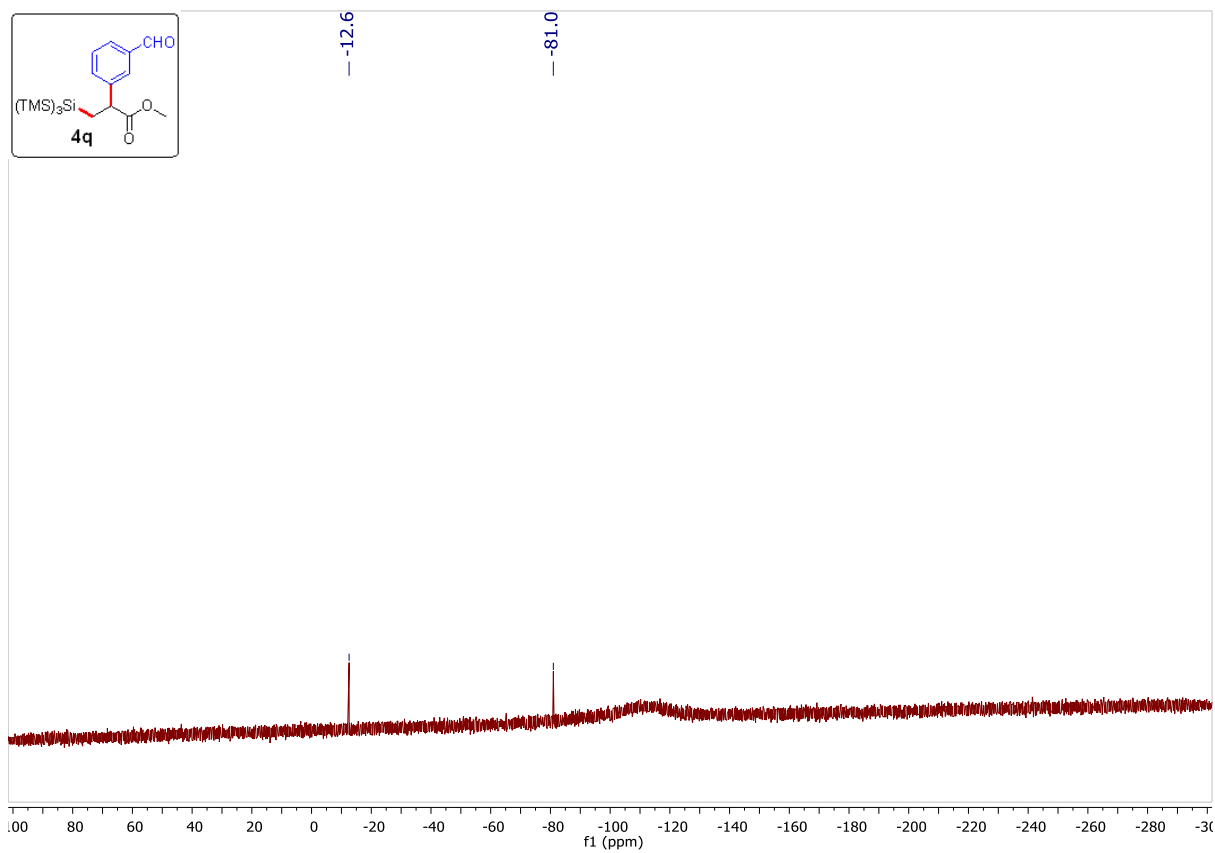
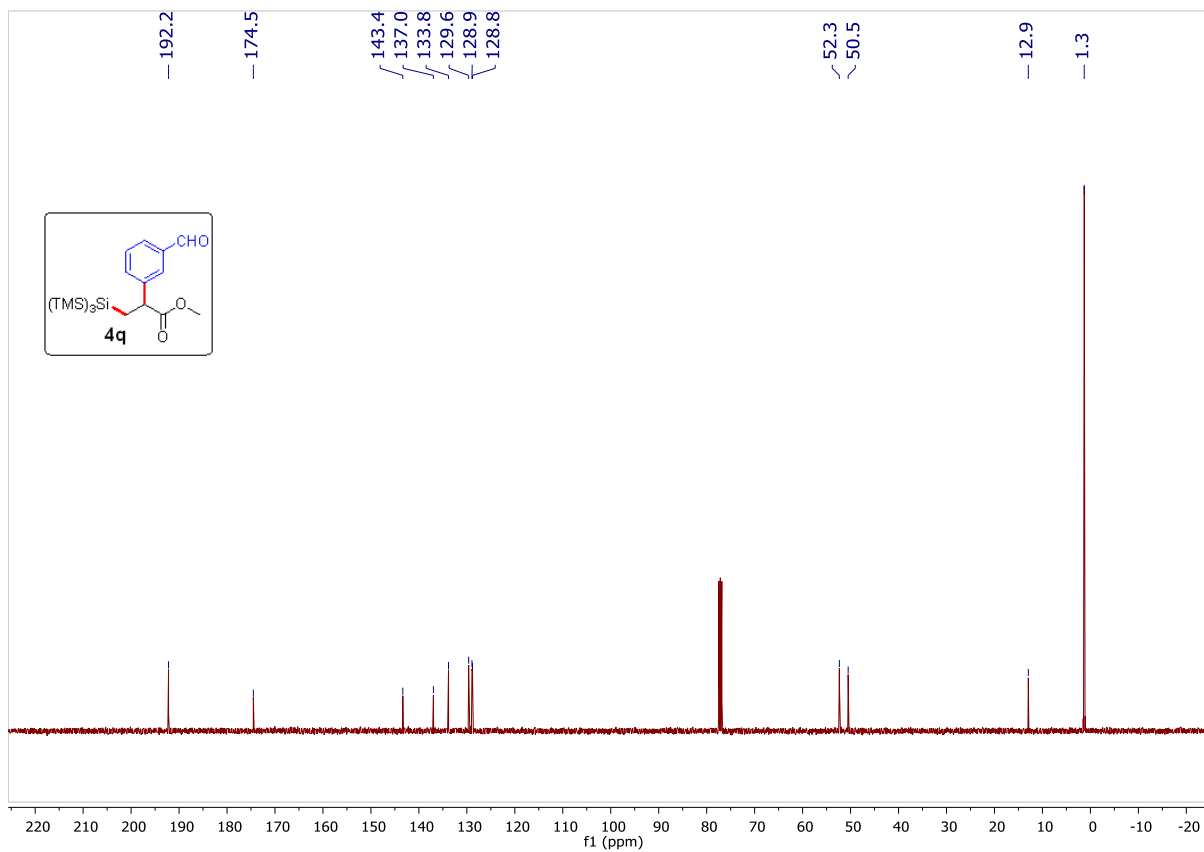
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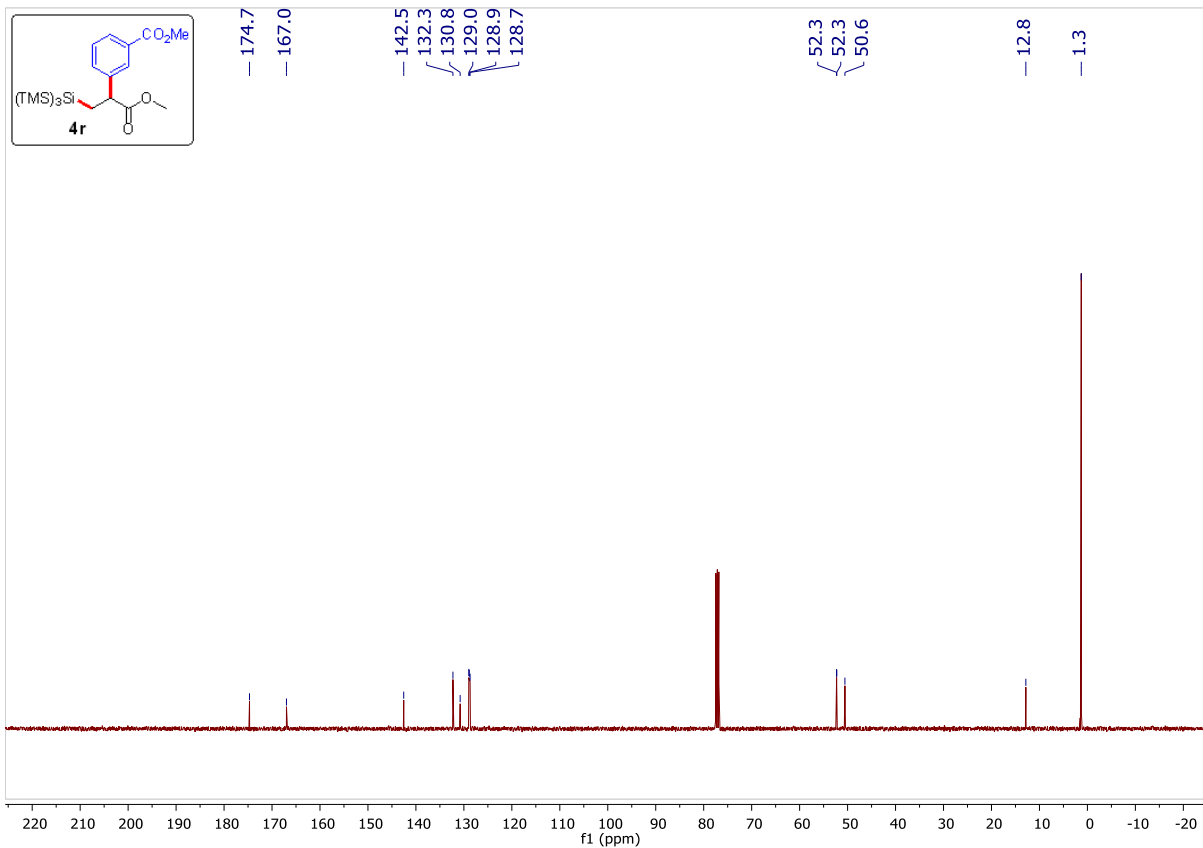
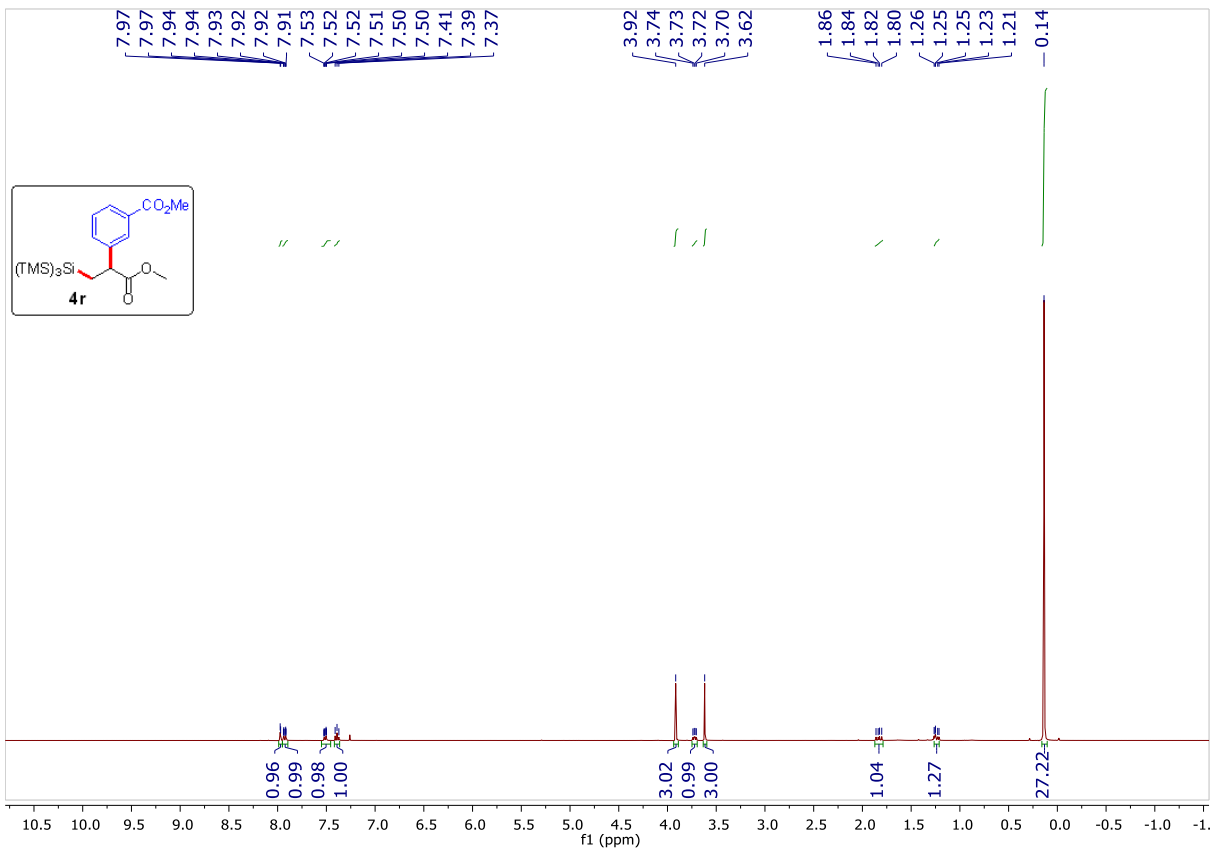
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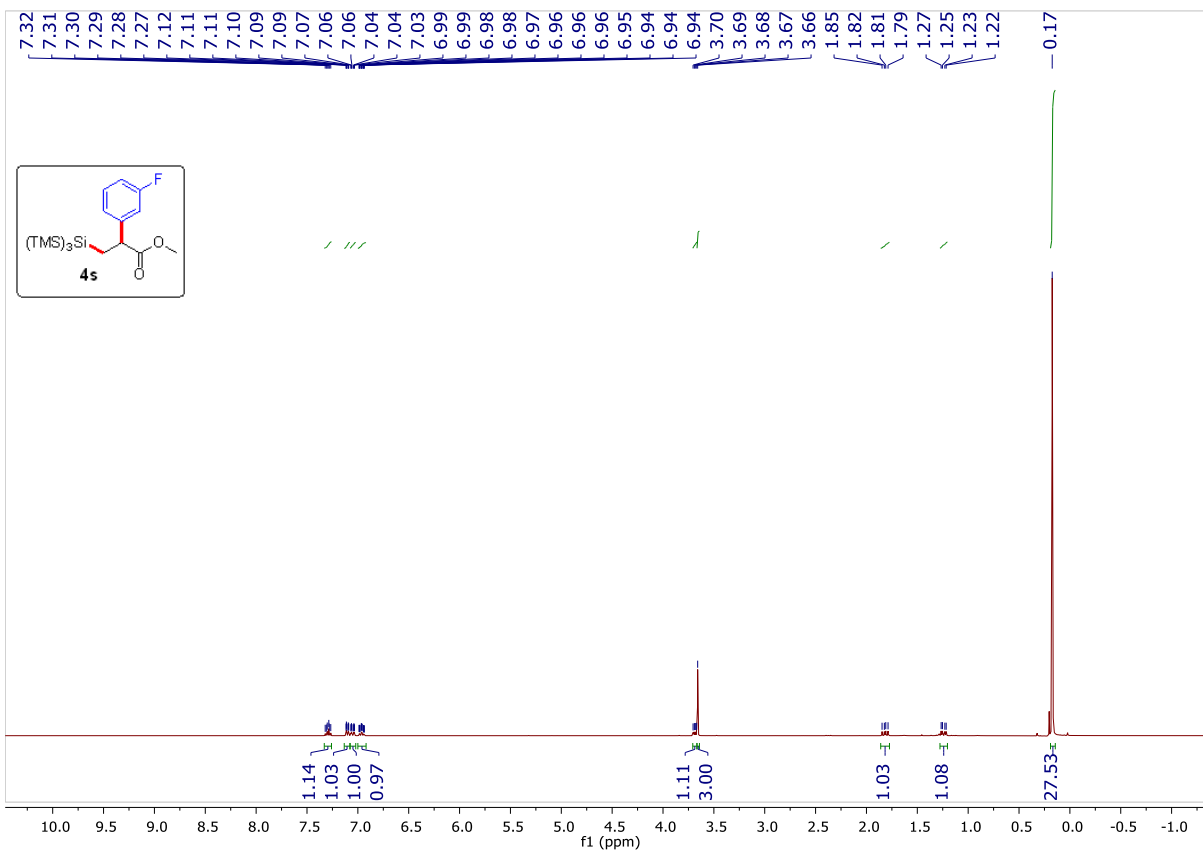
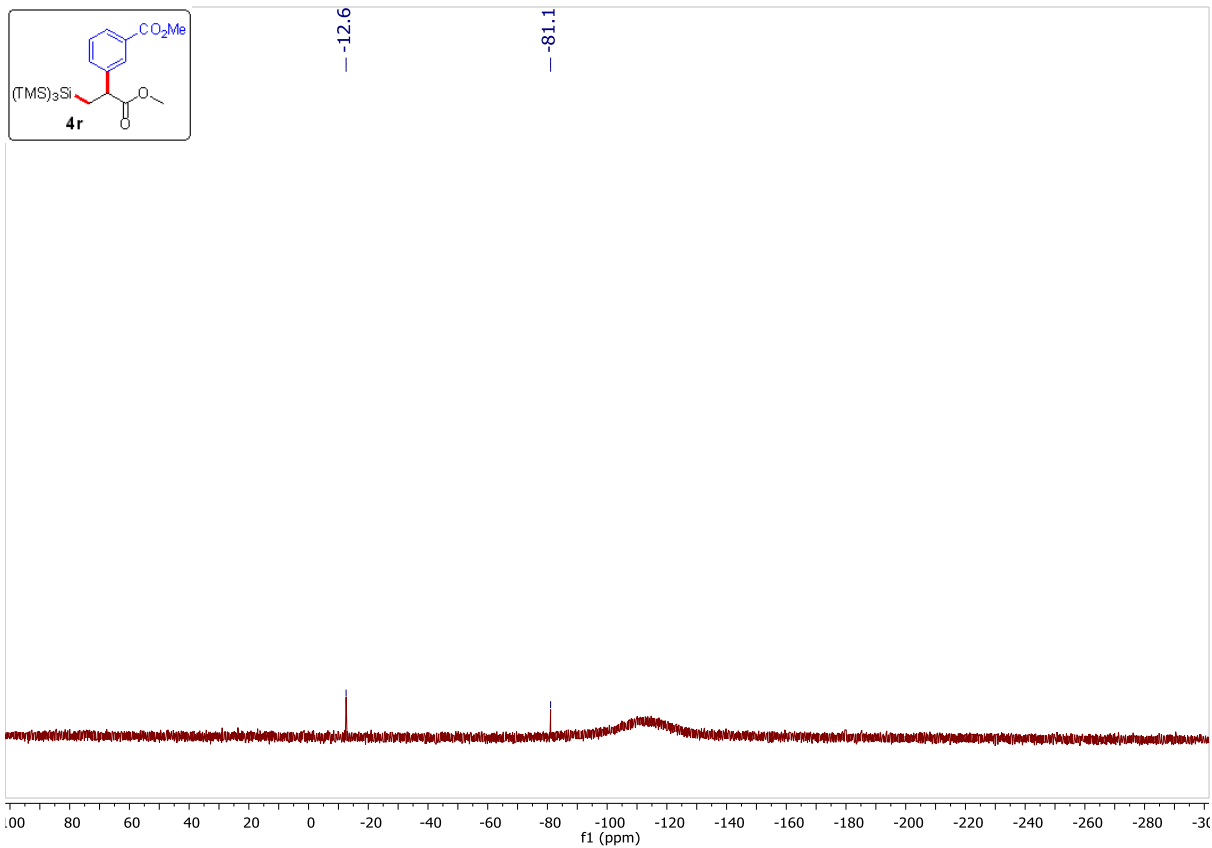


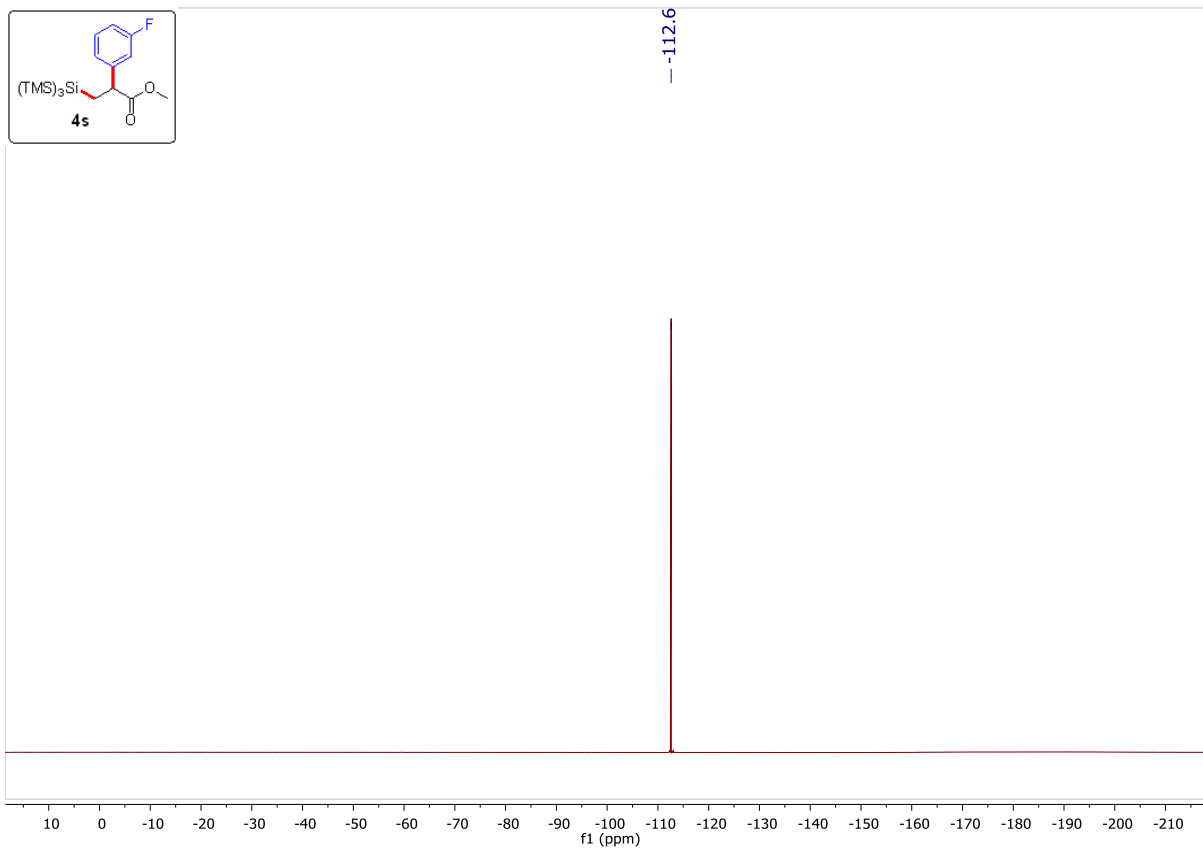
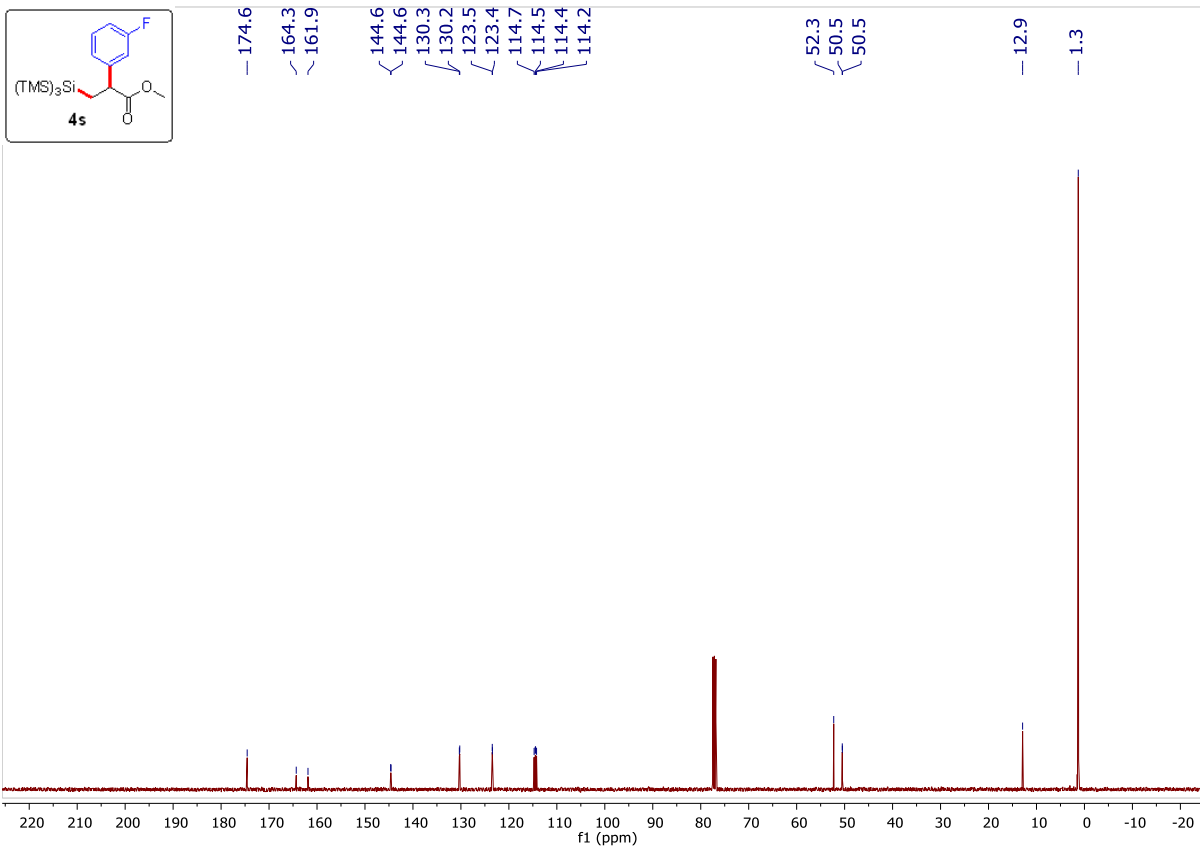




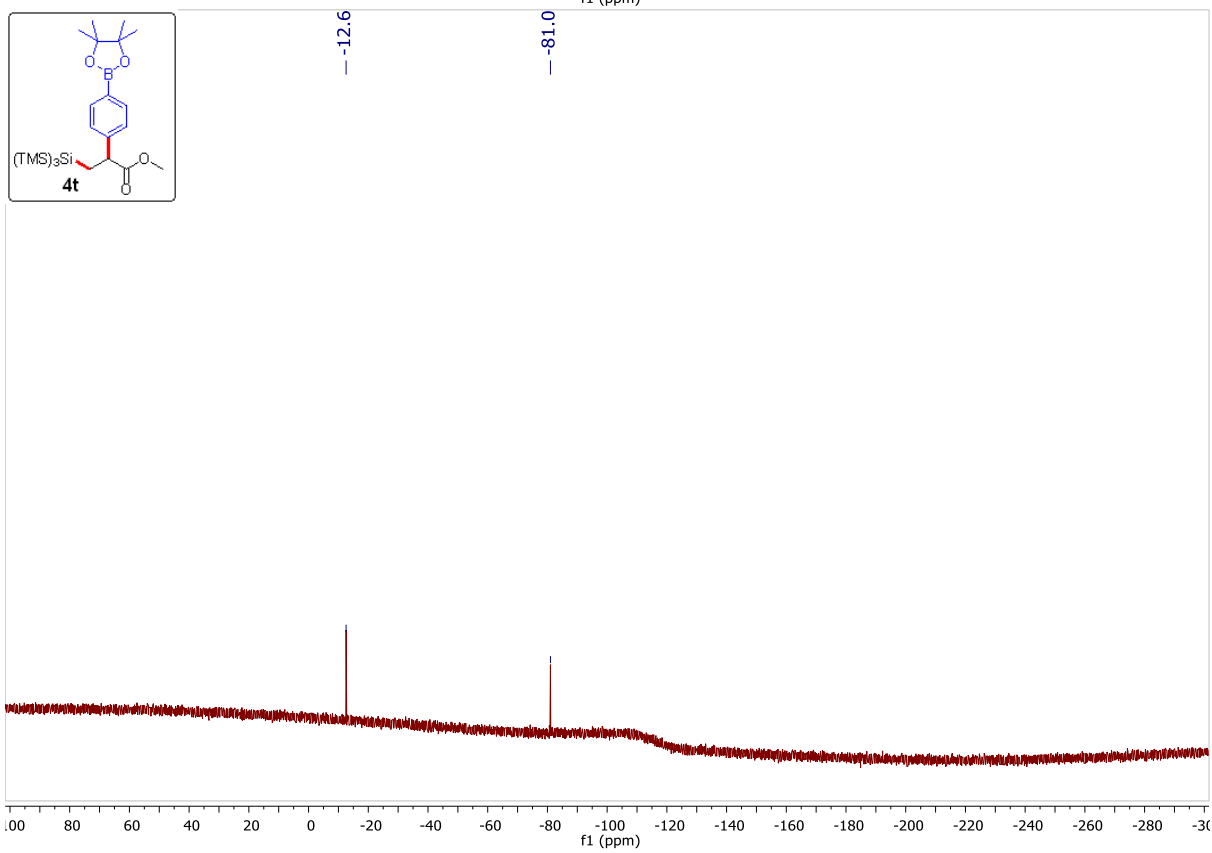
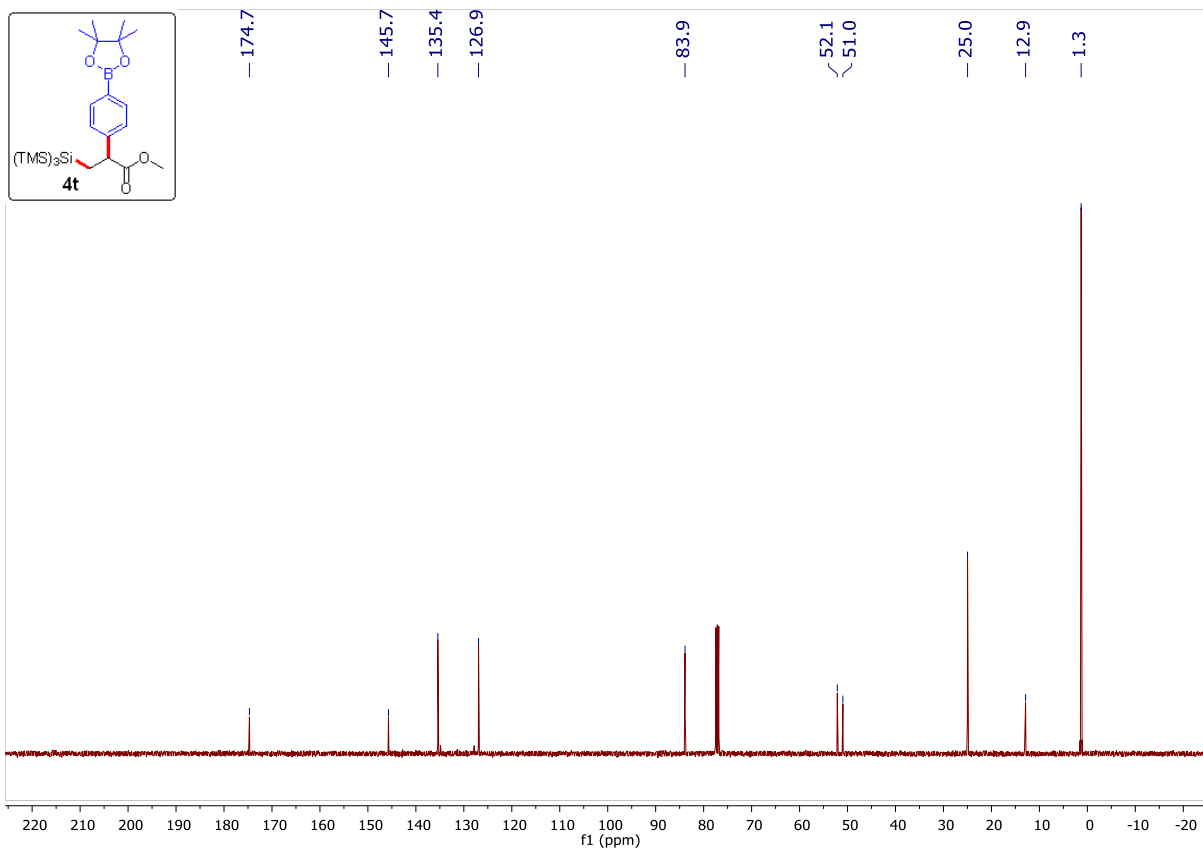
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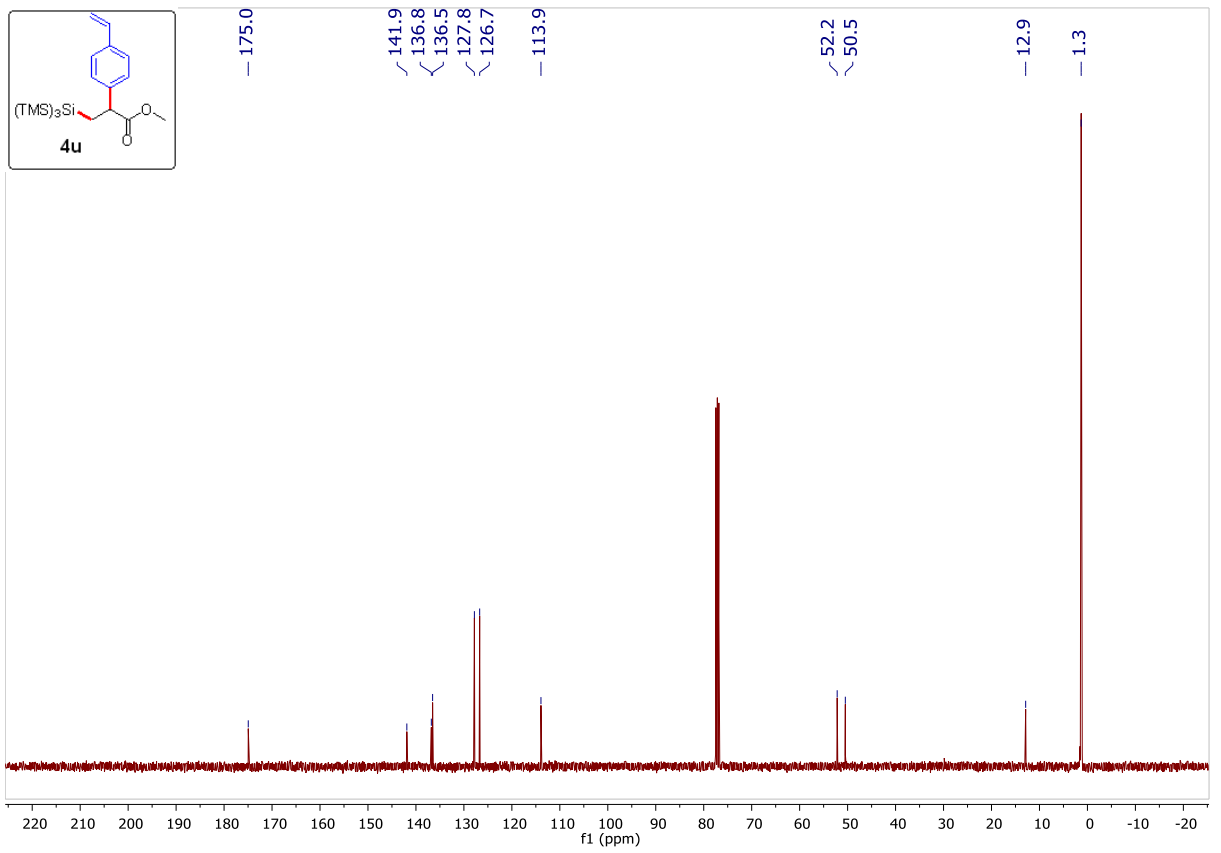
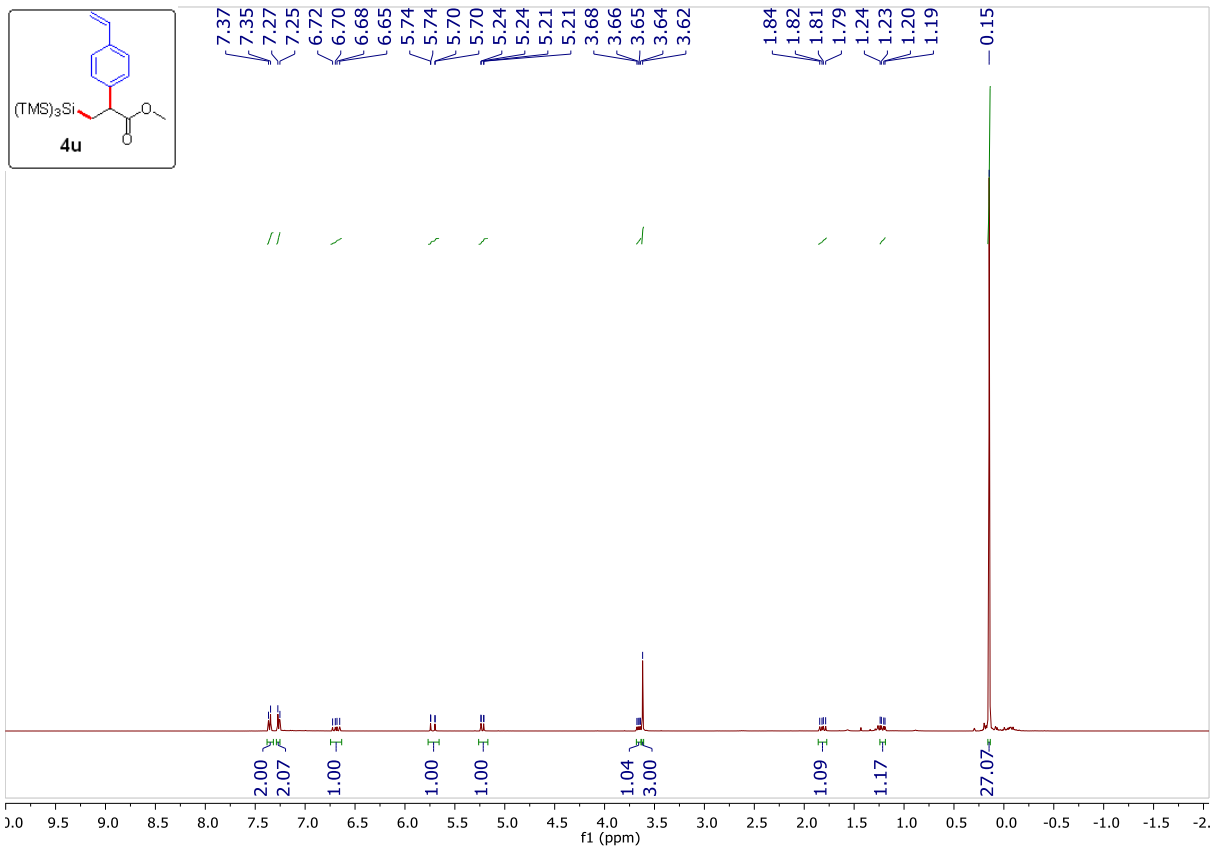


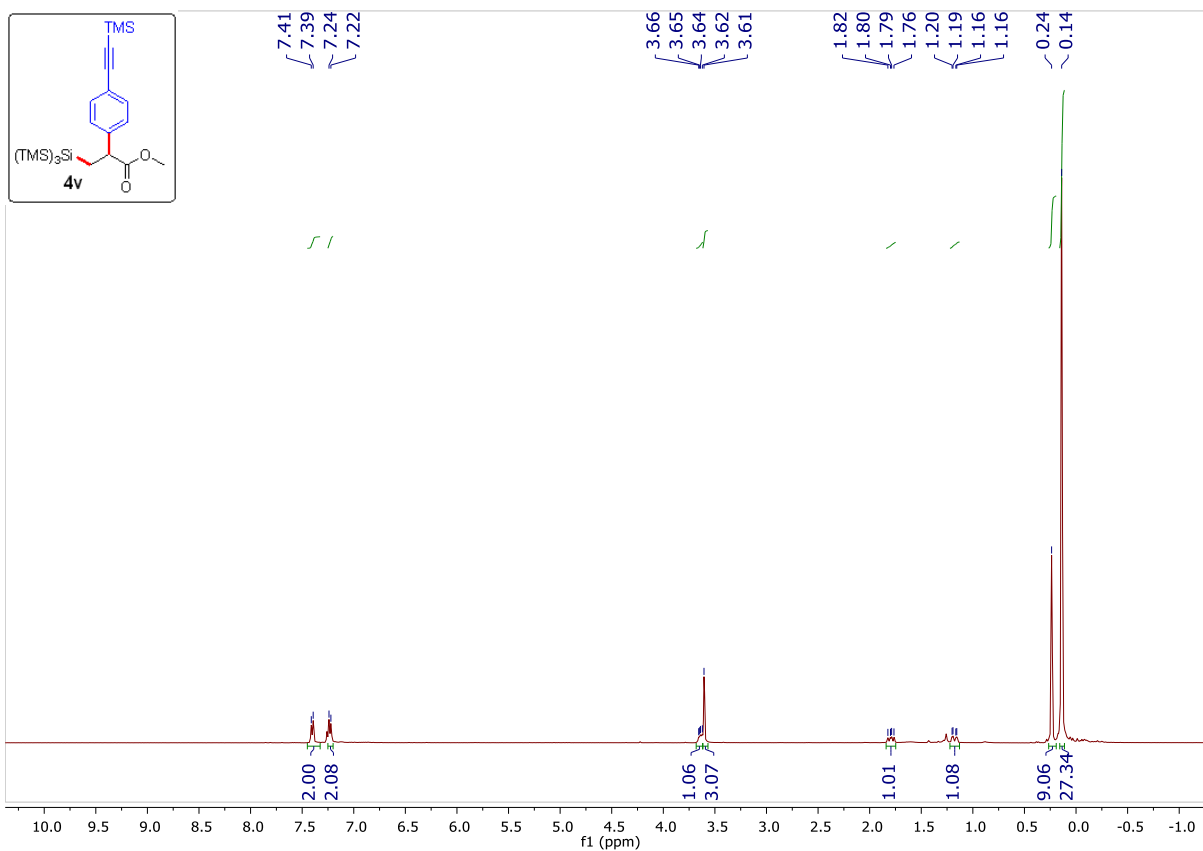
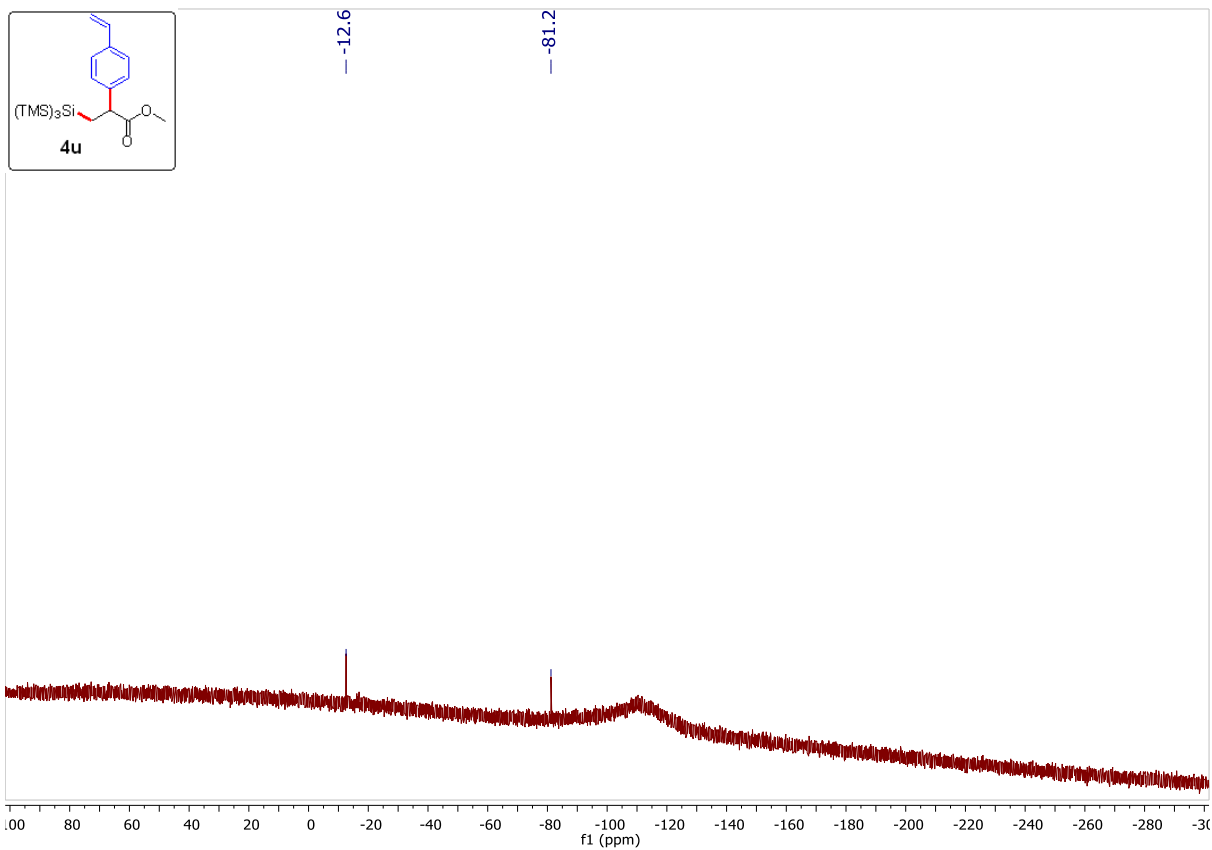


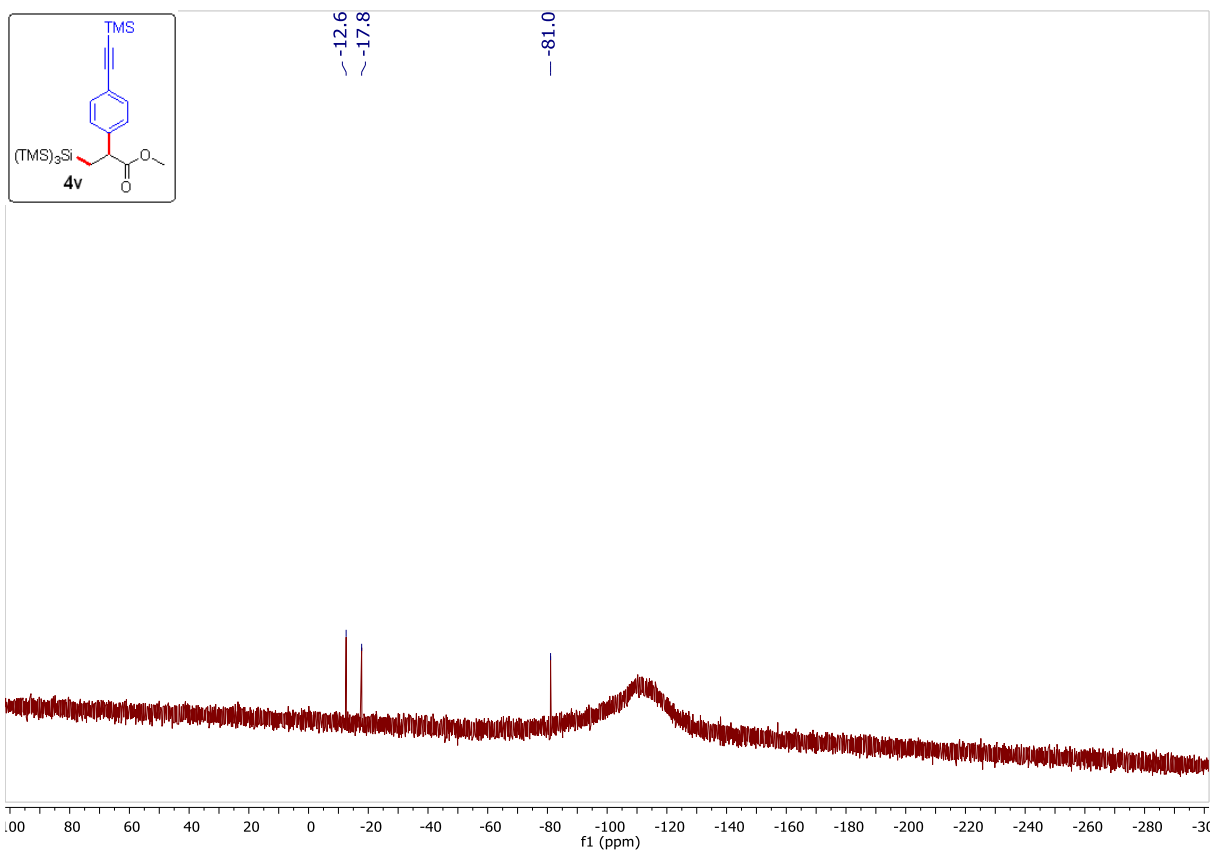
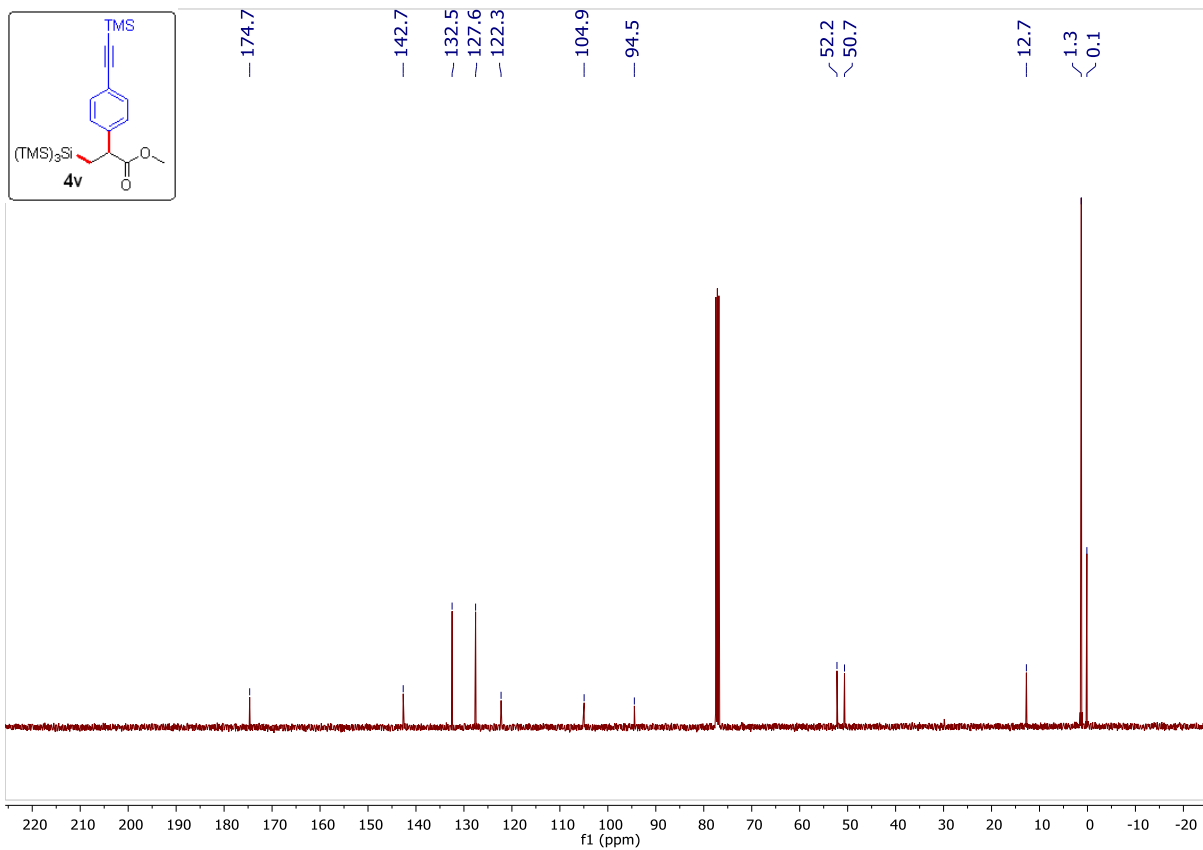


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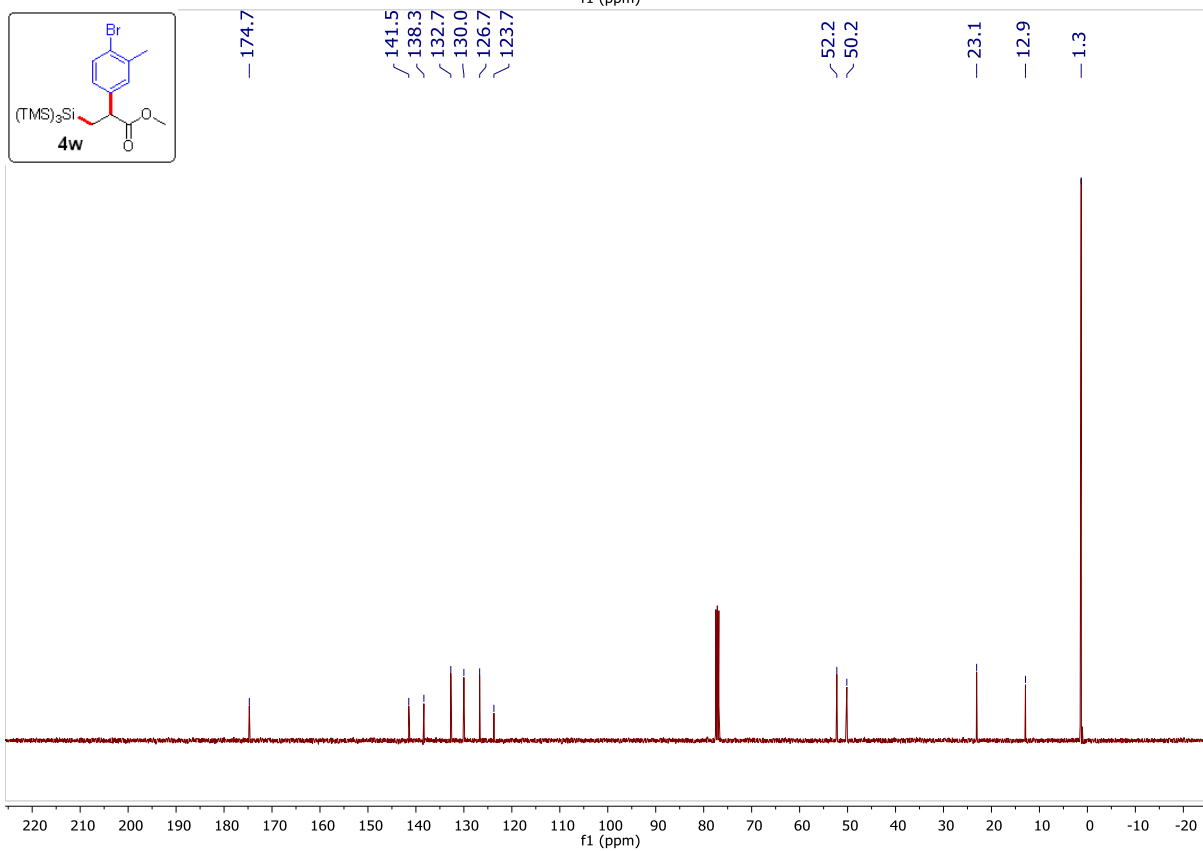
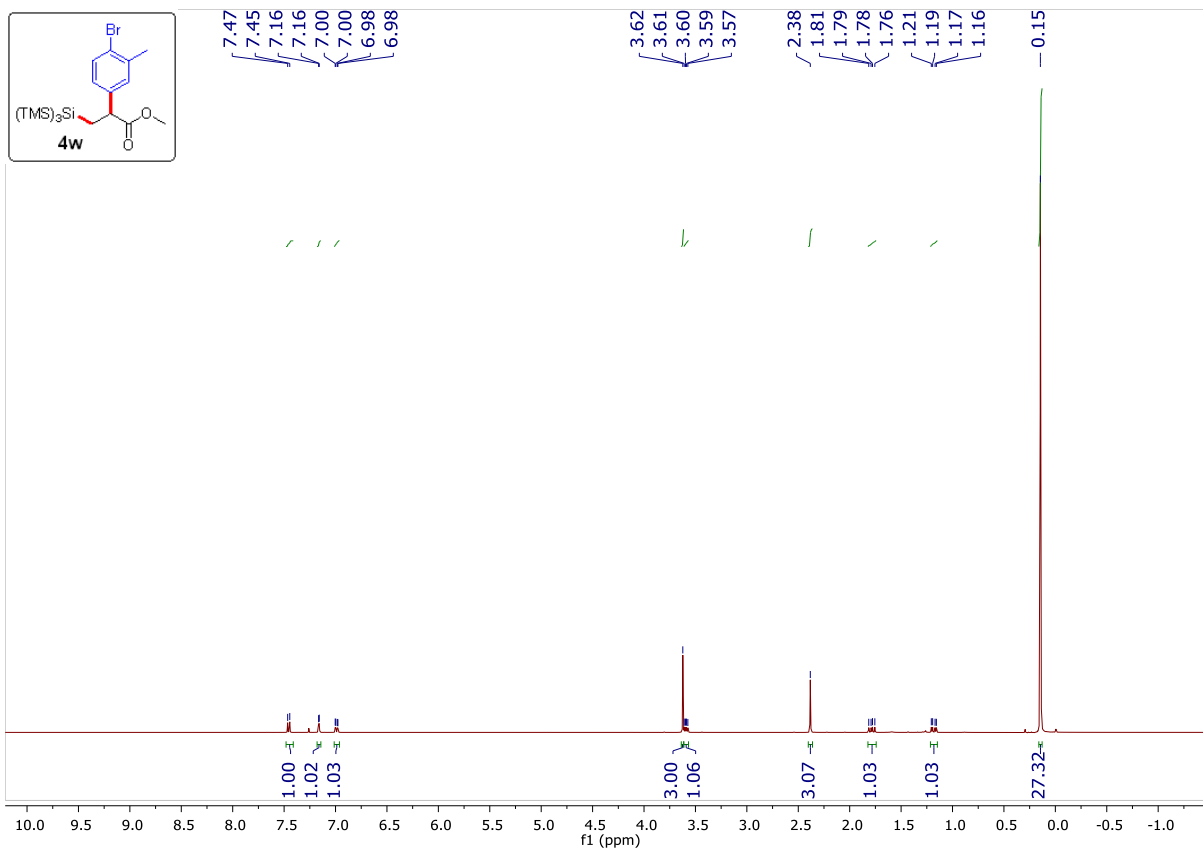


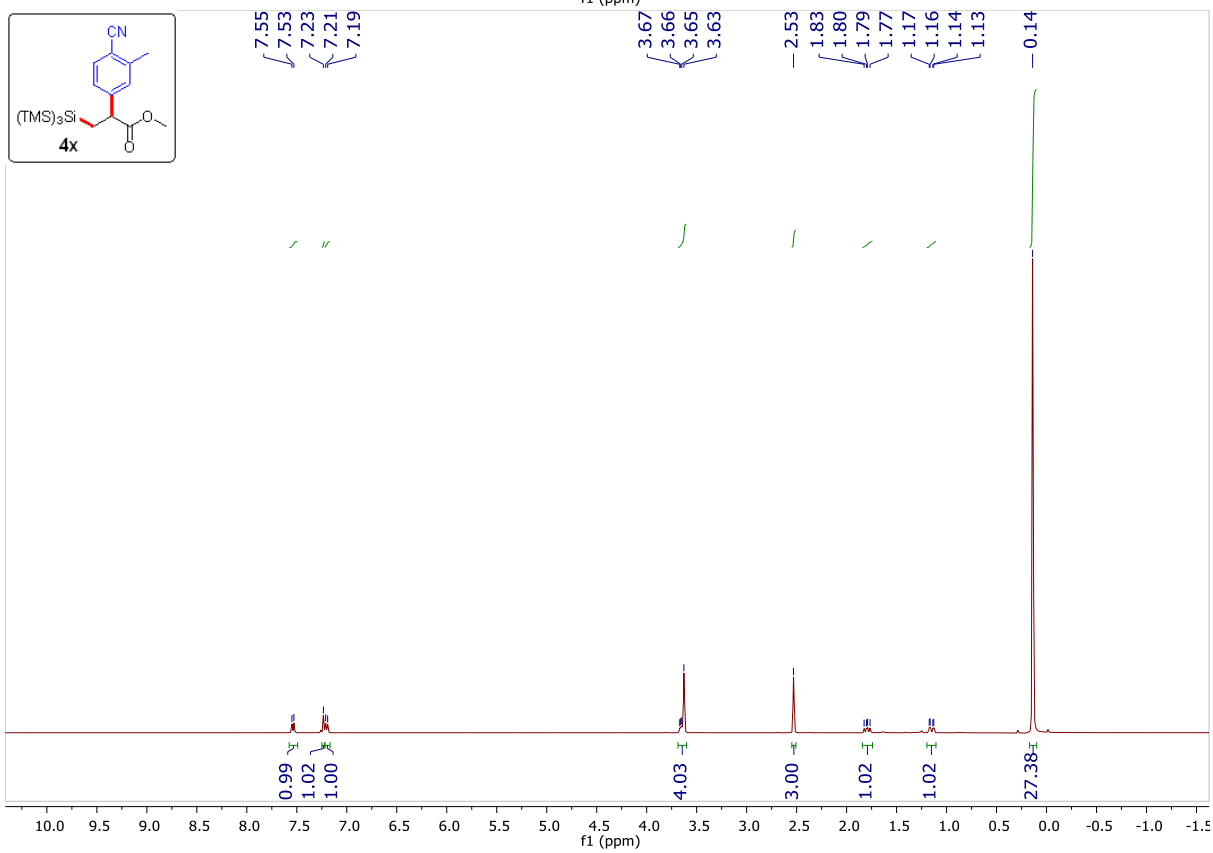
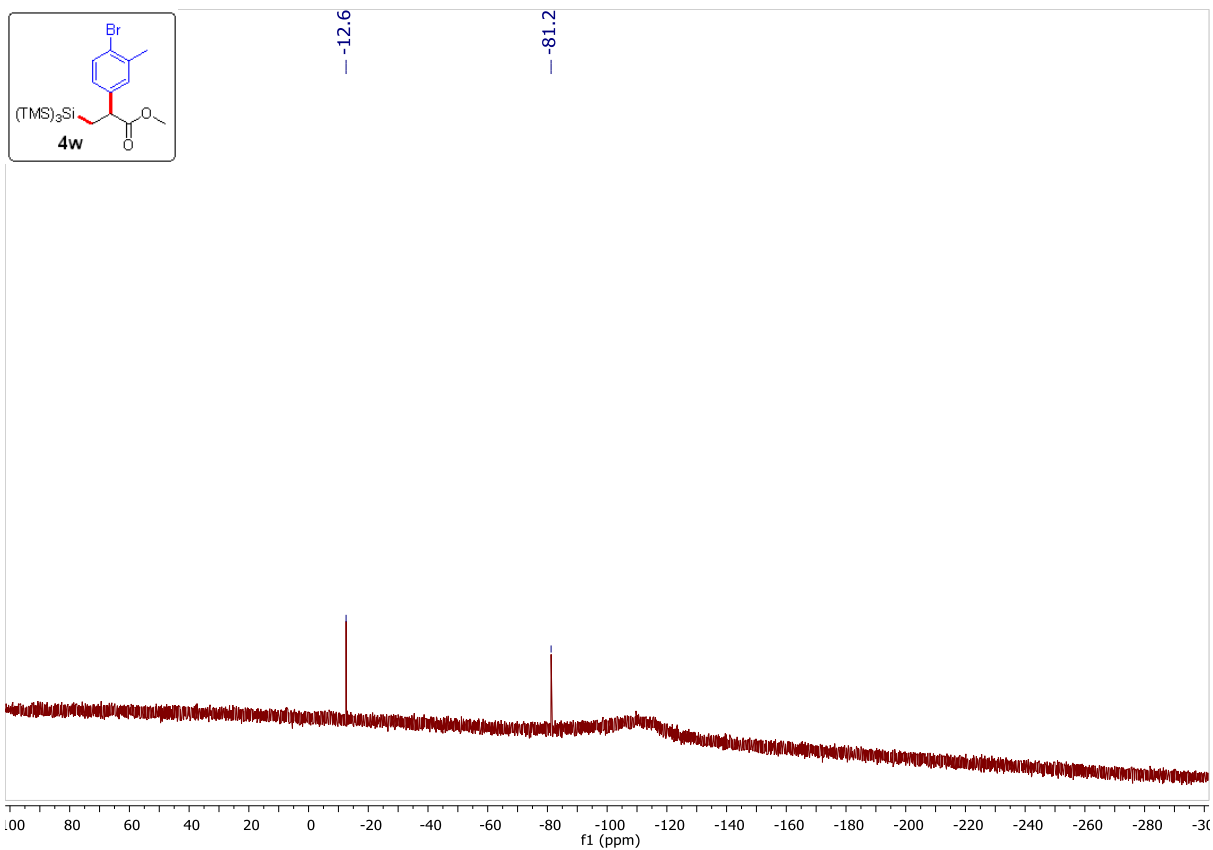


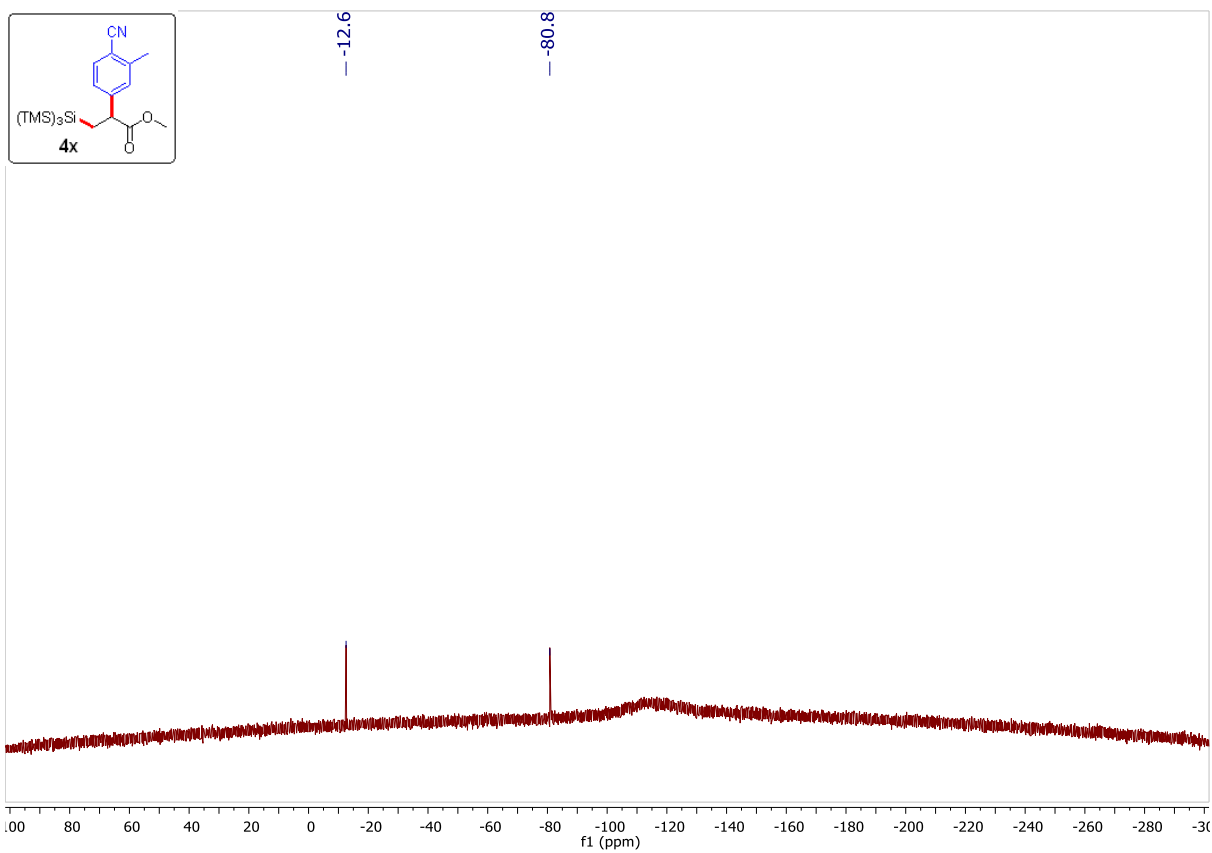
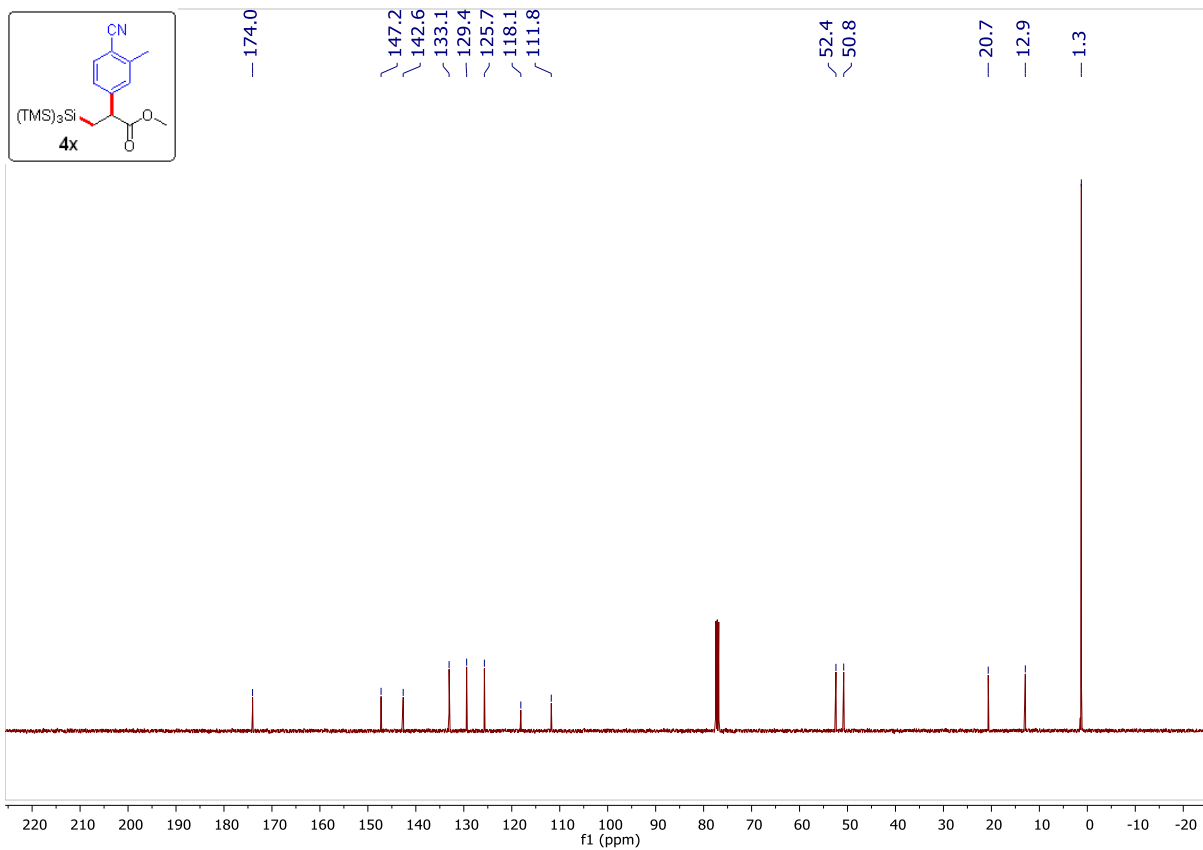




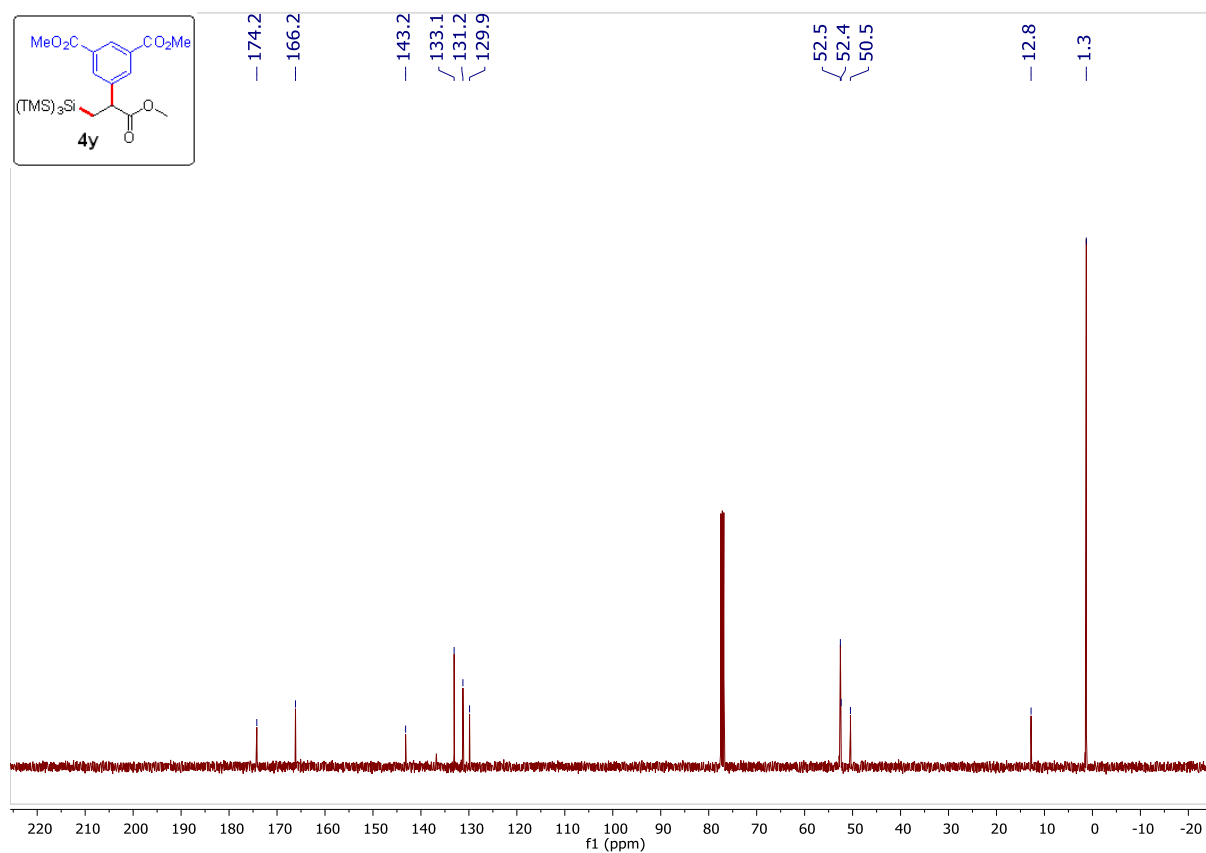
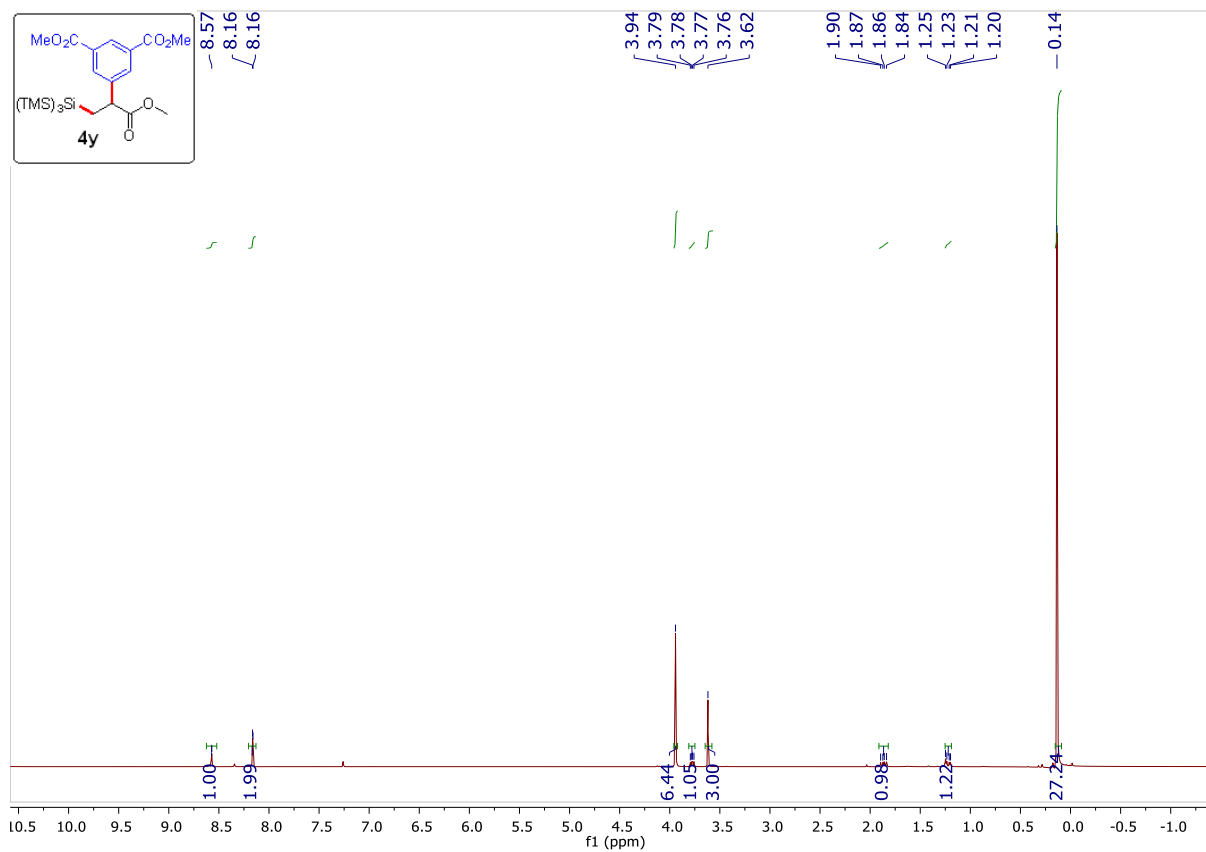
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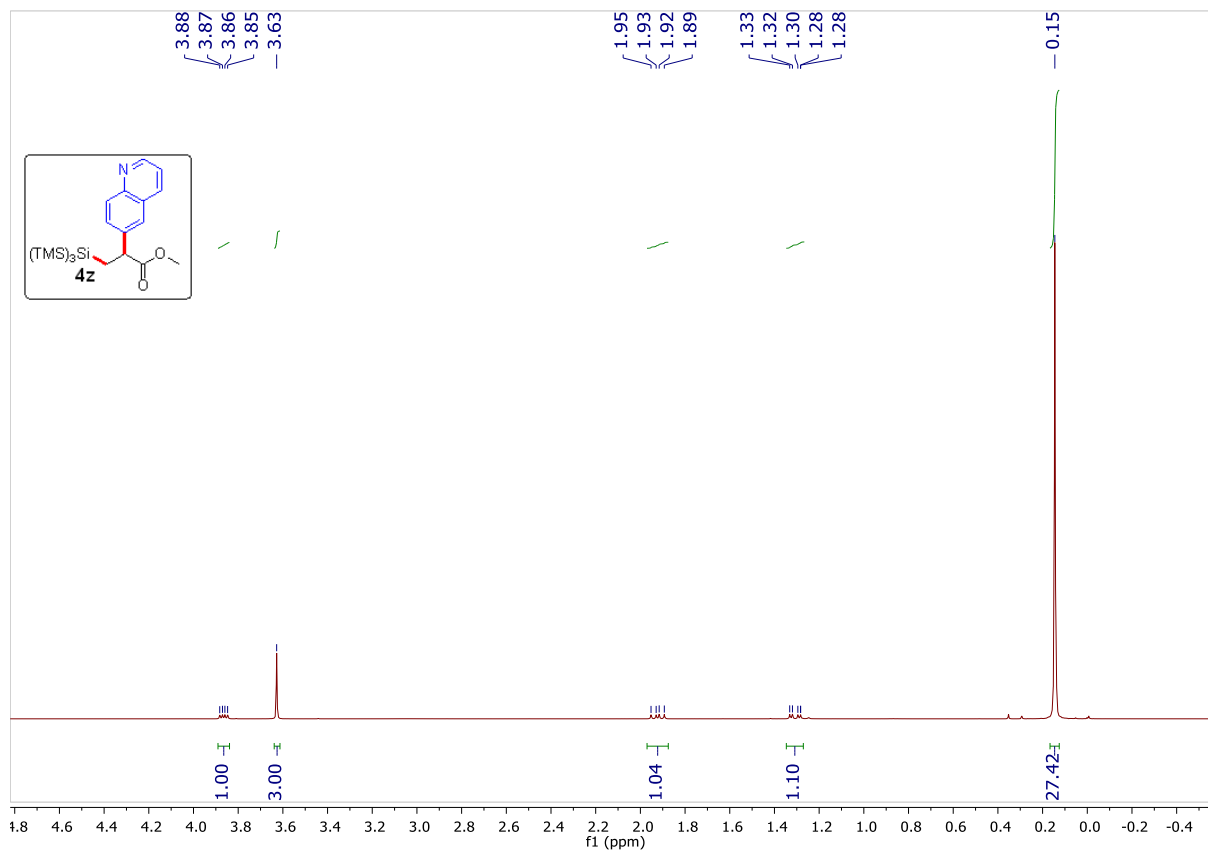
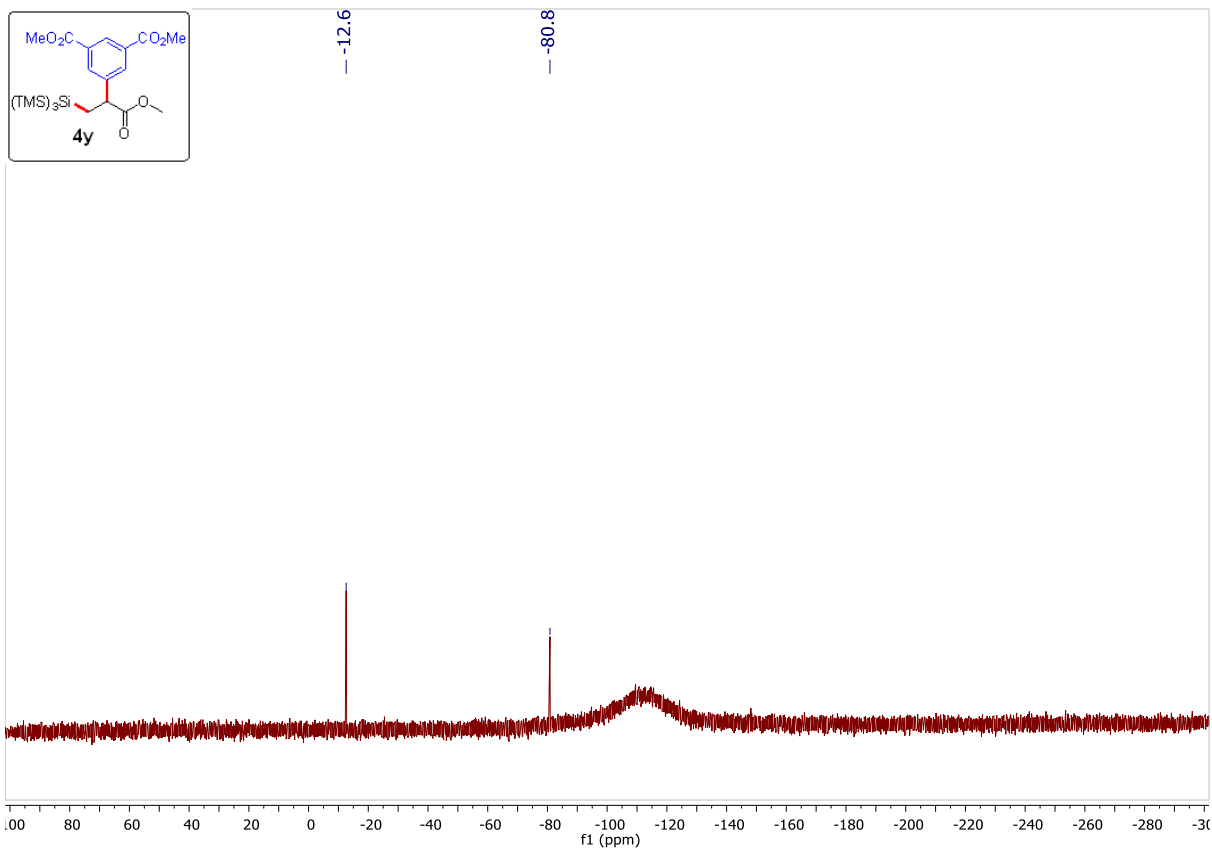


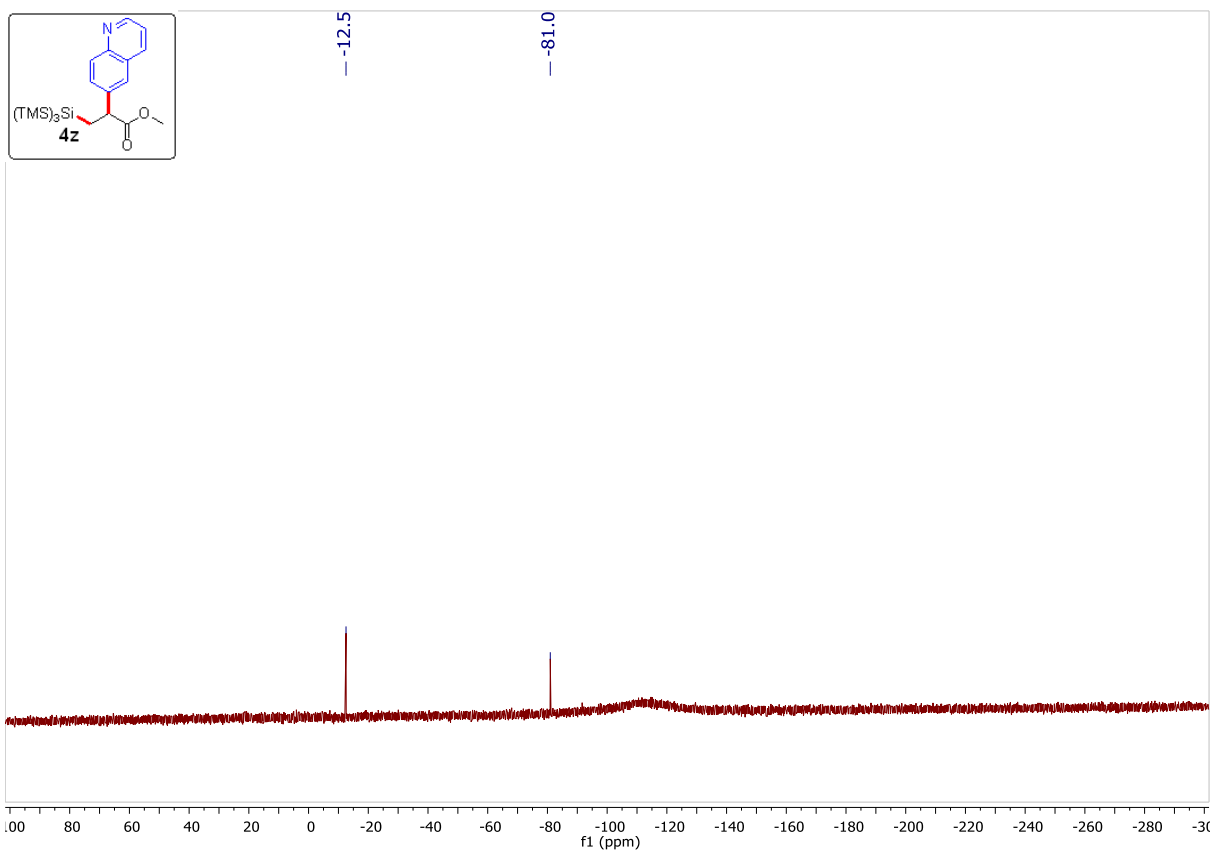
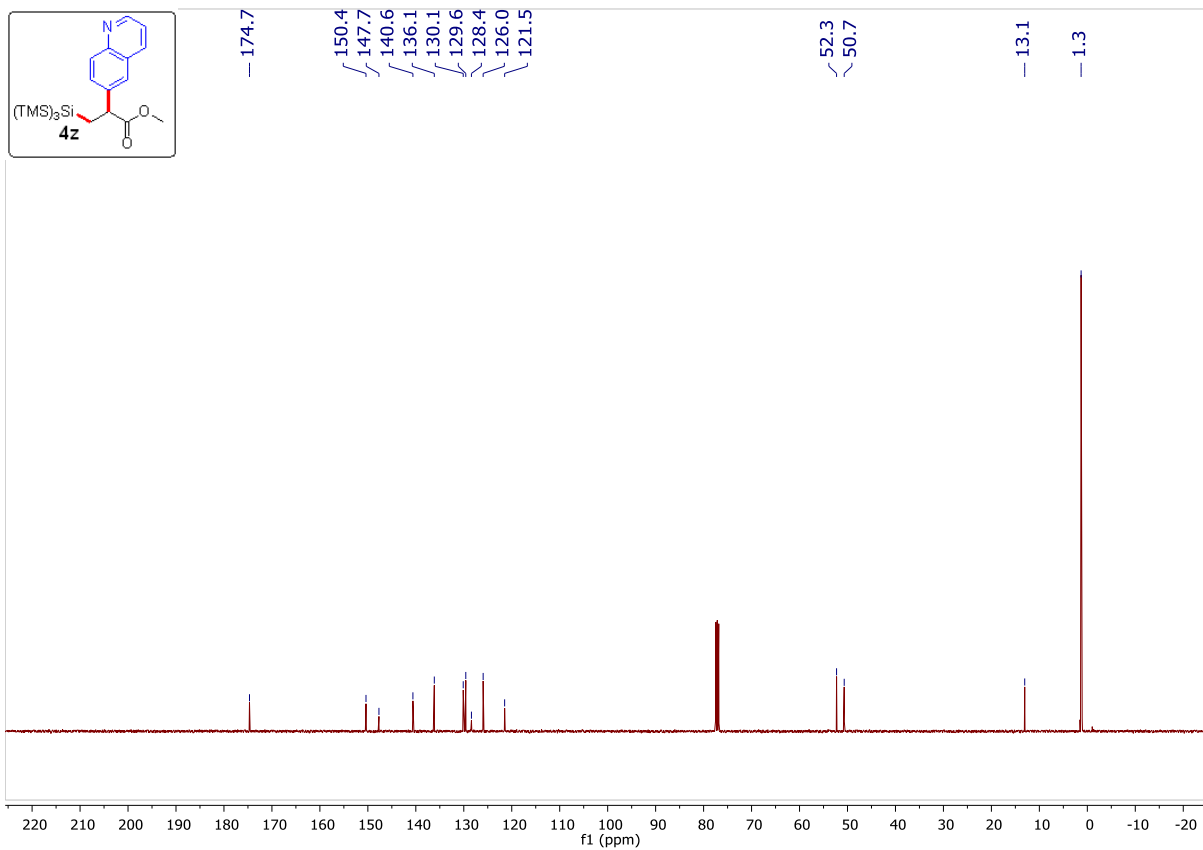




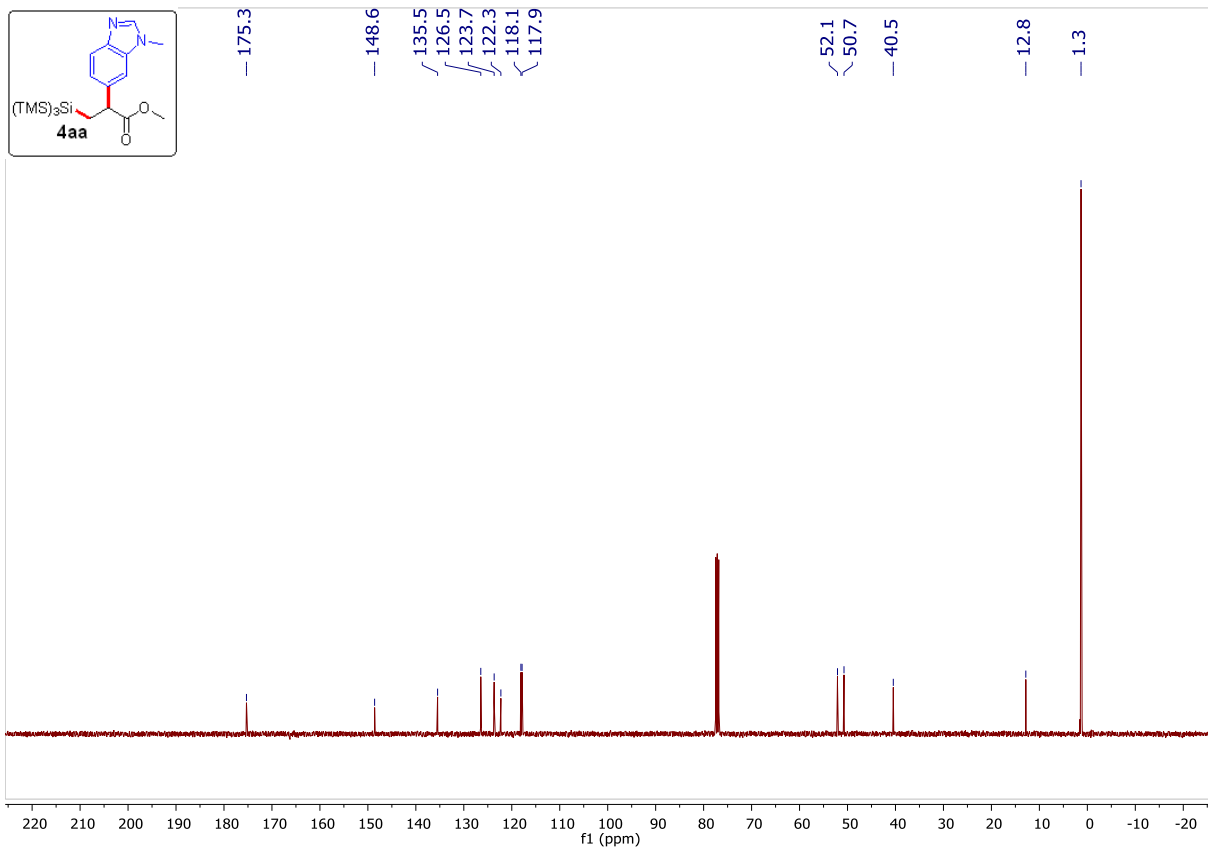
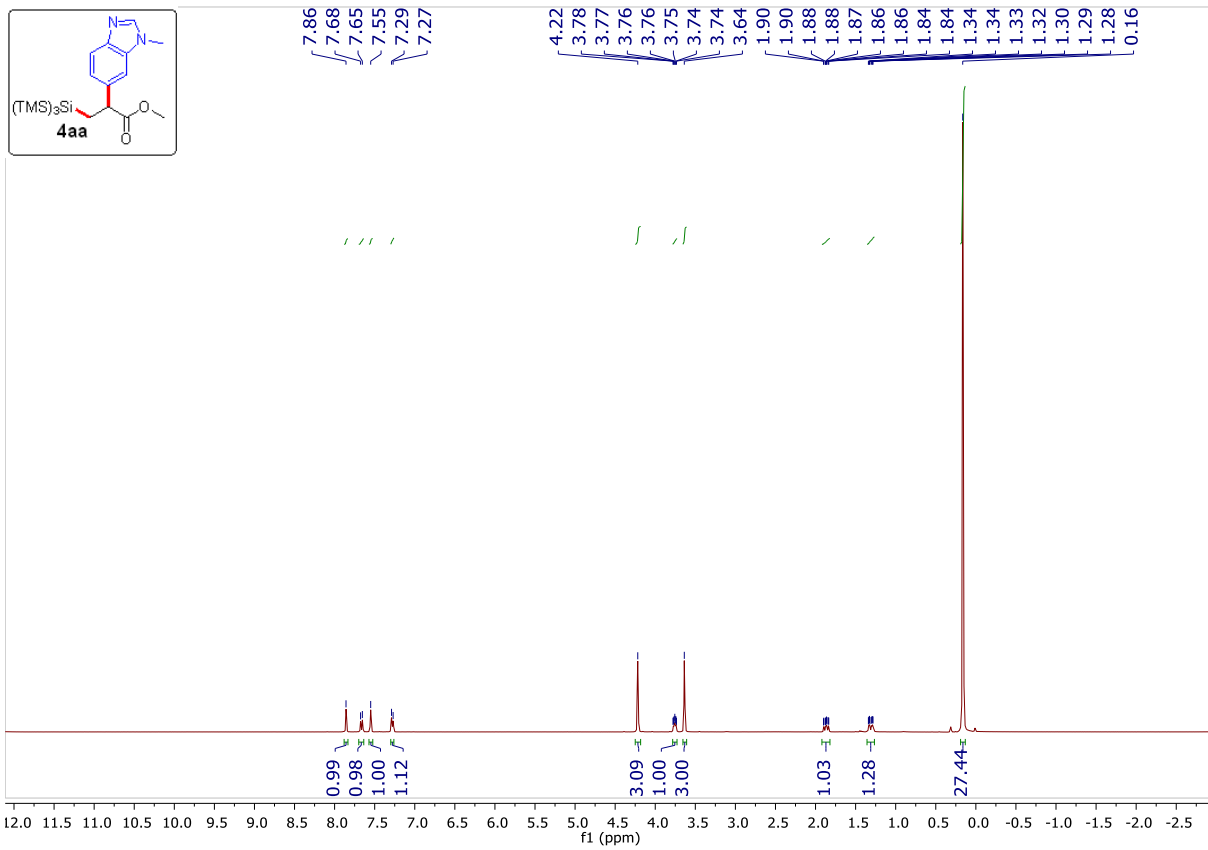
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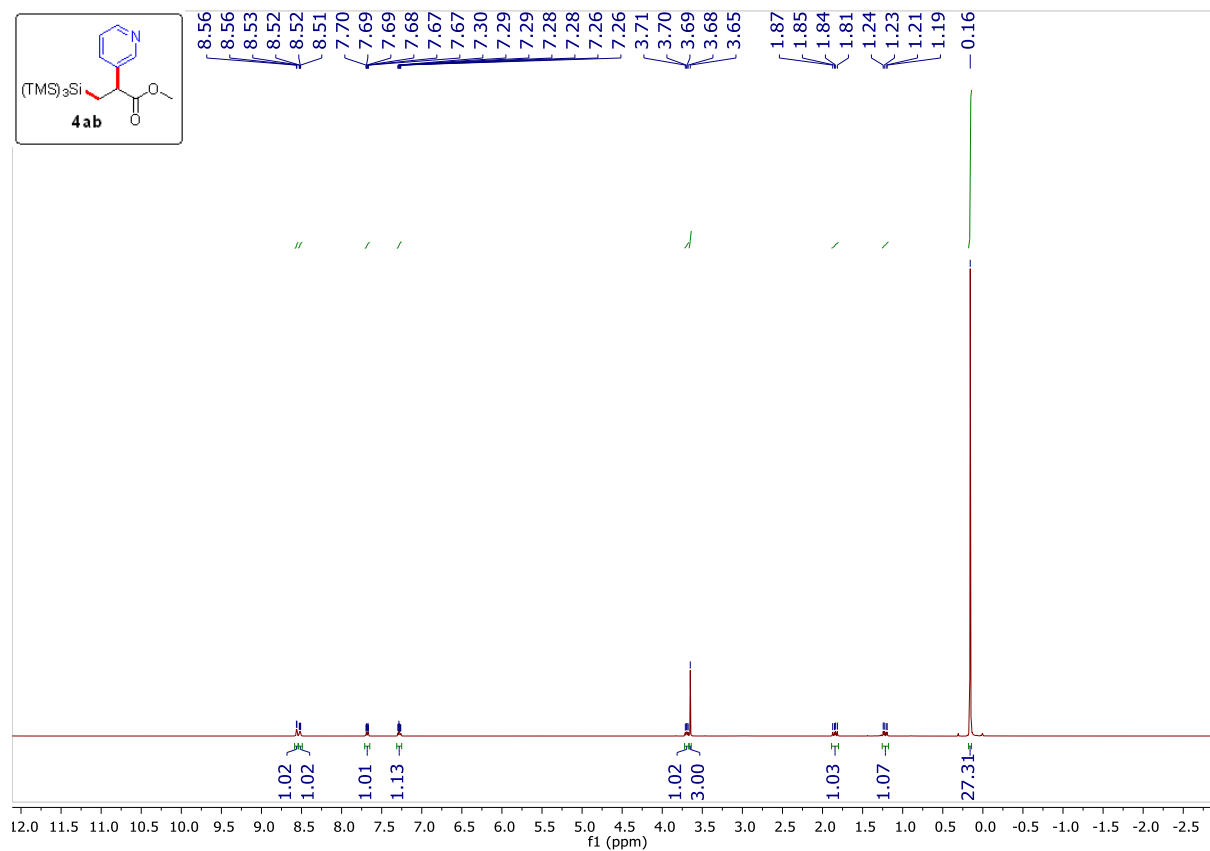
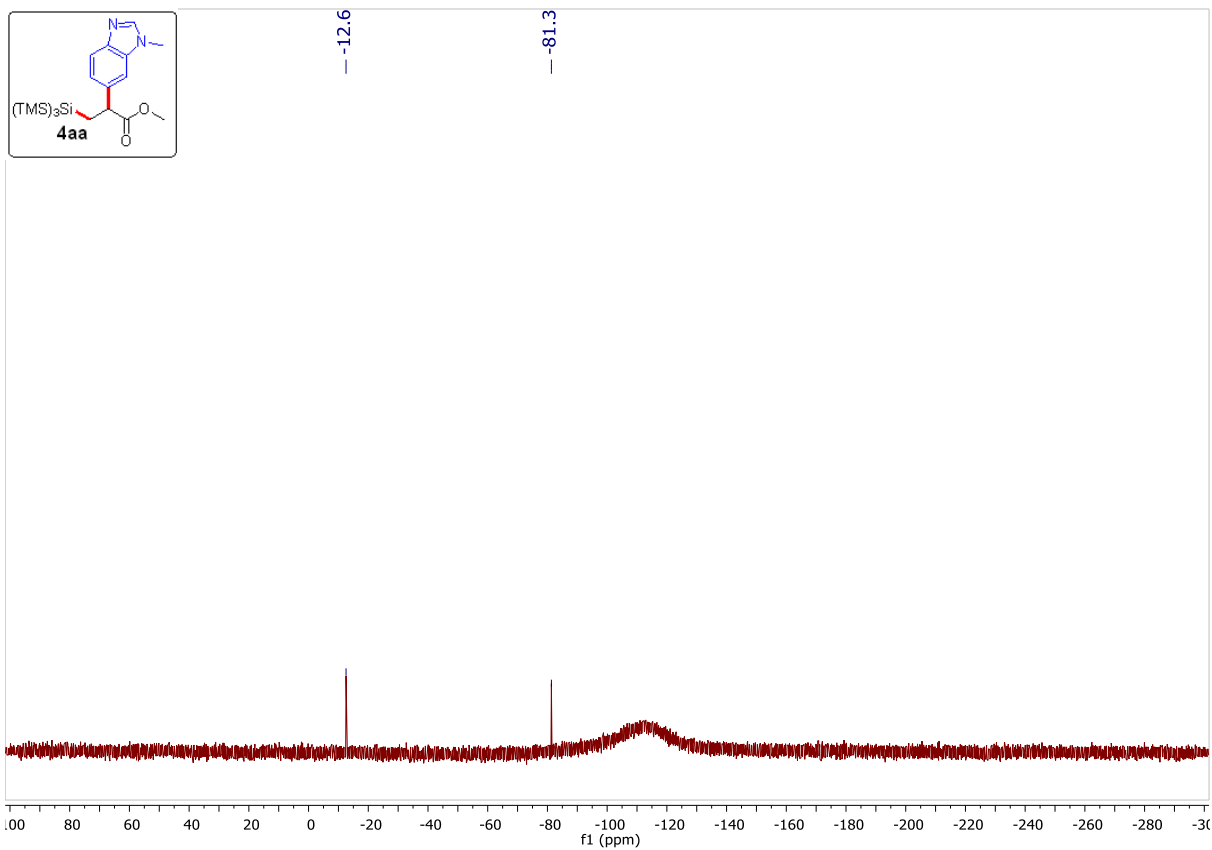


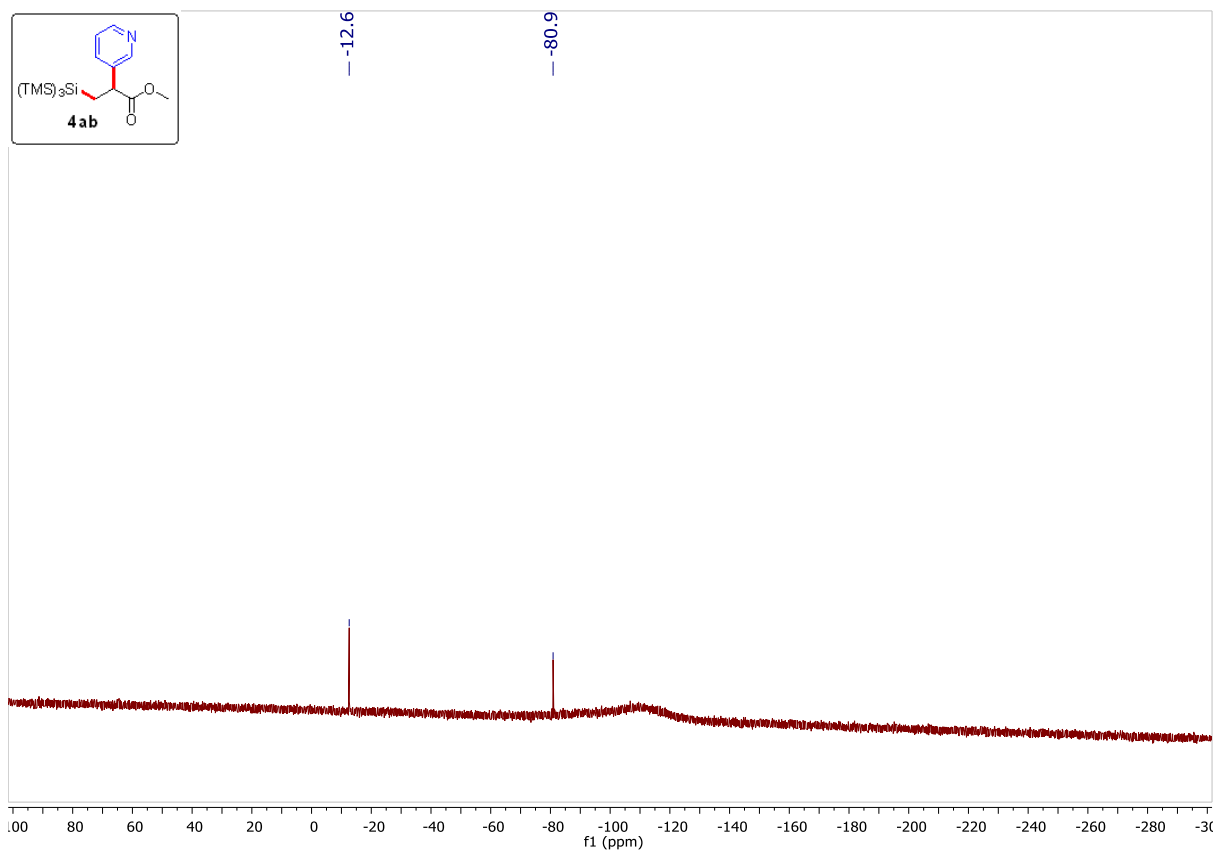
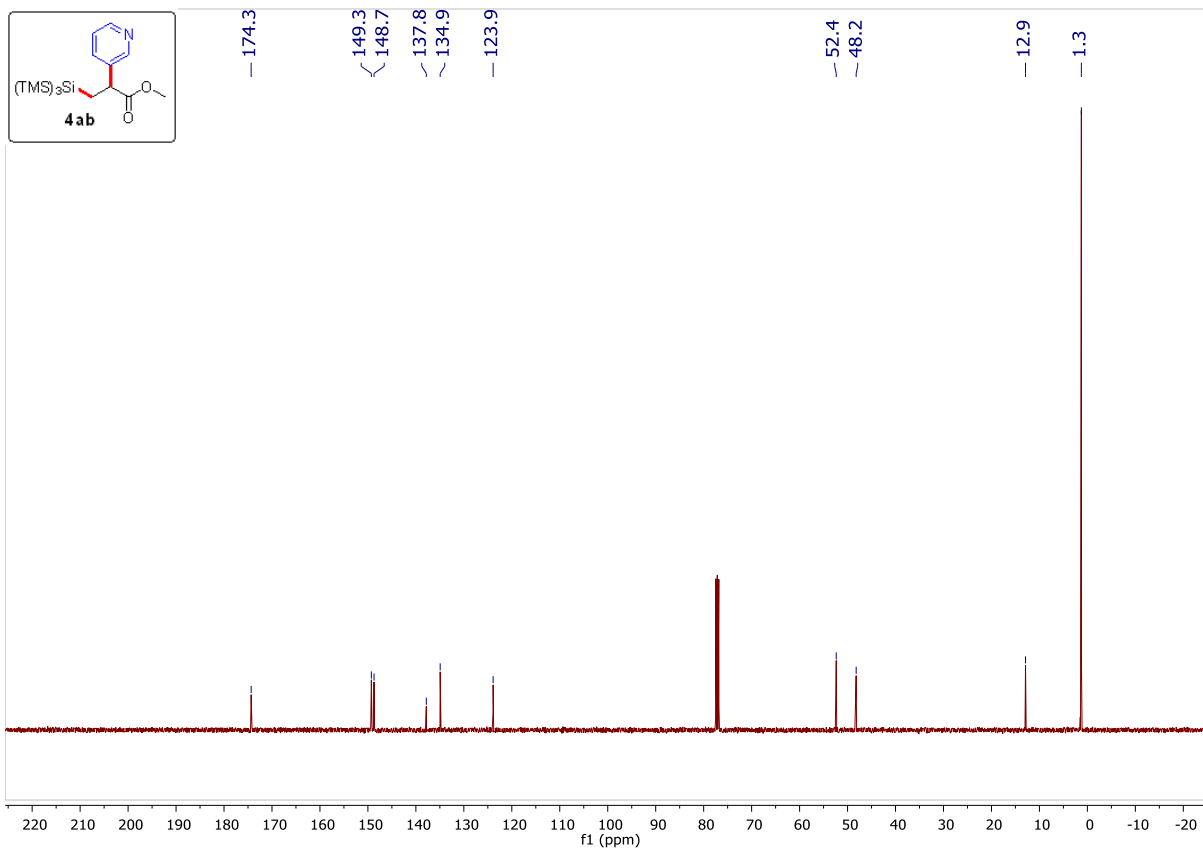




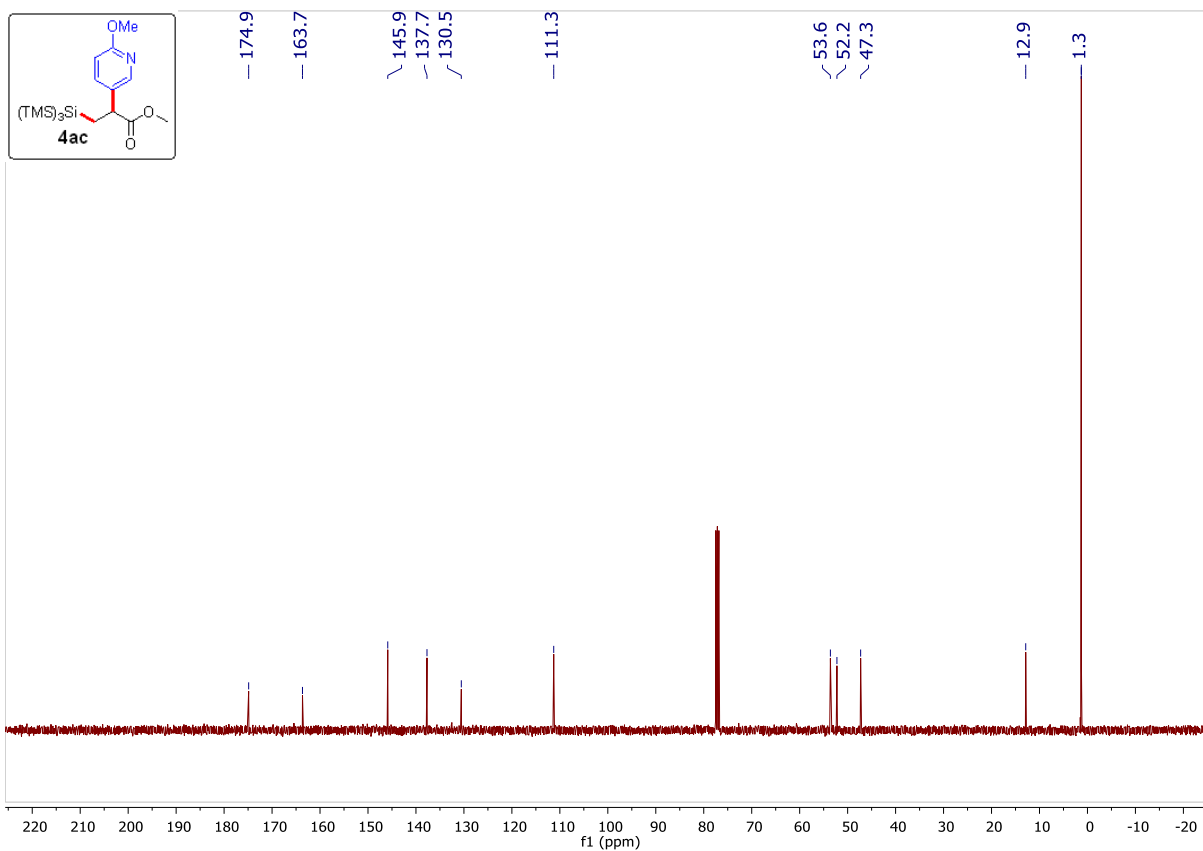
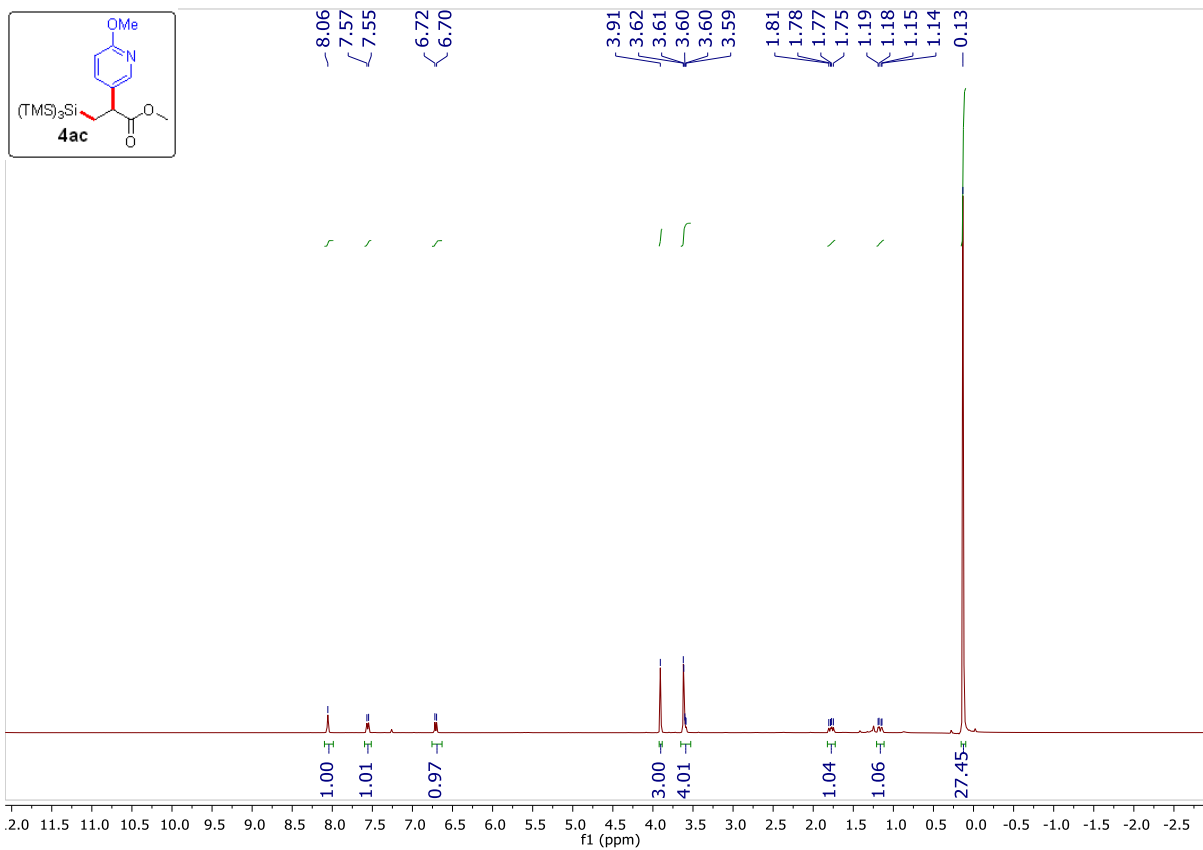
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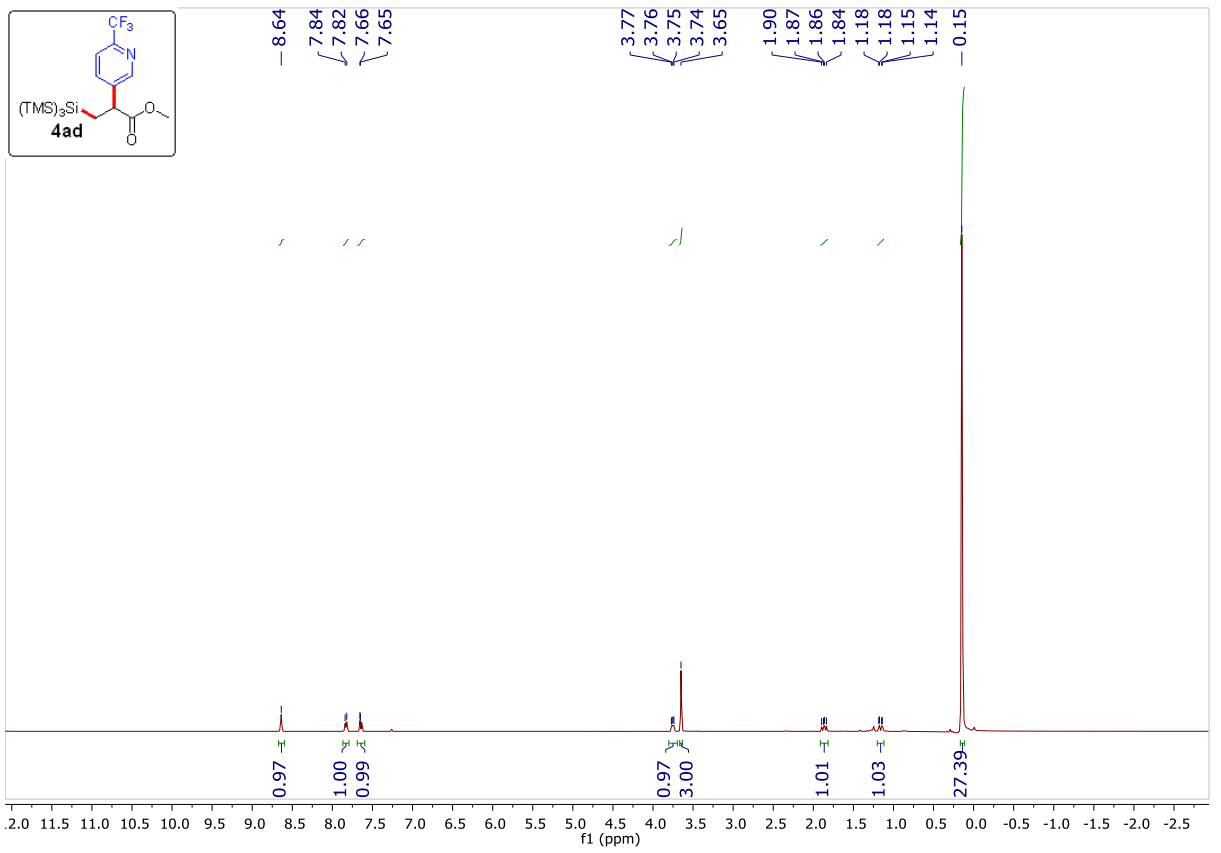
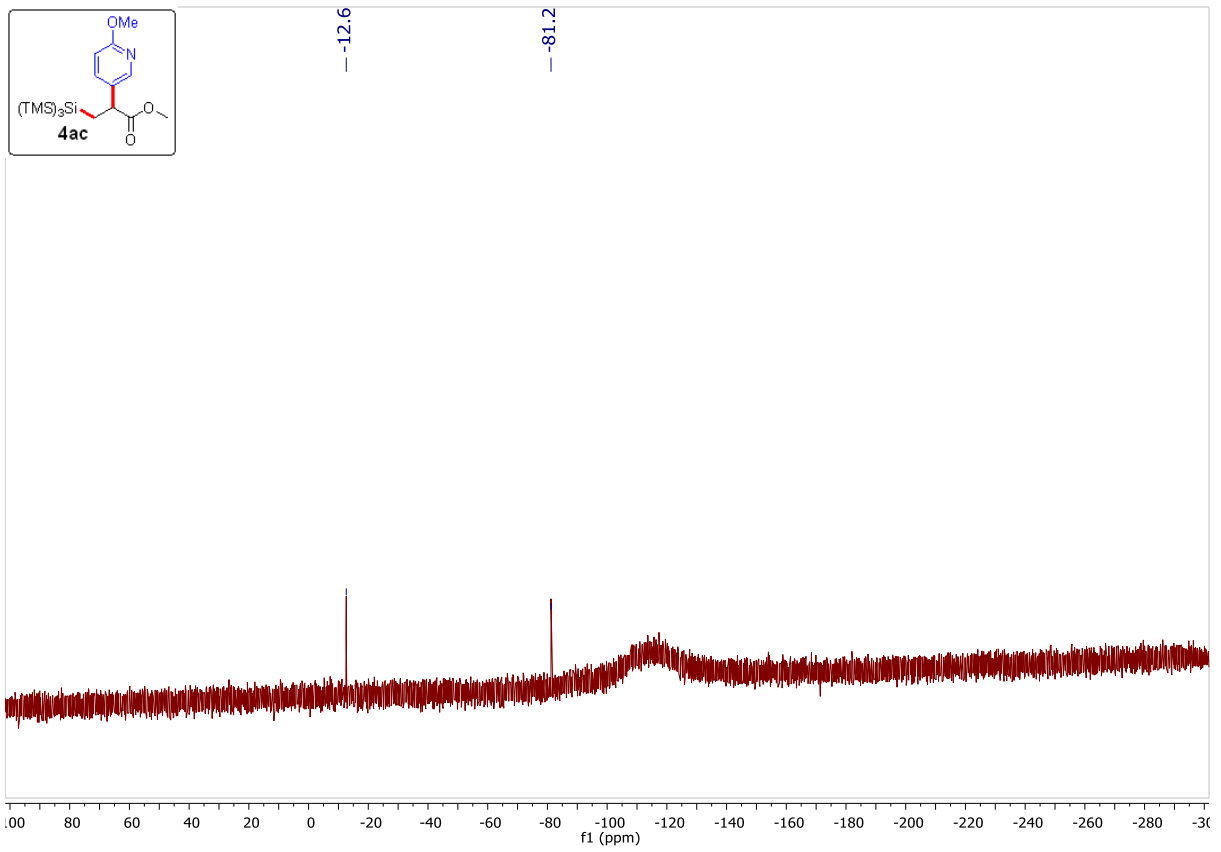


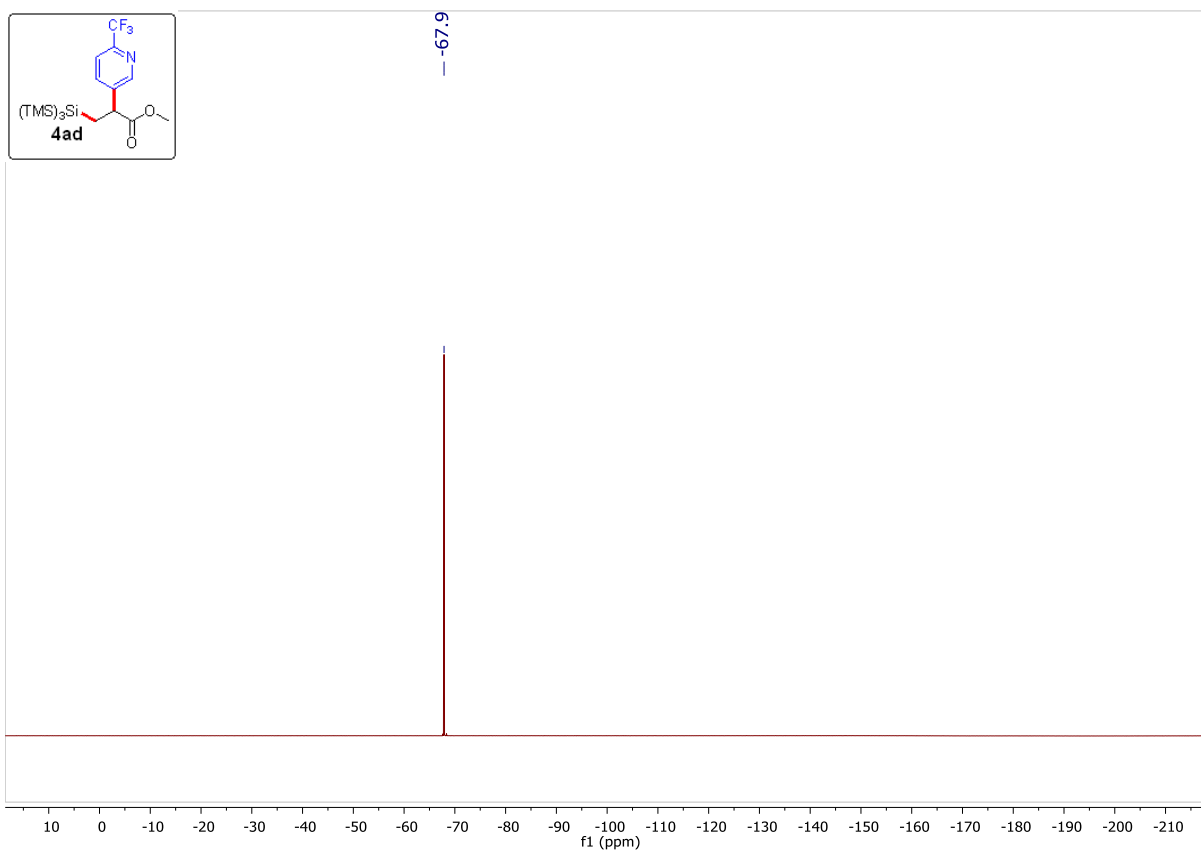
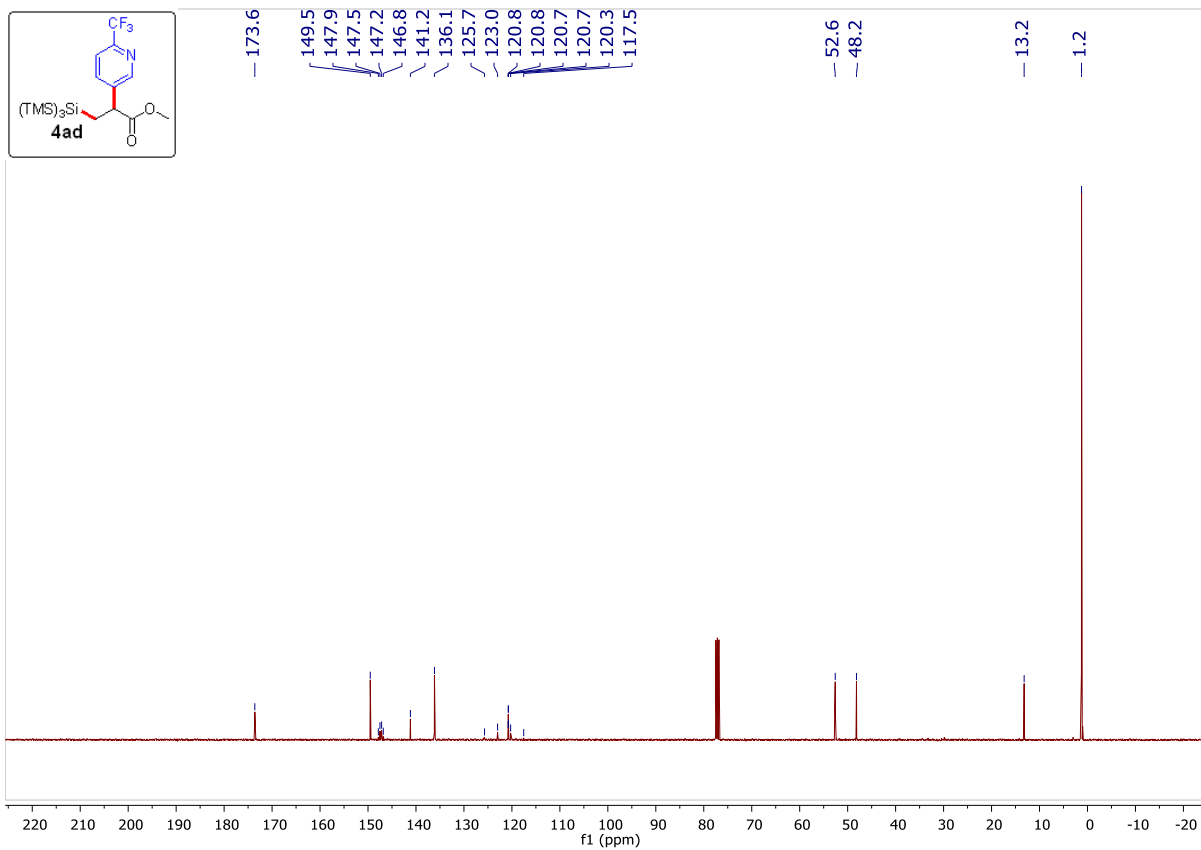


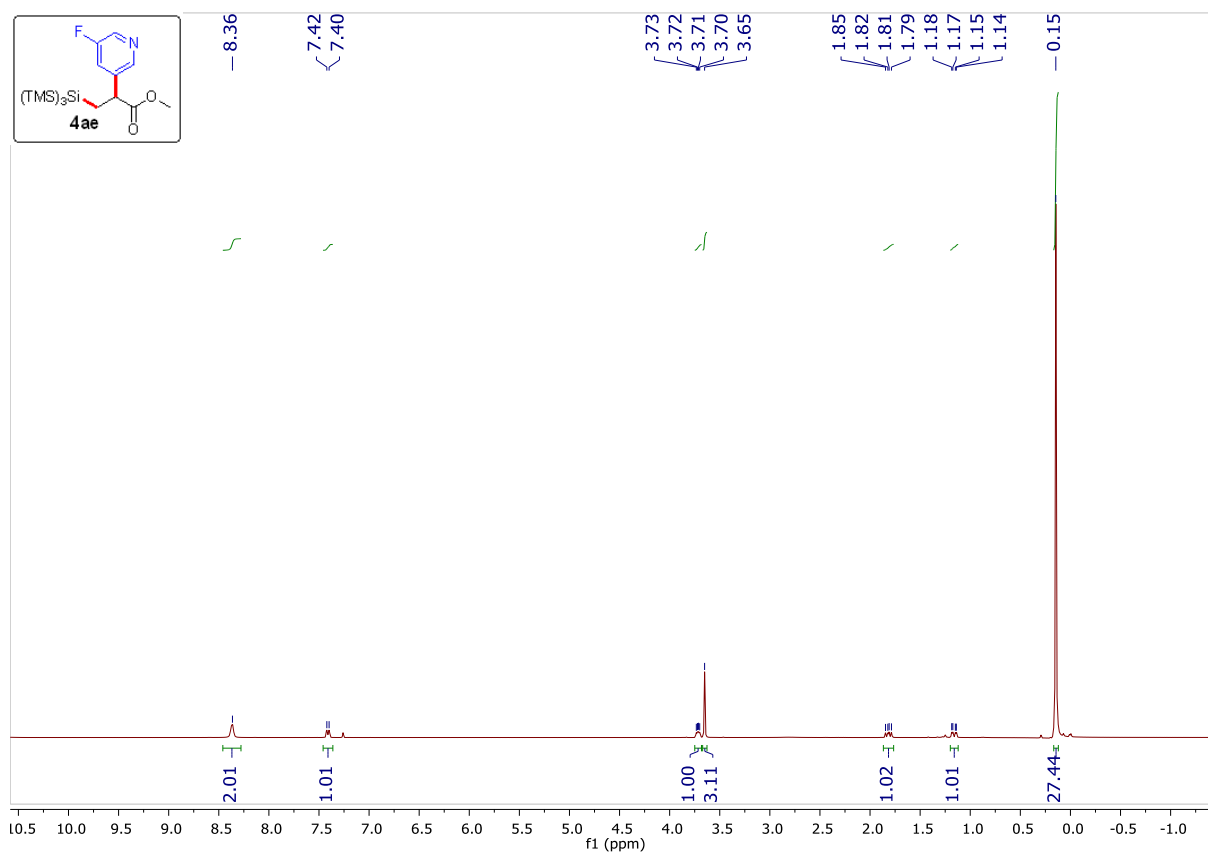
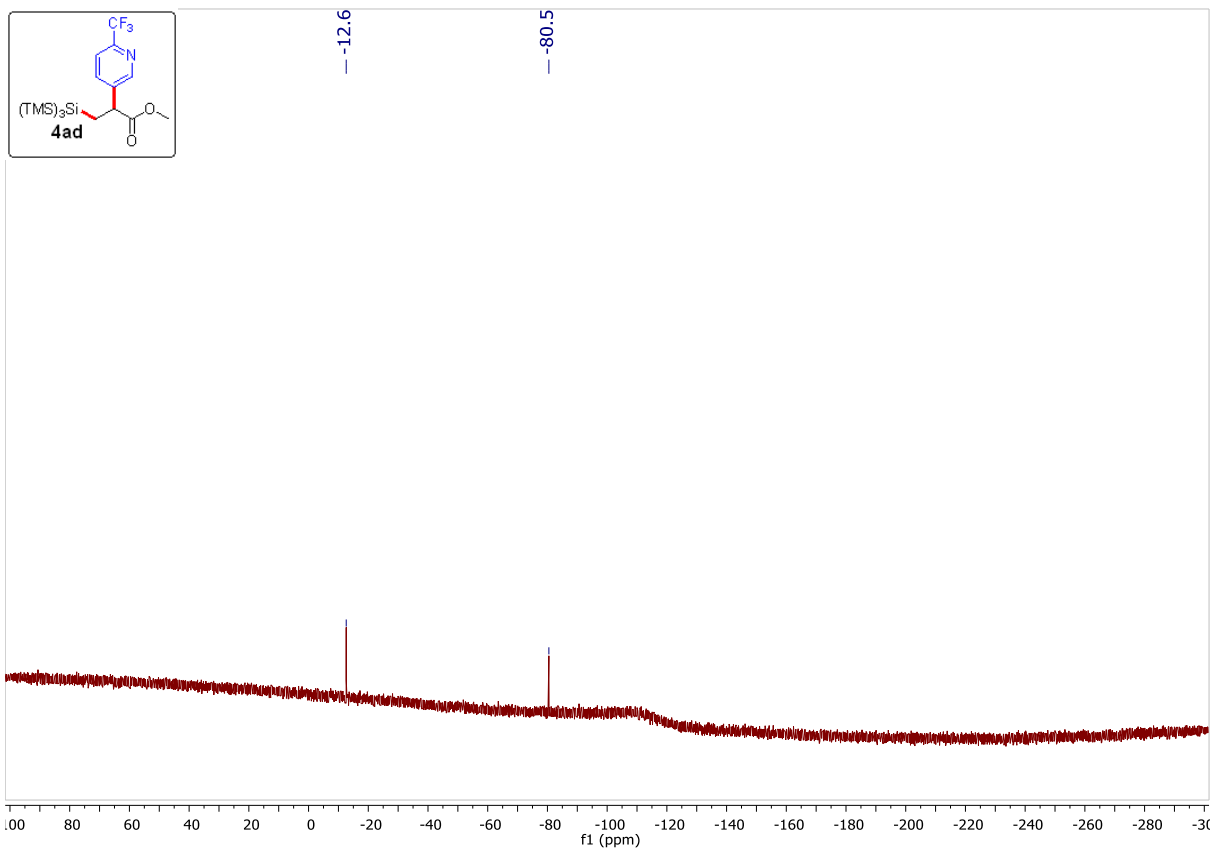


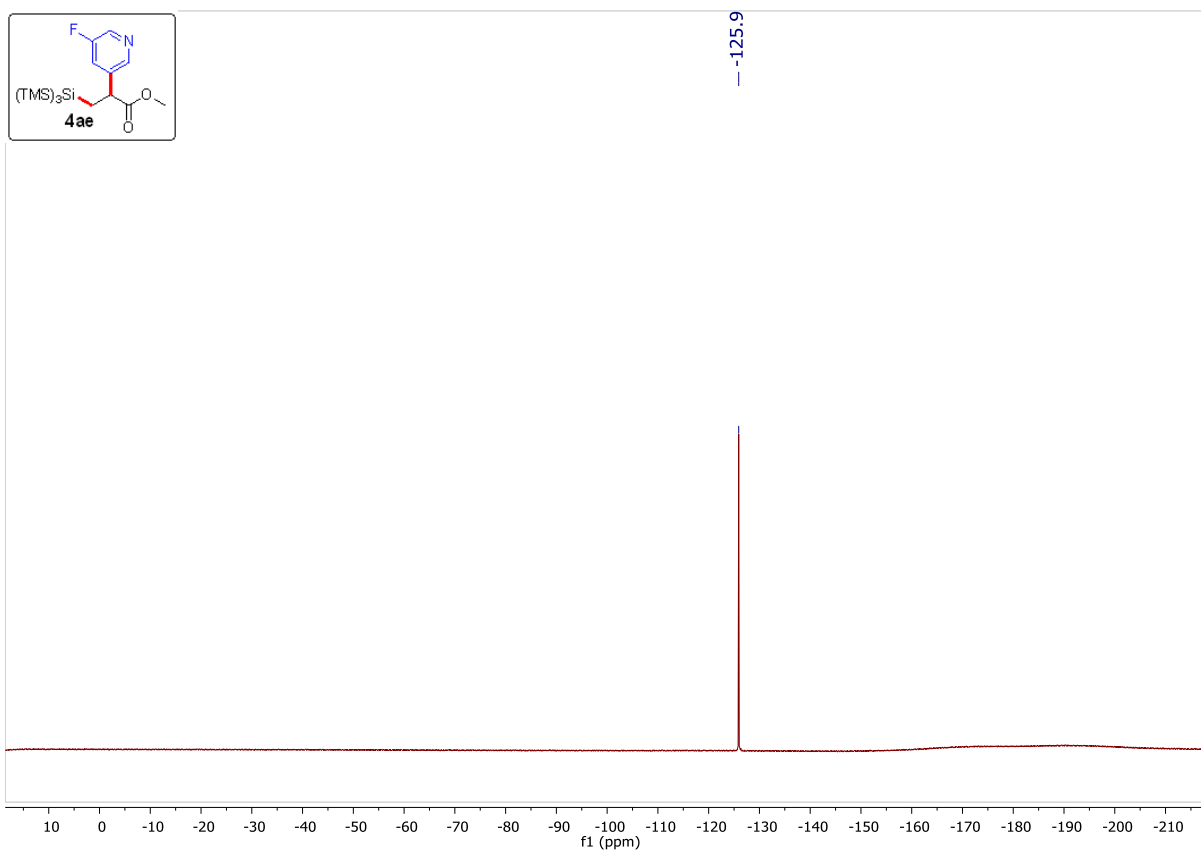
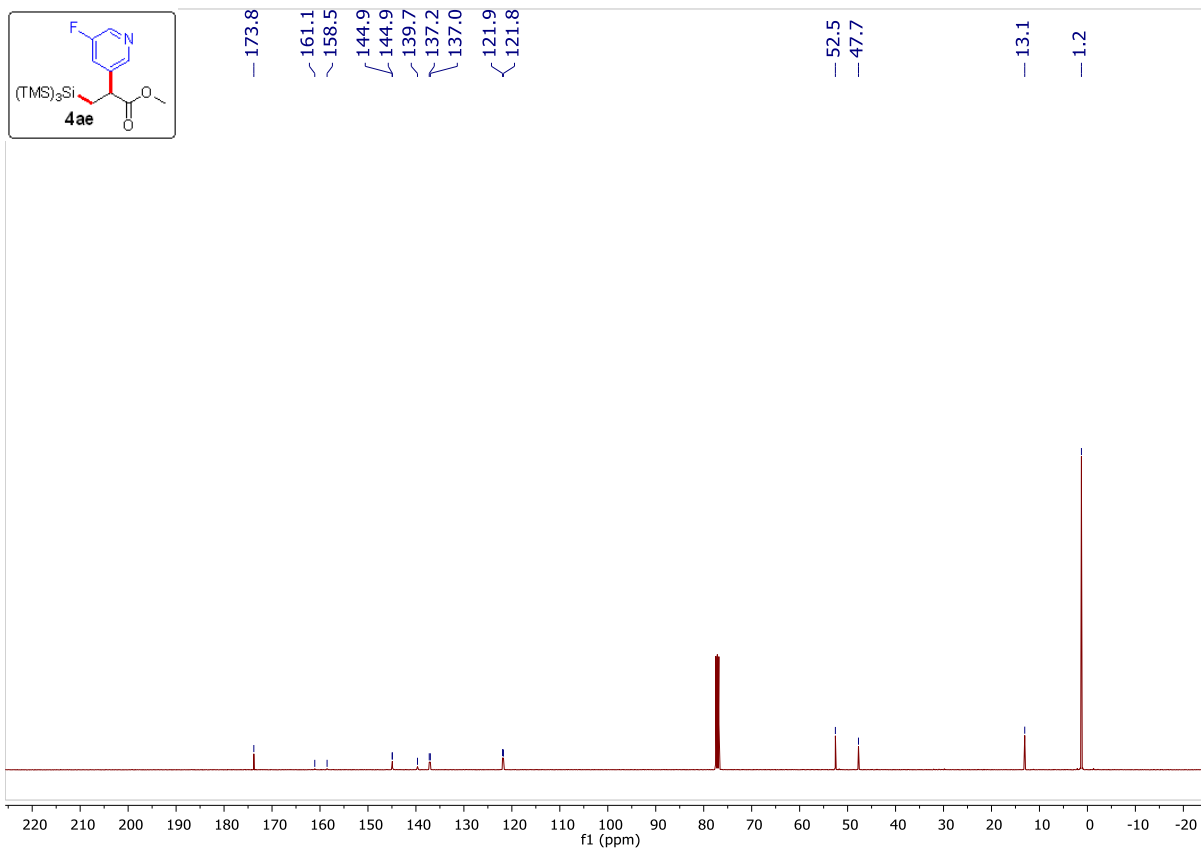
S73



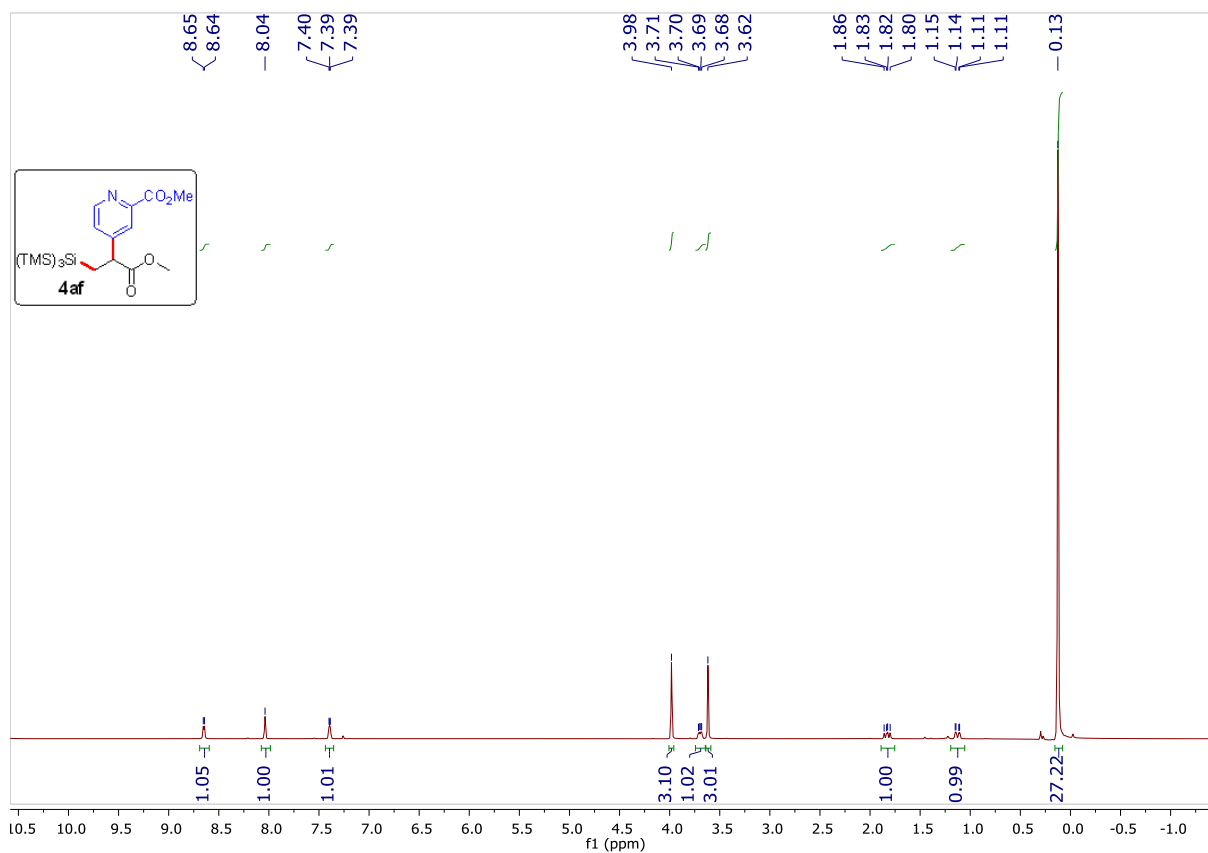
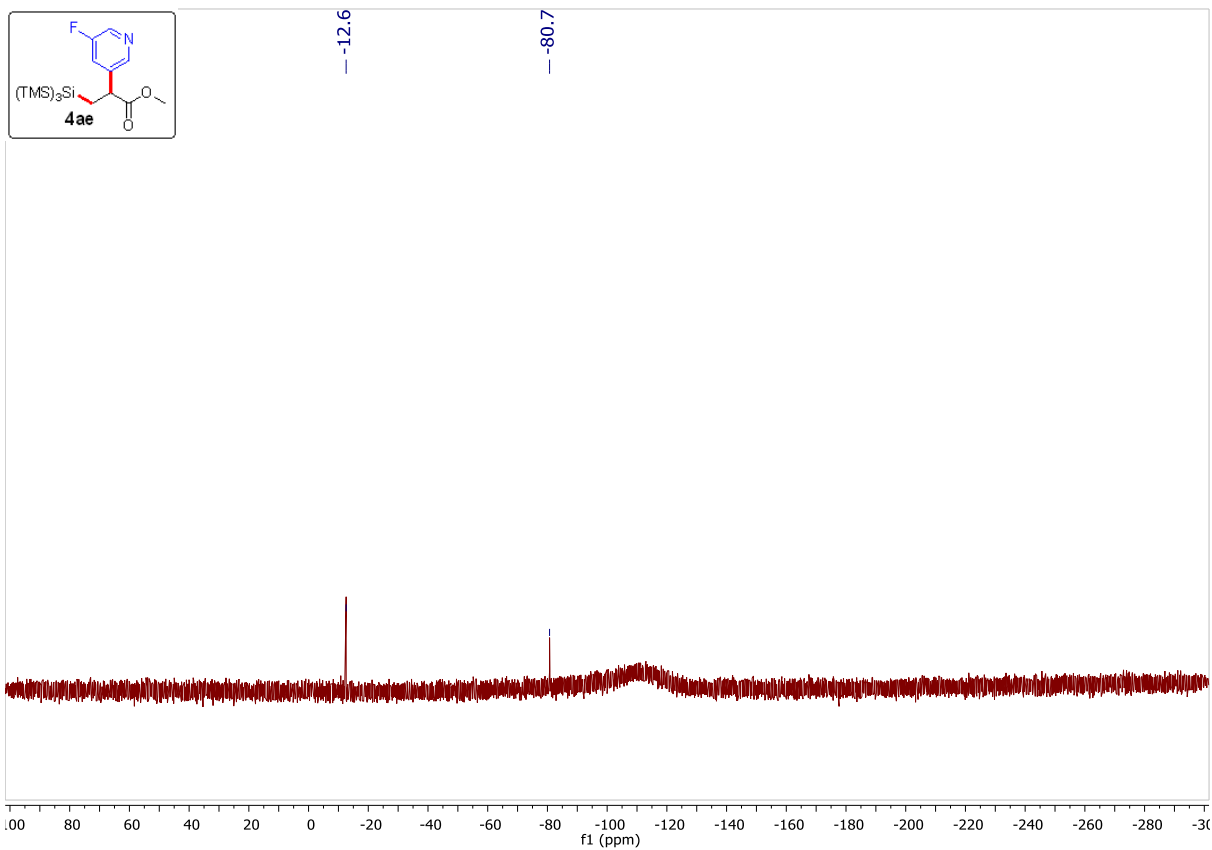


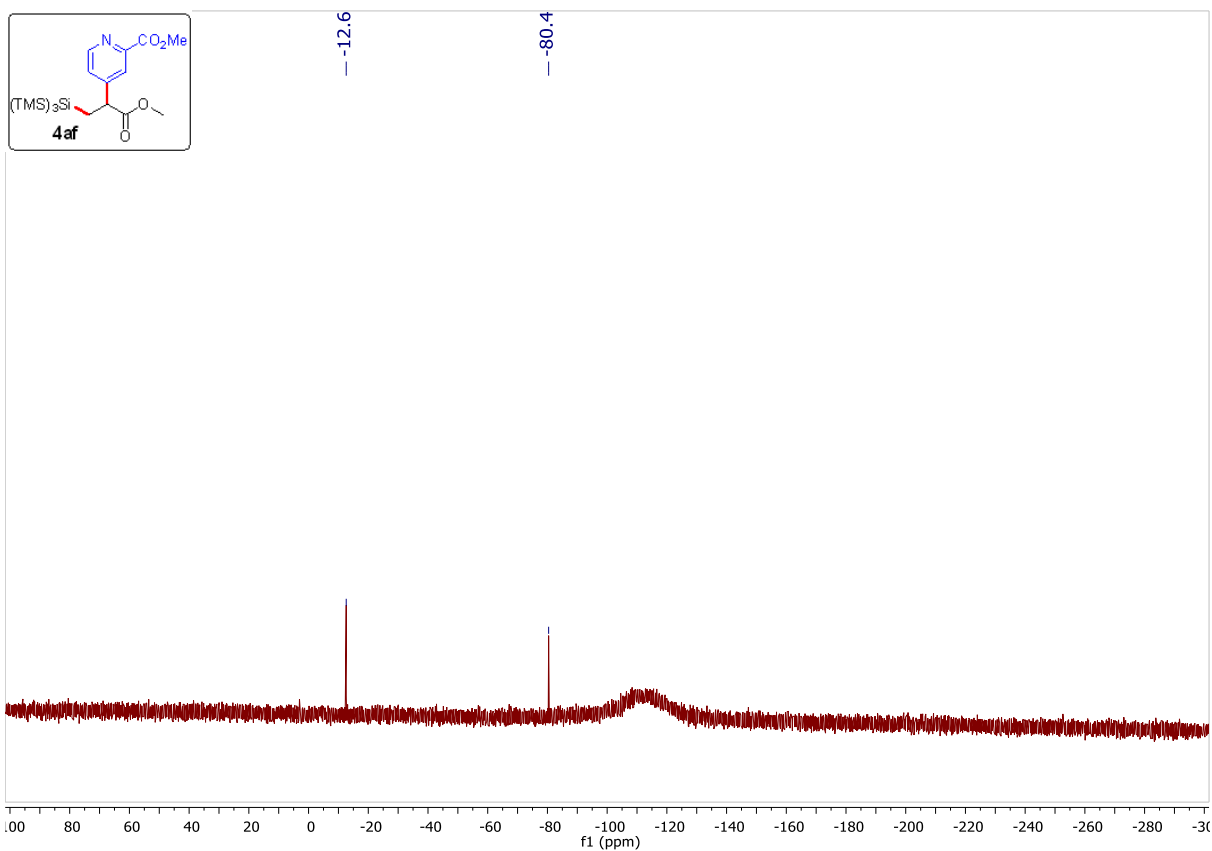
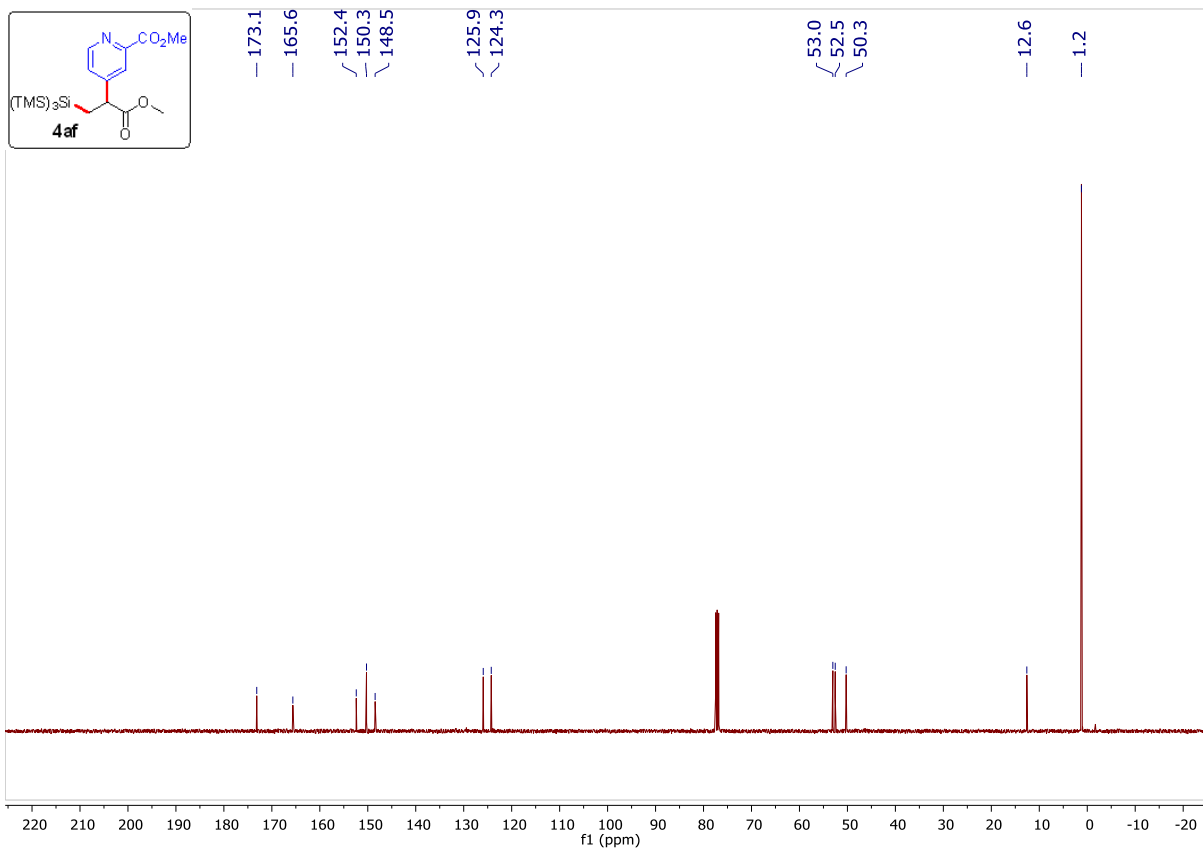




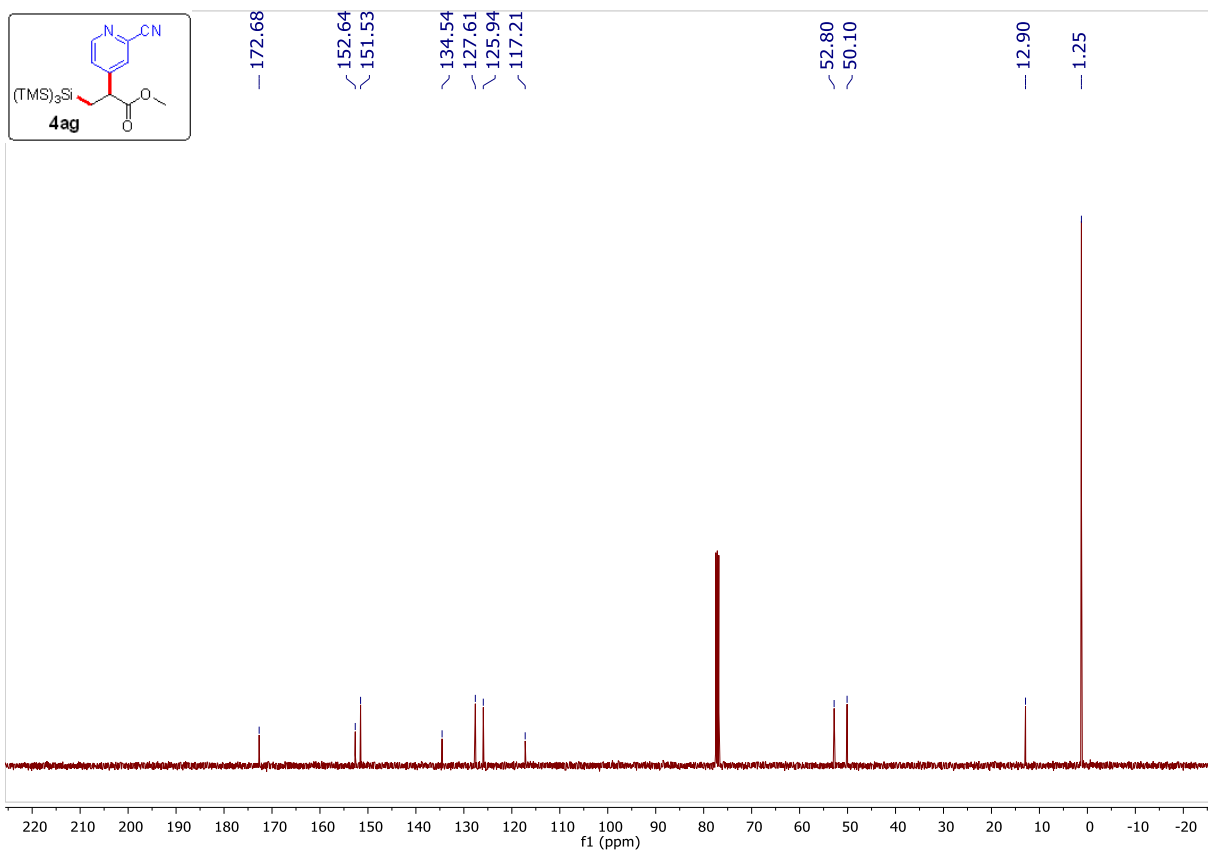
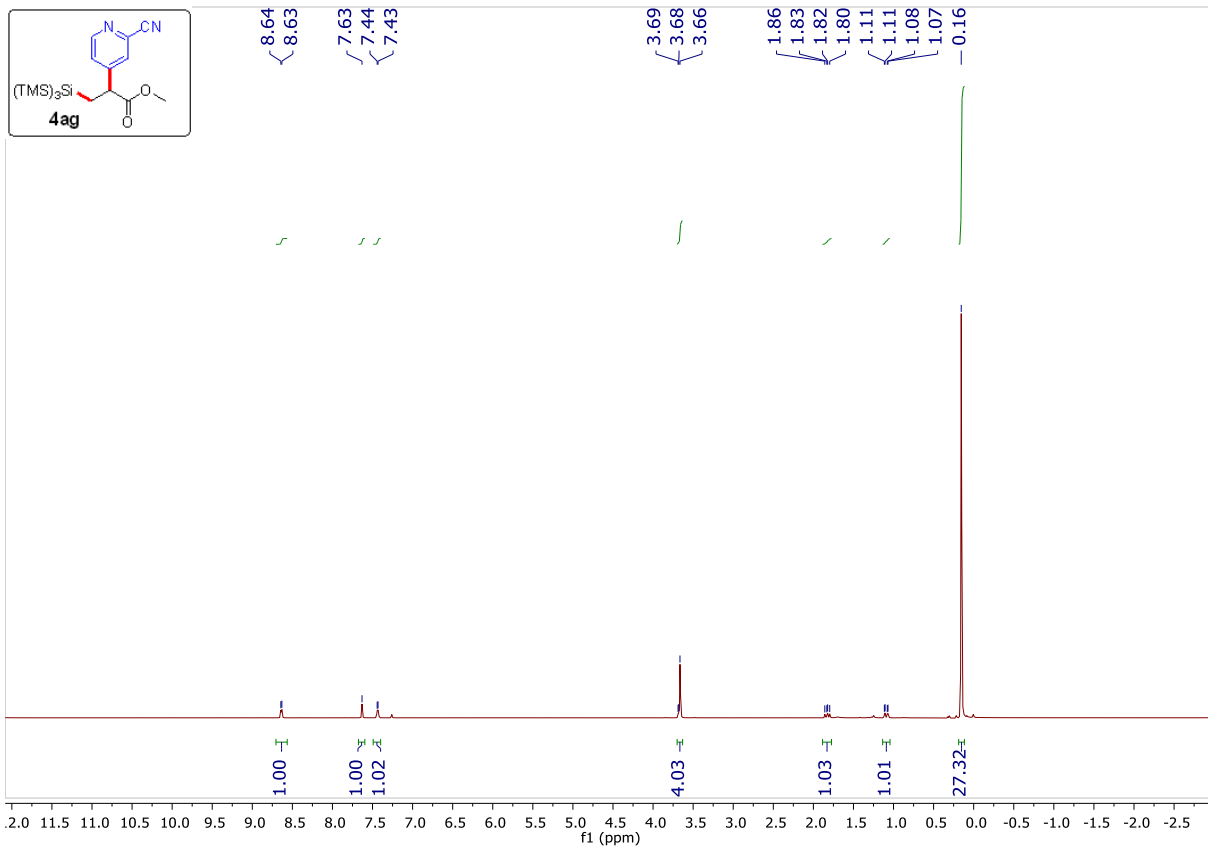


S78

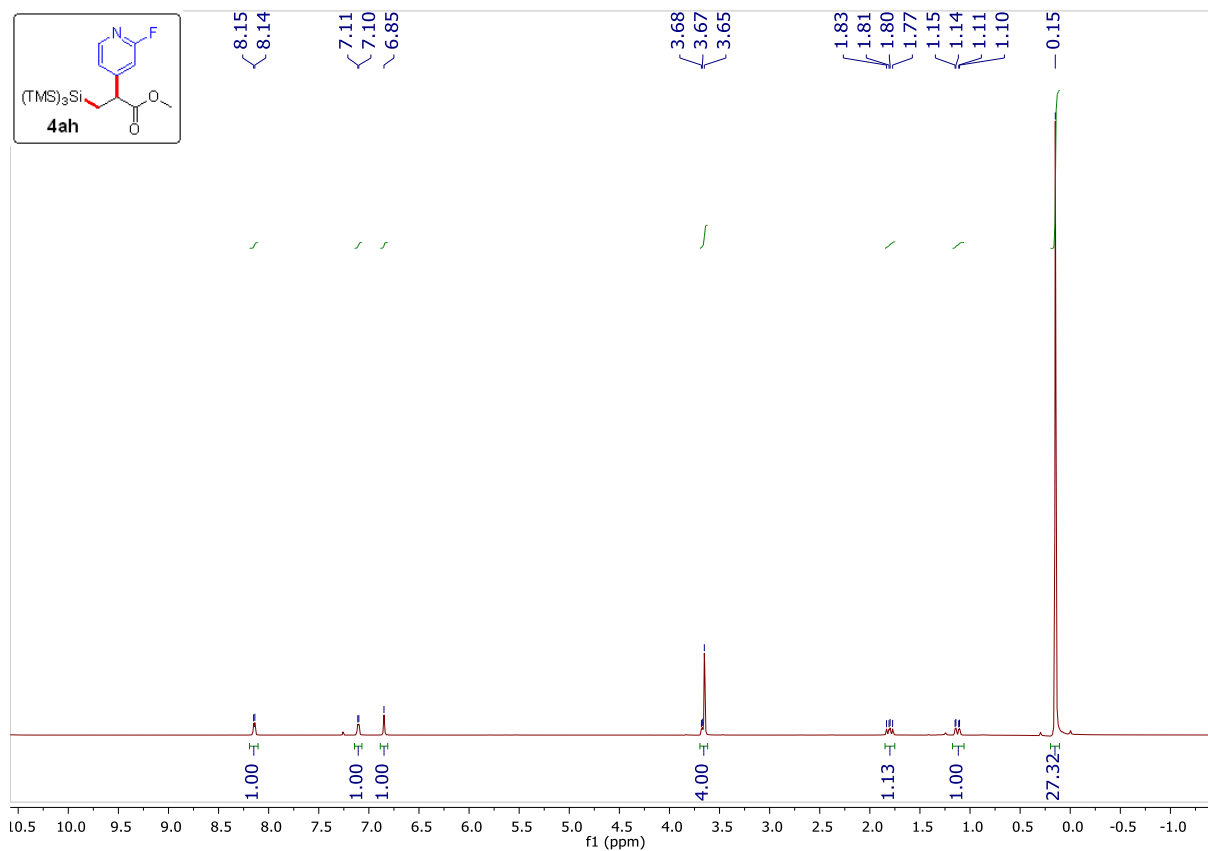
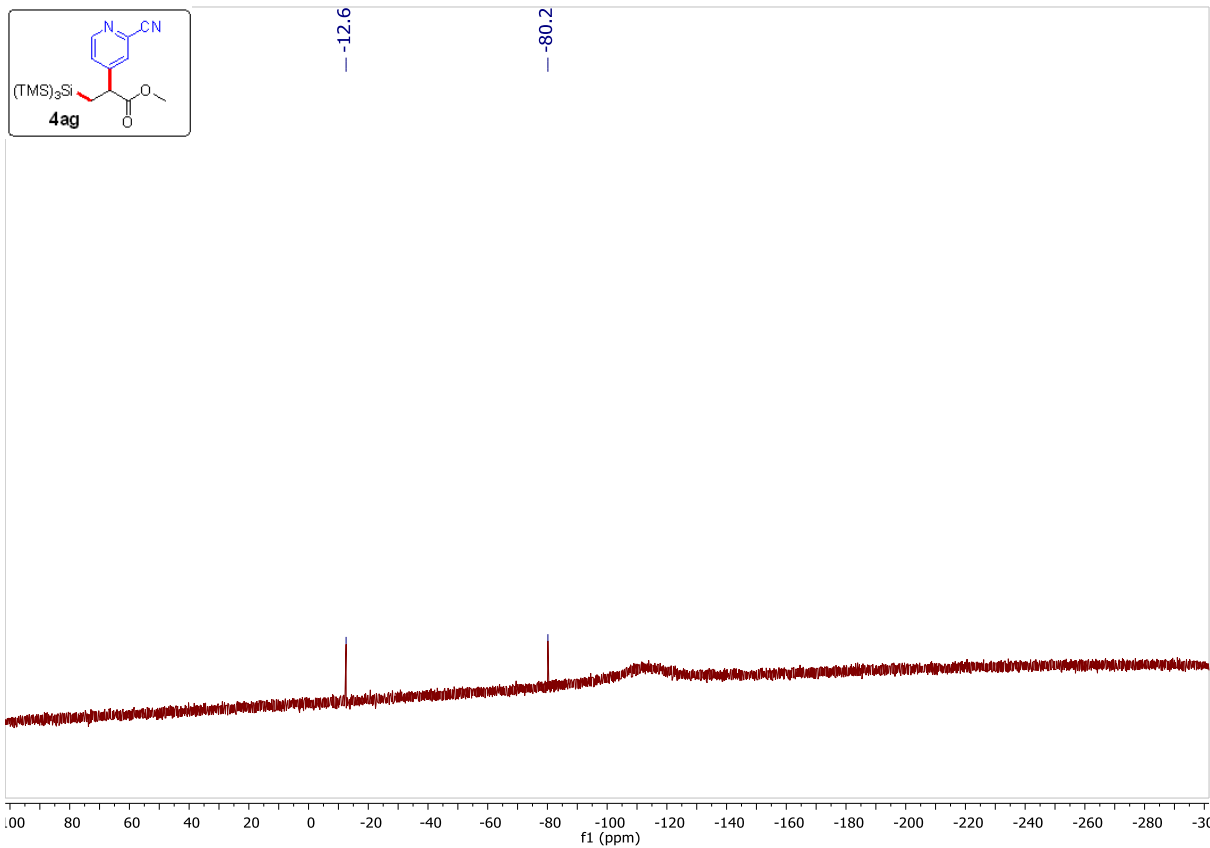




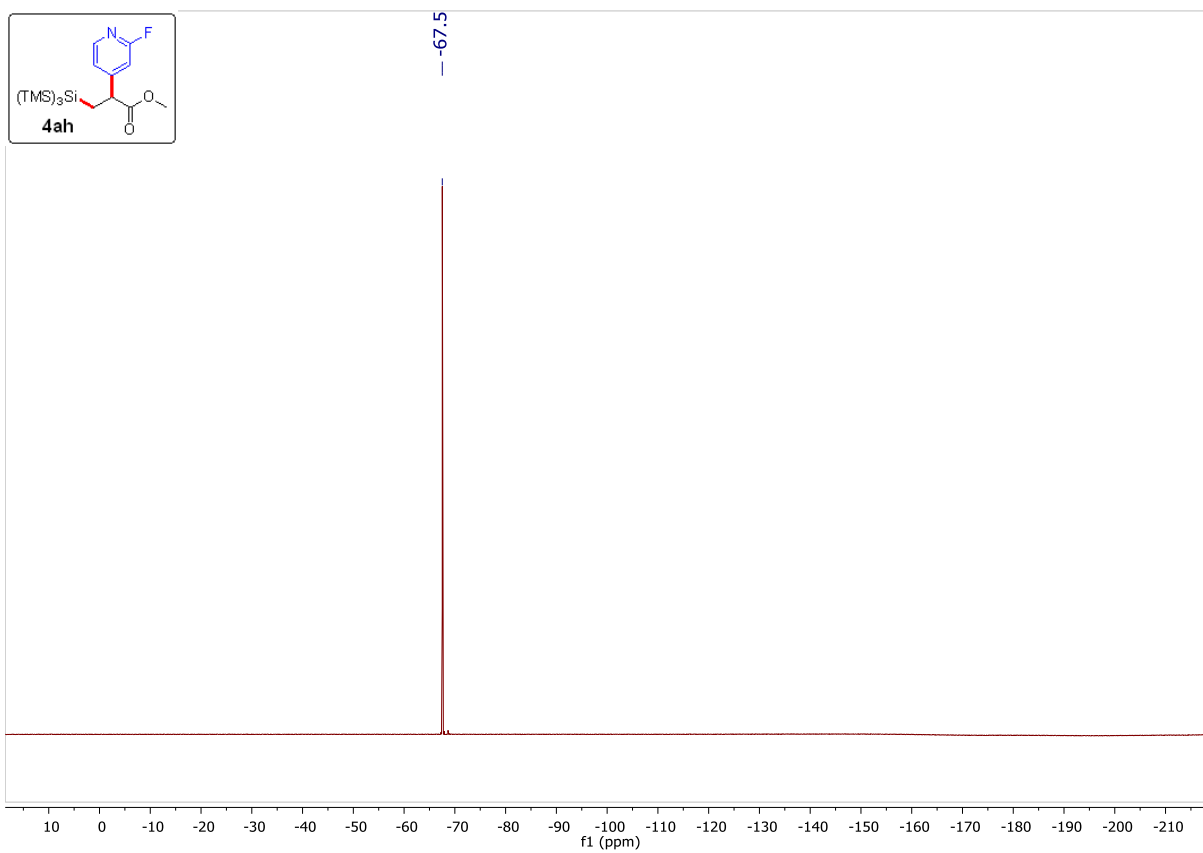
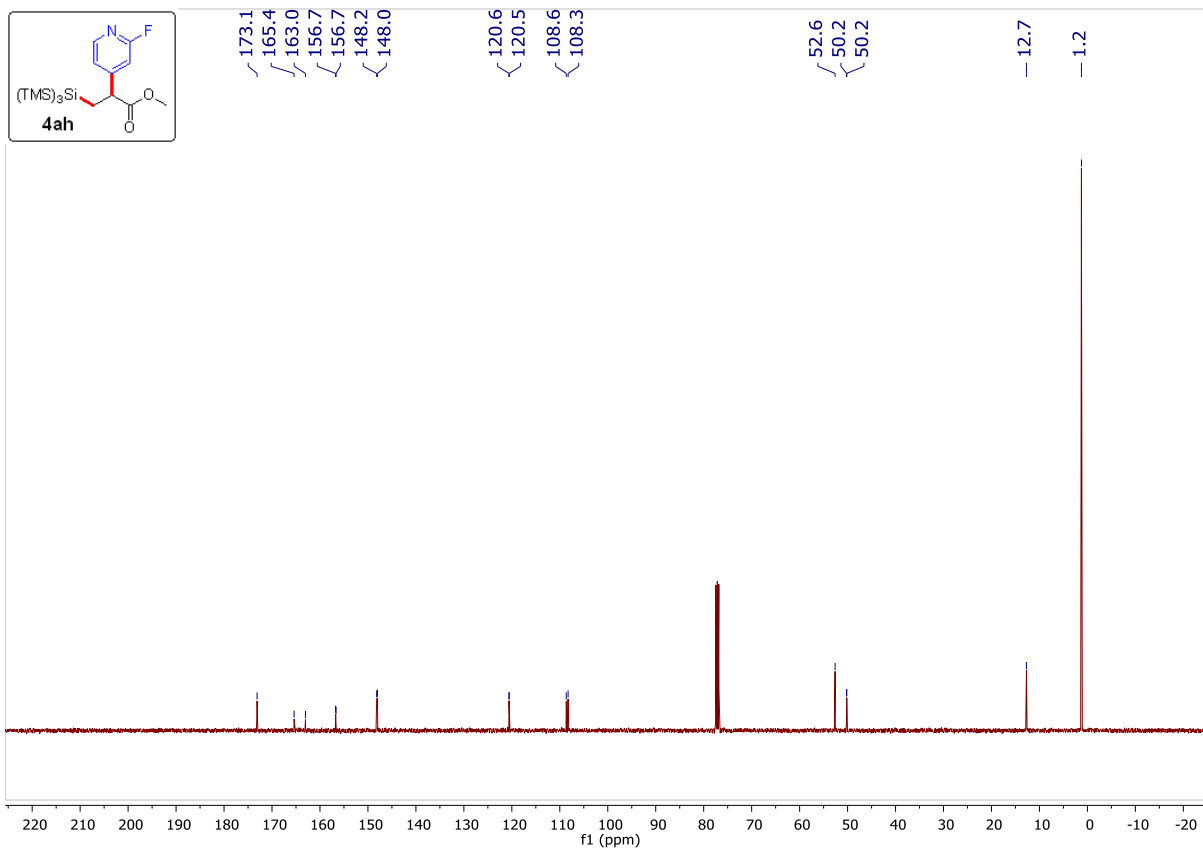
S80



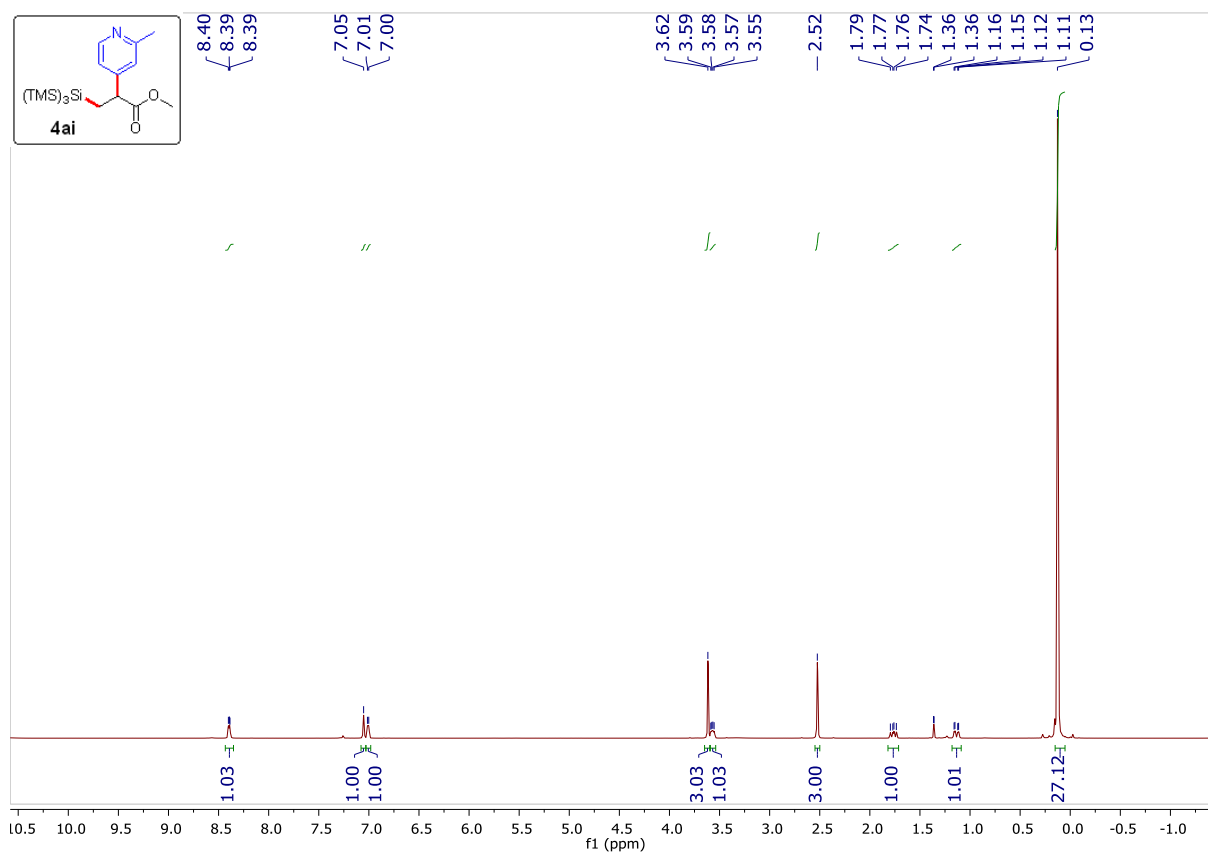
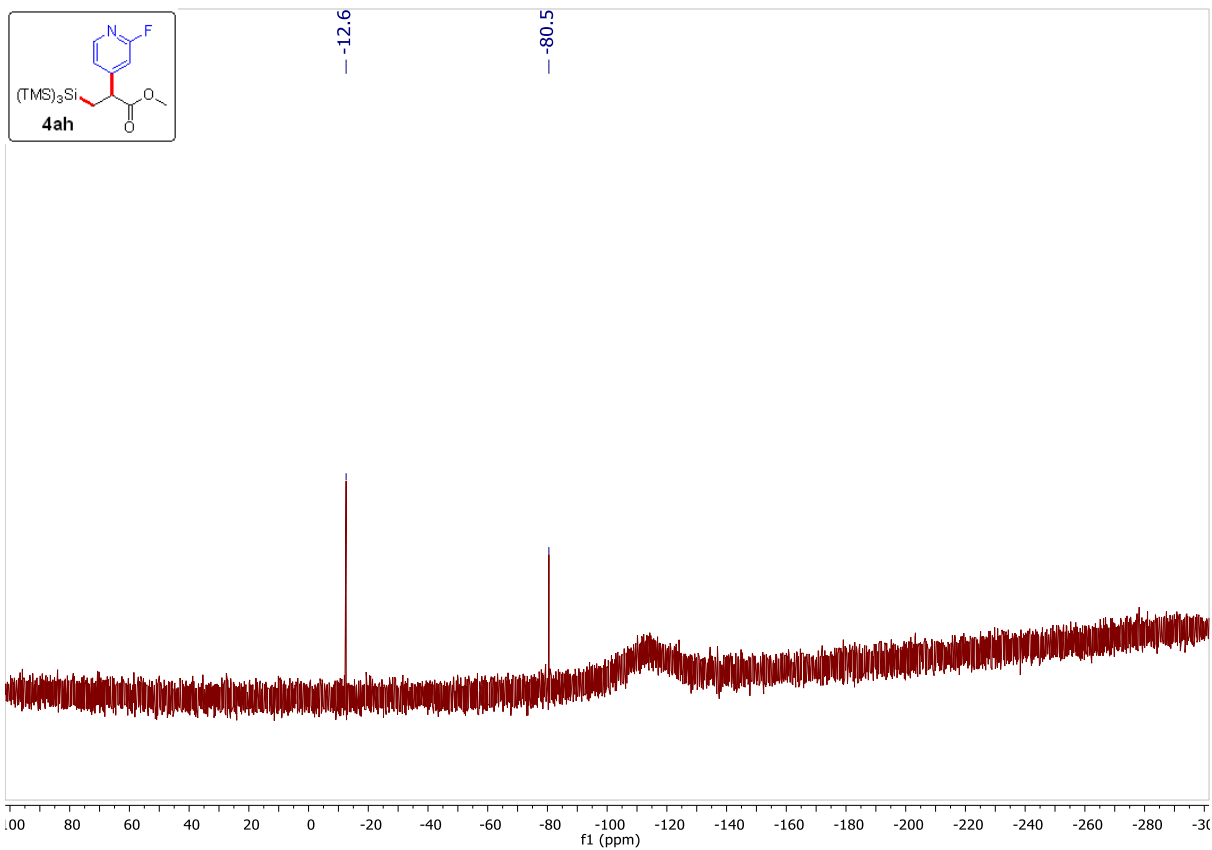
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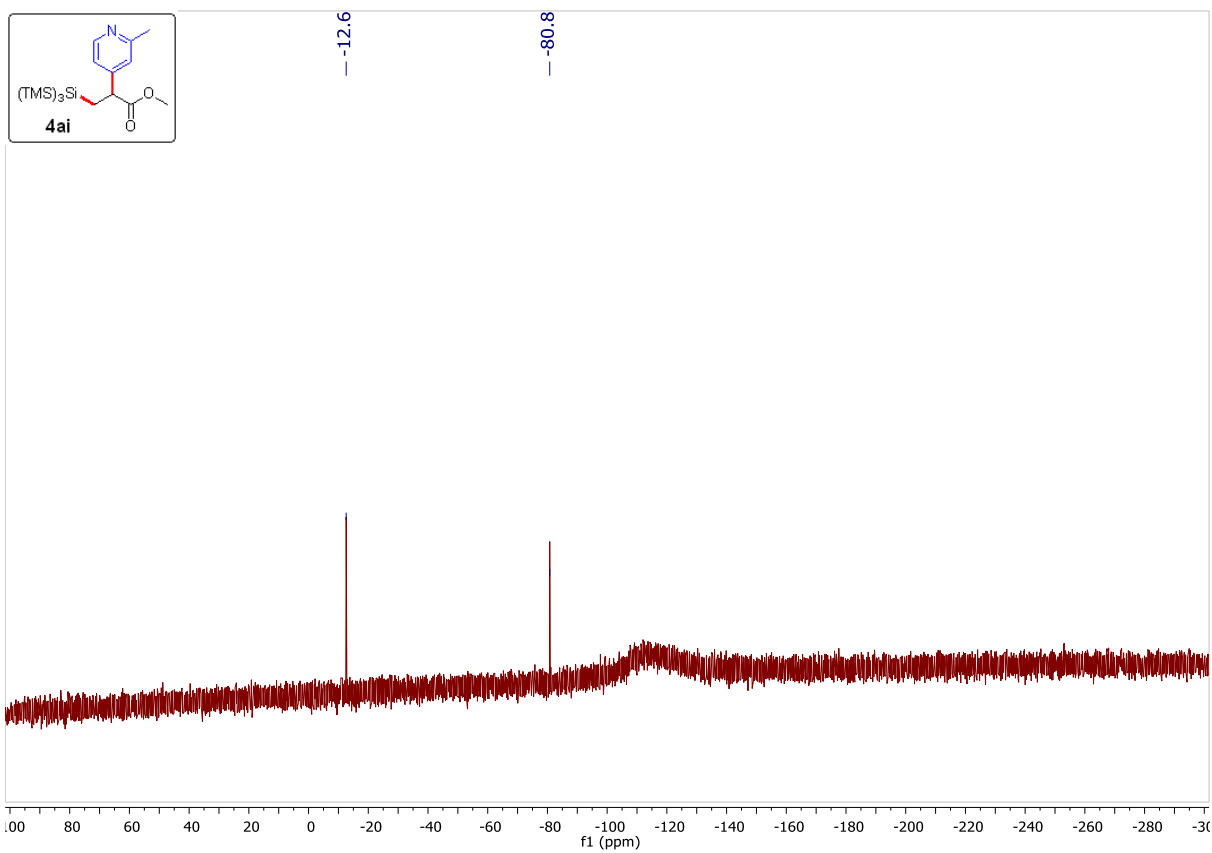
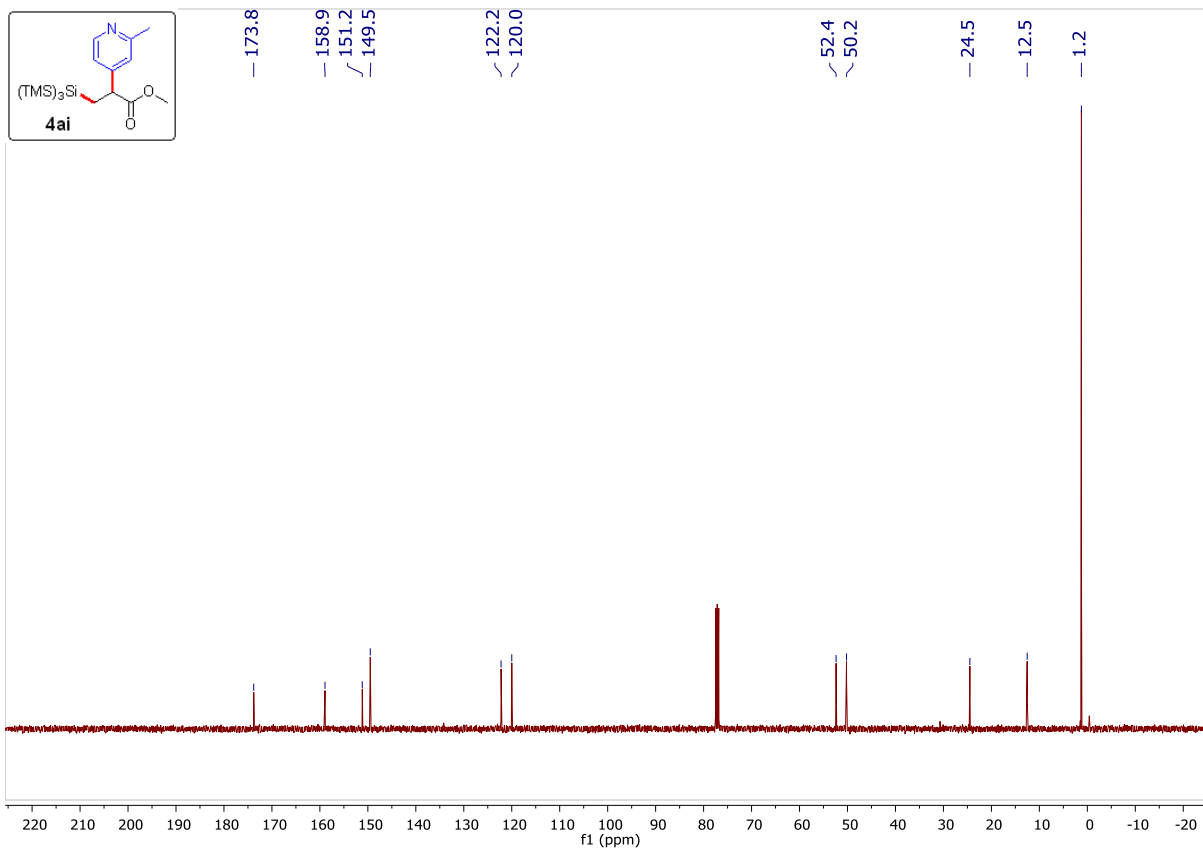


S82

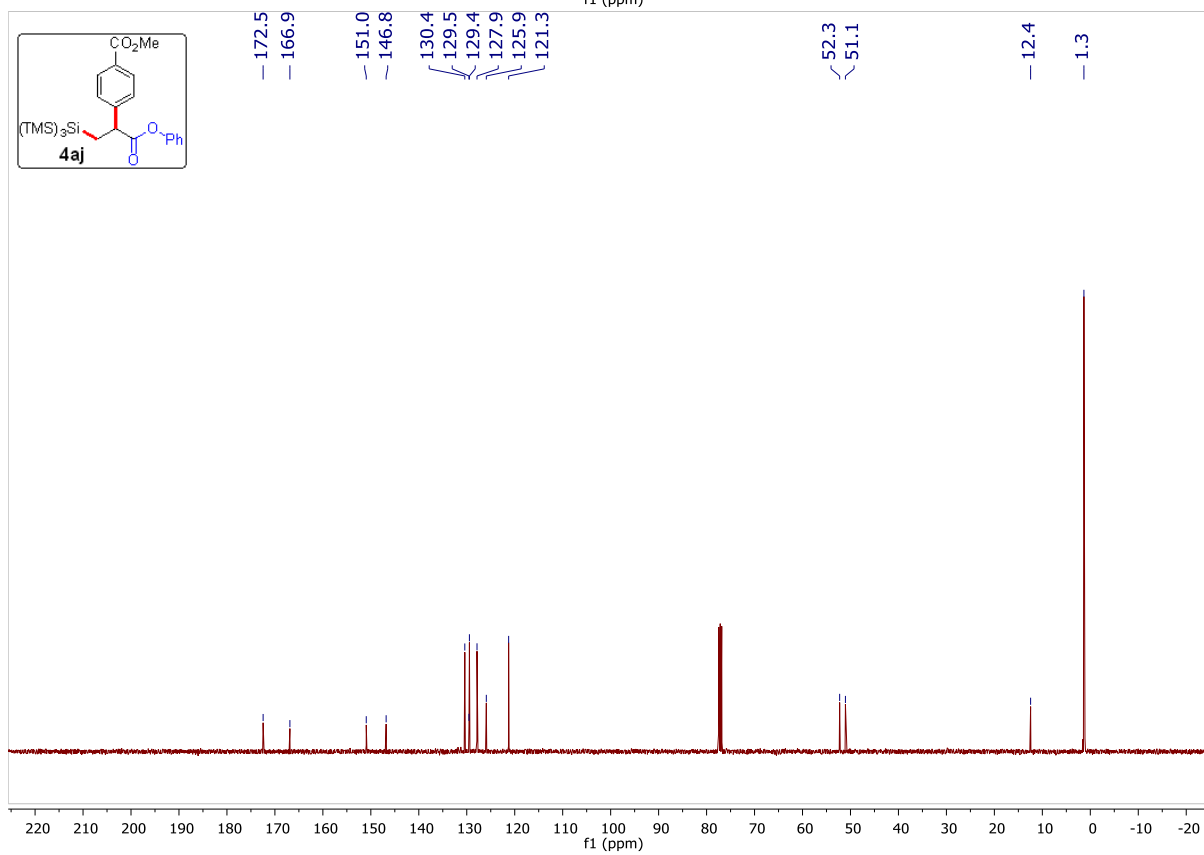
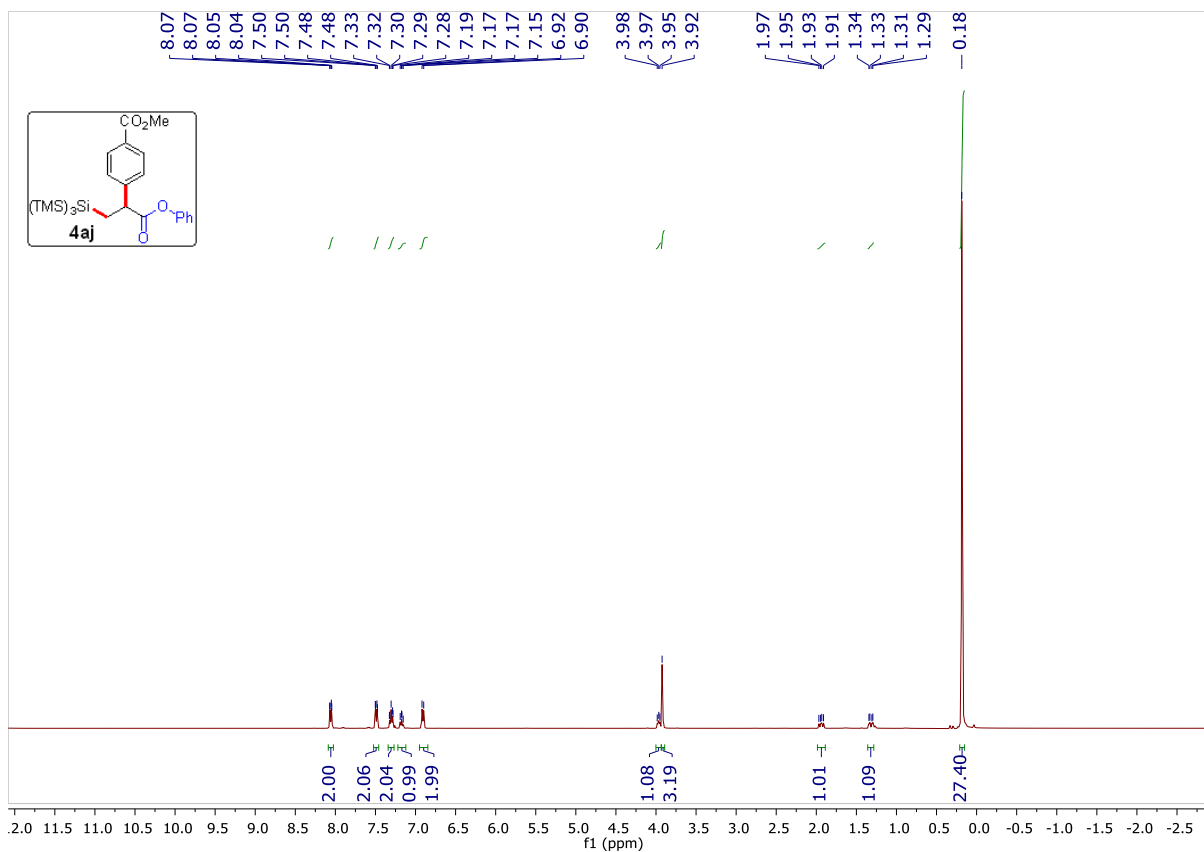


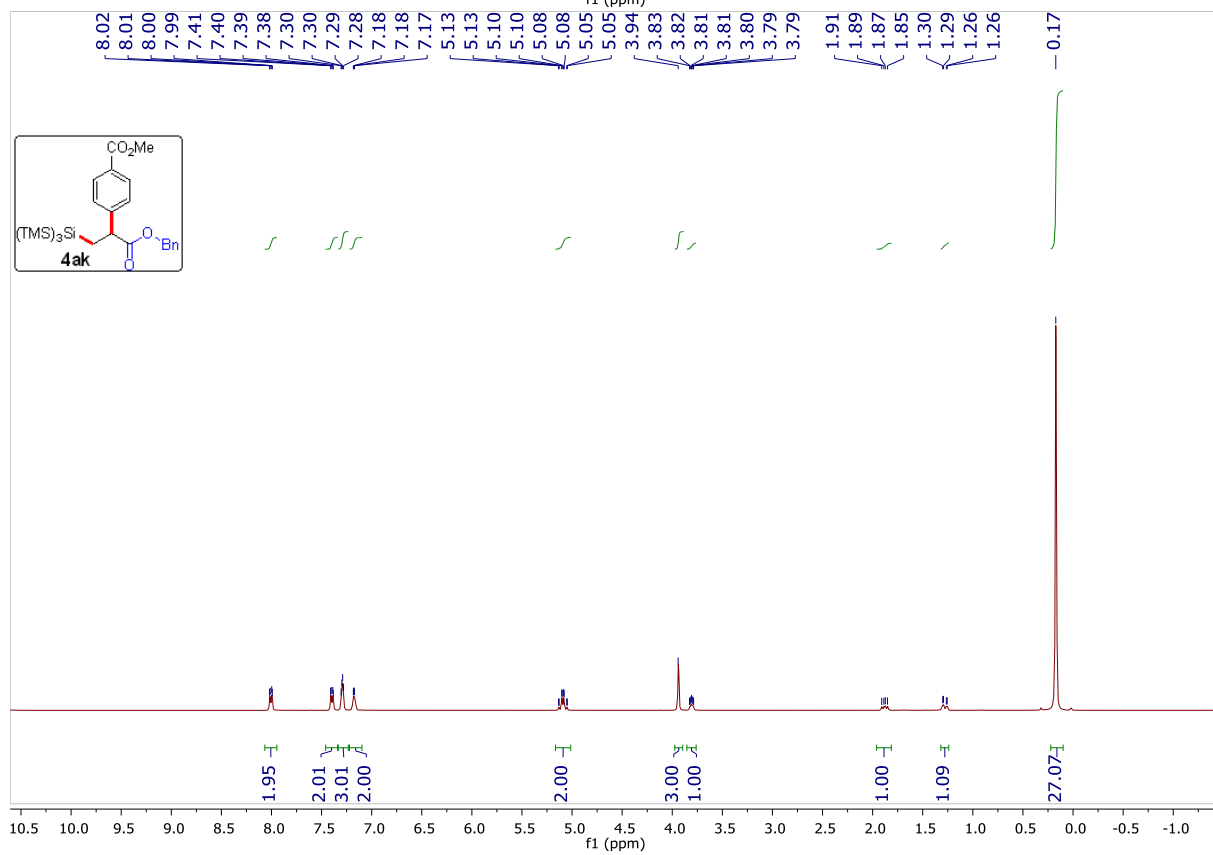
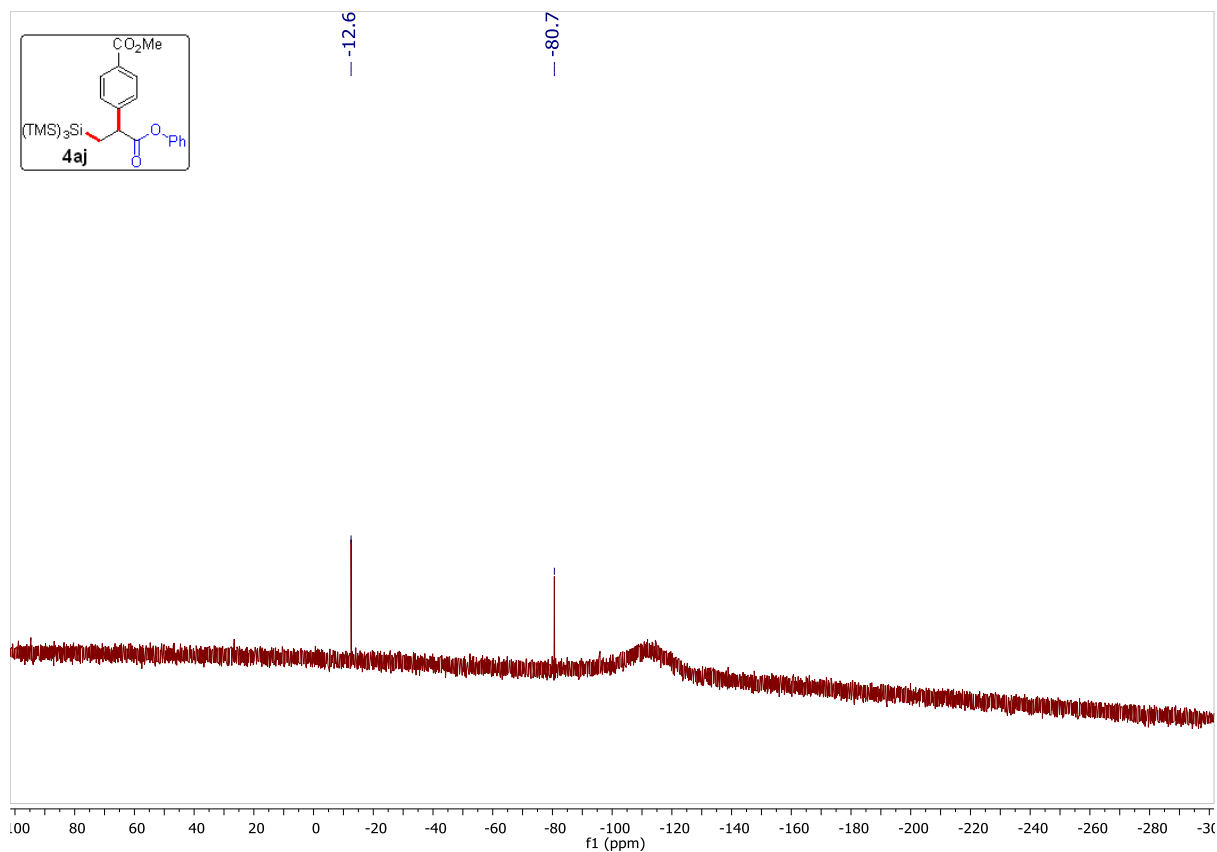
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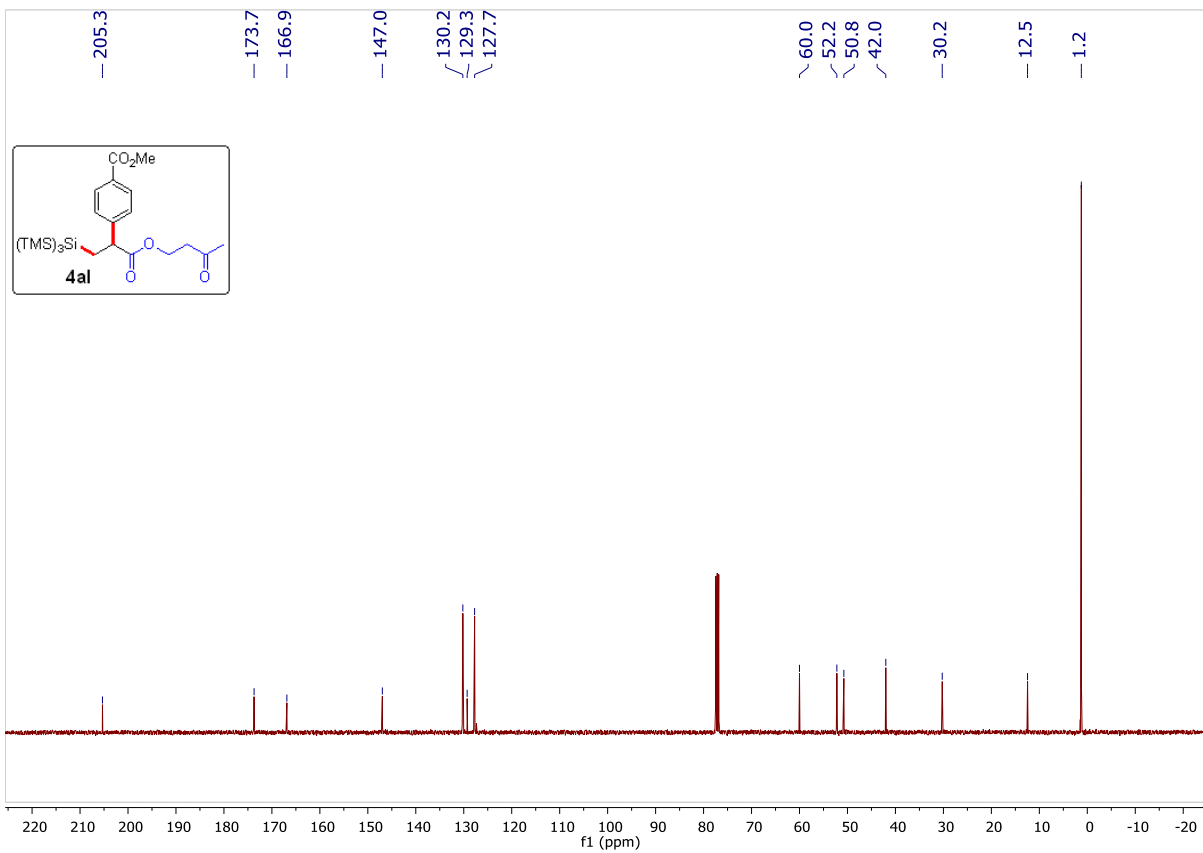
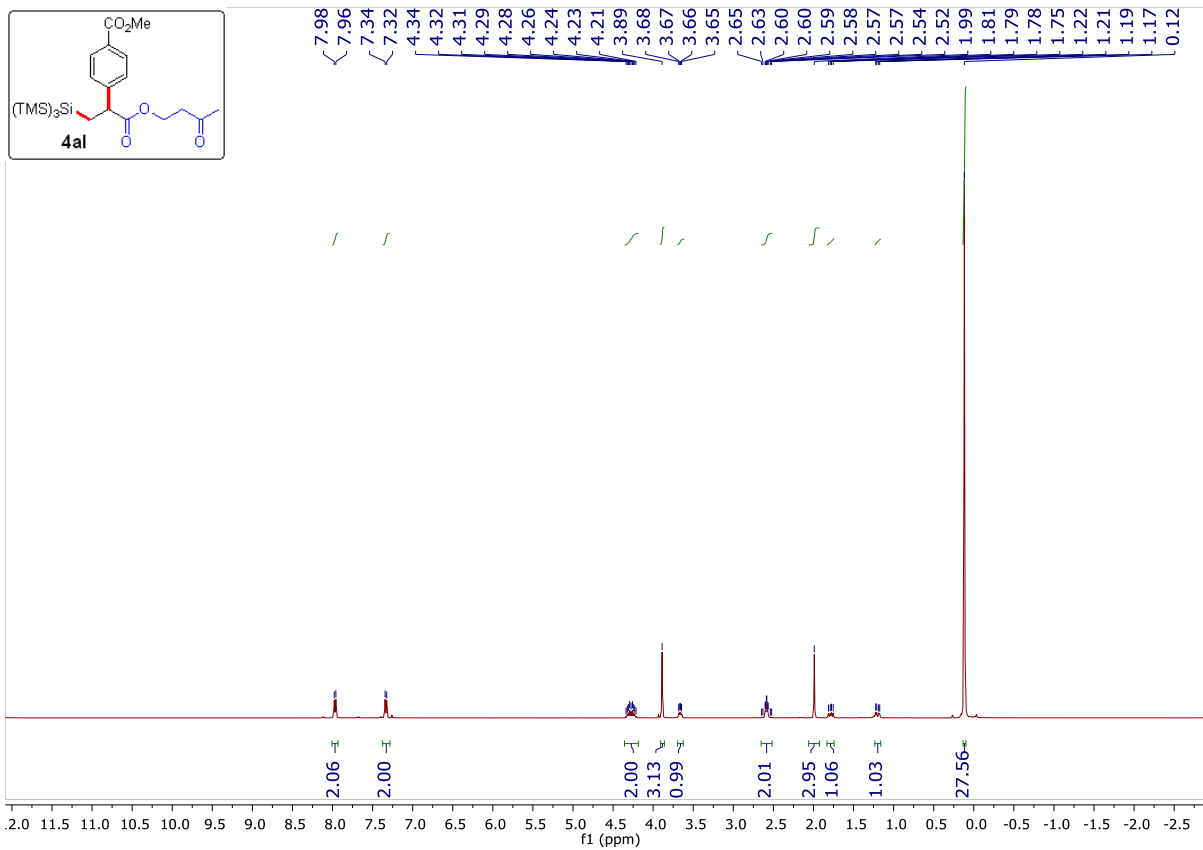


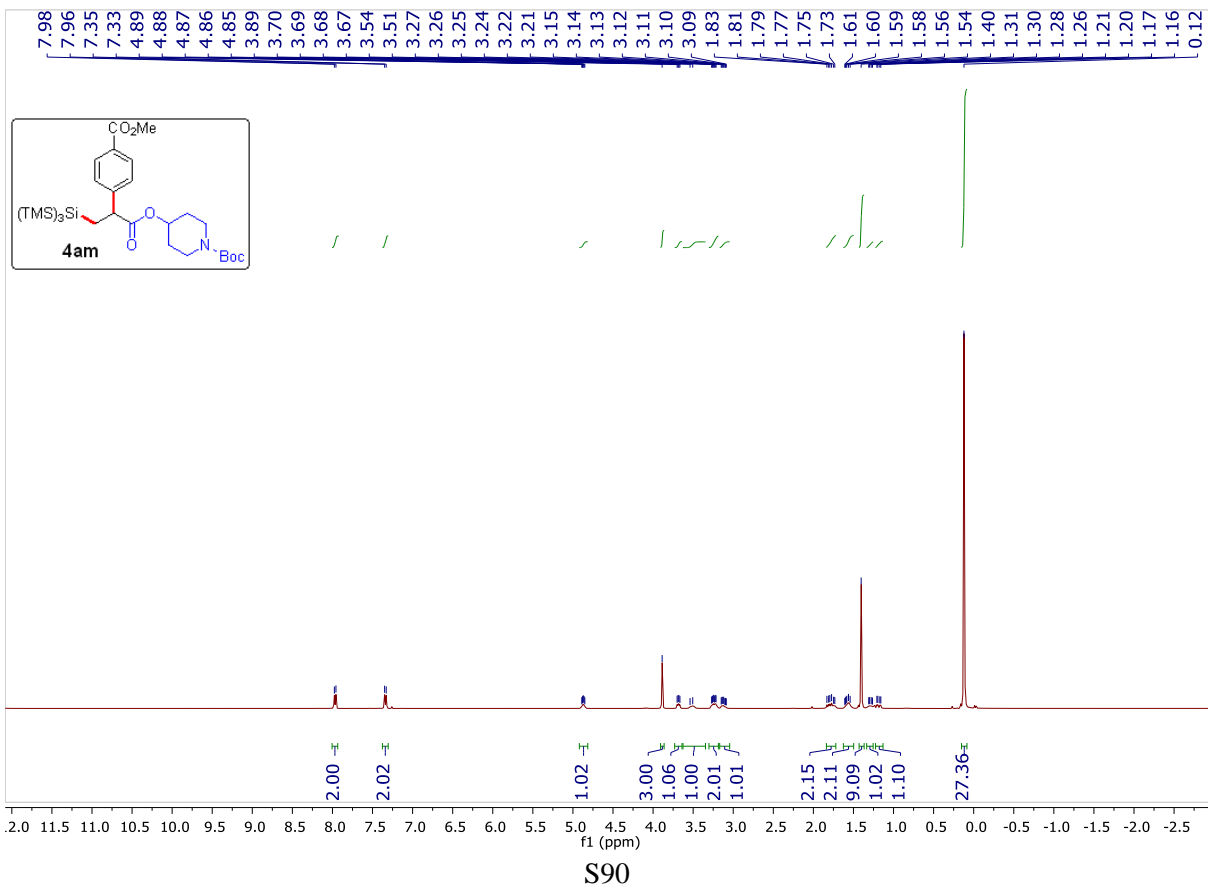
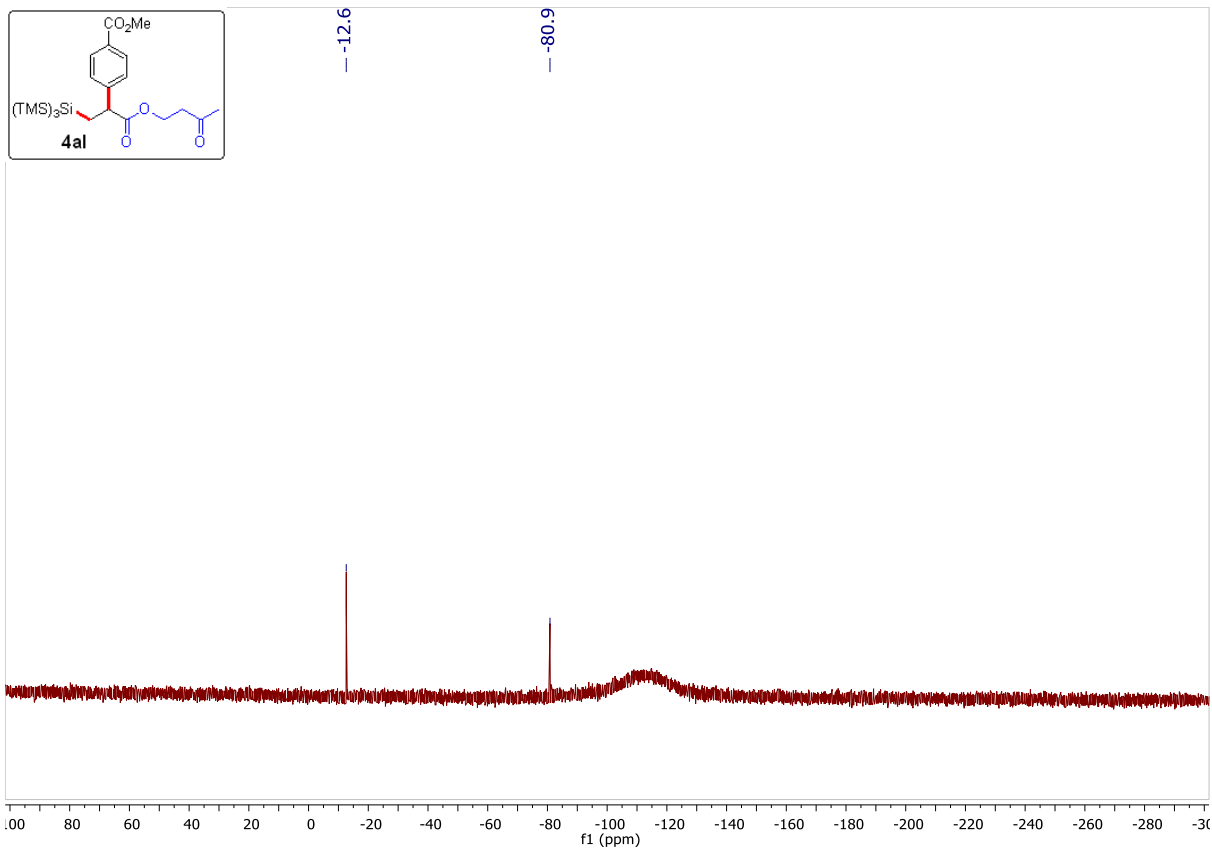


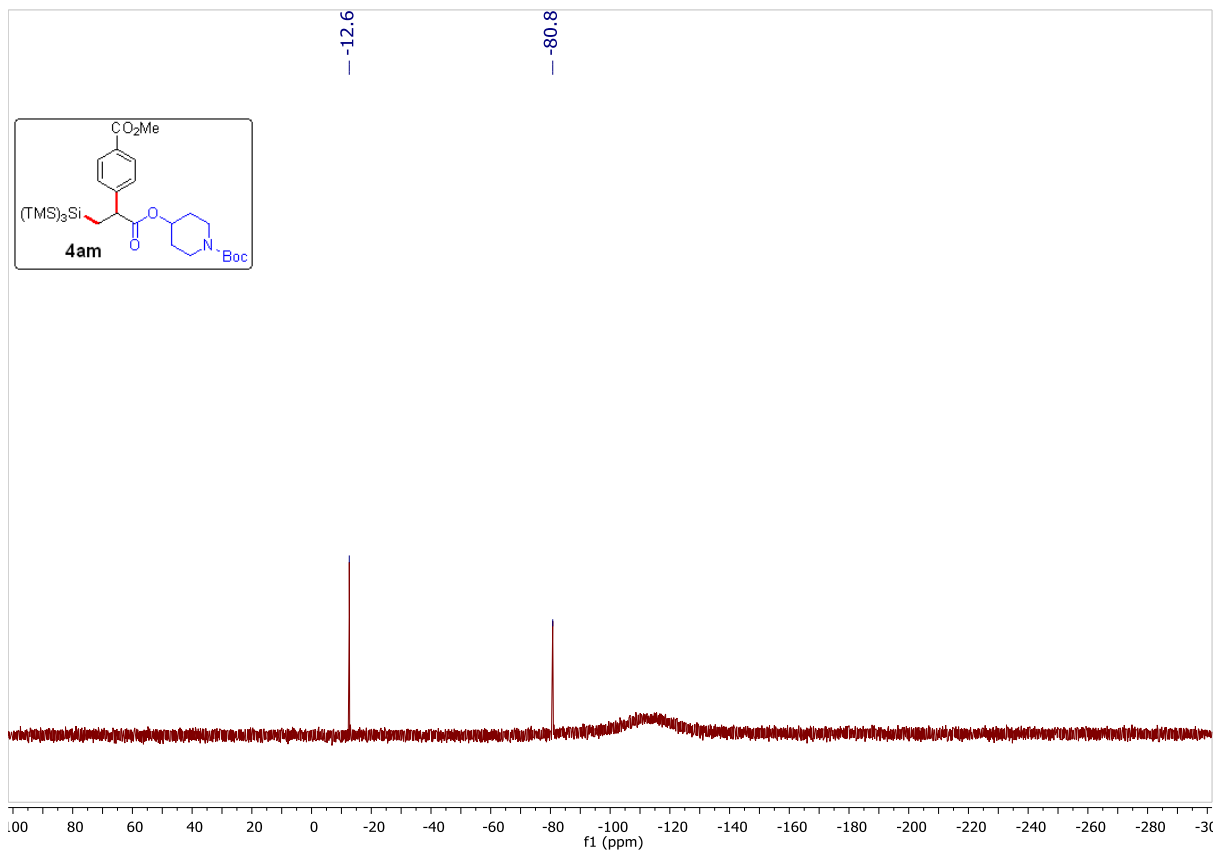
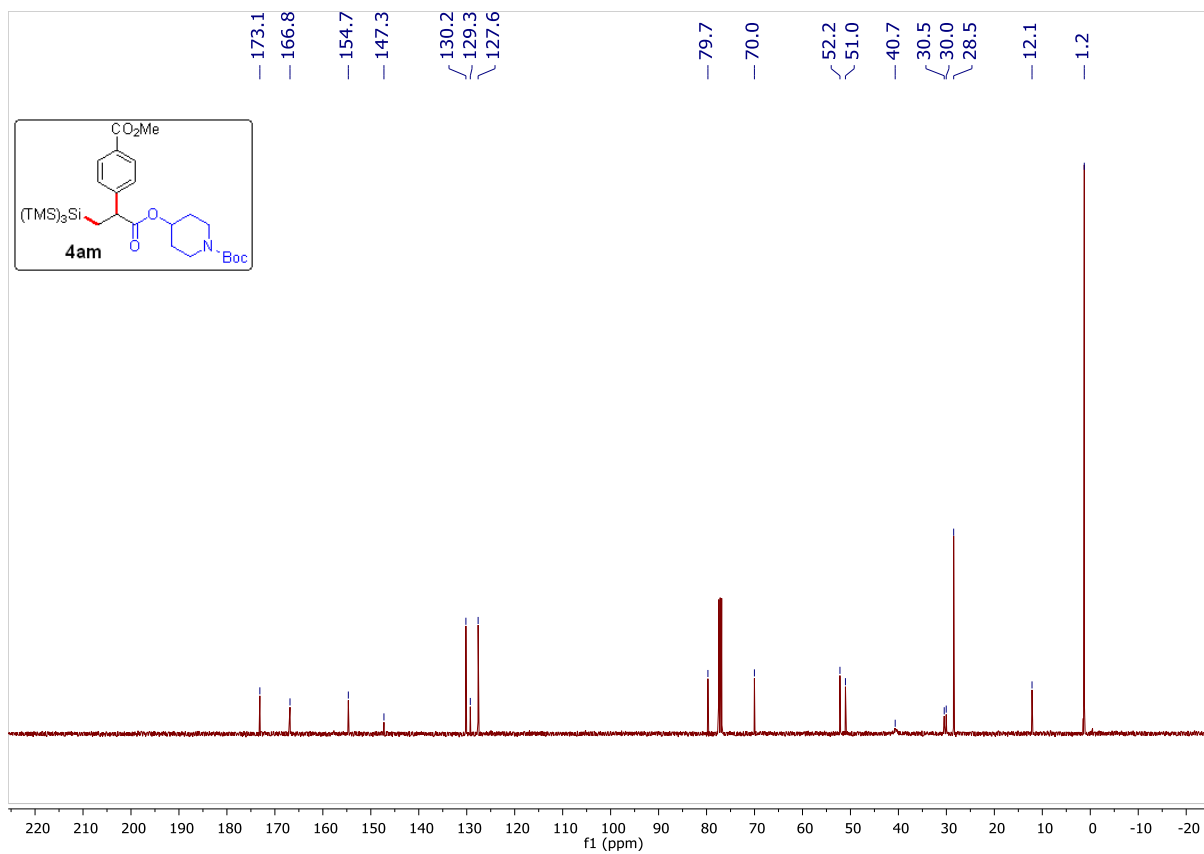
S85



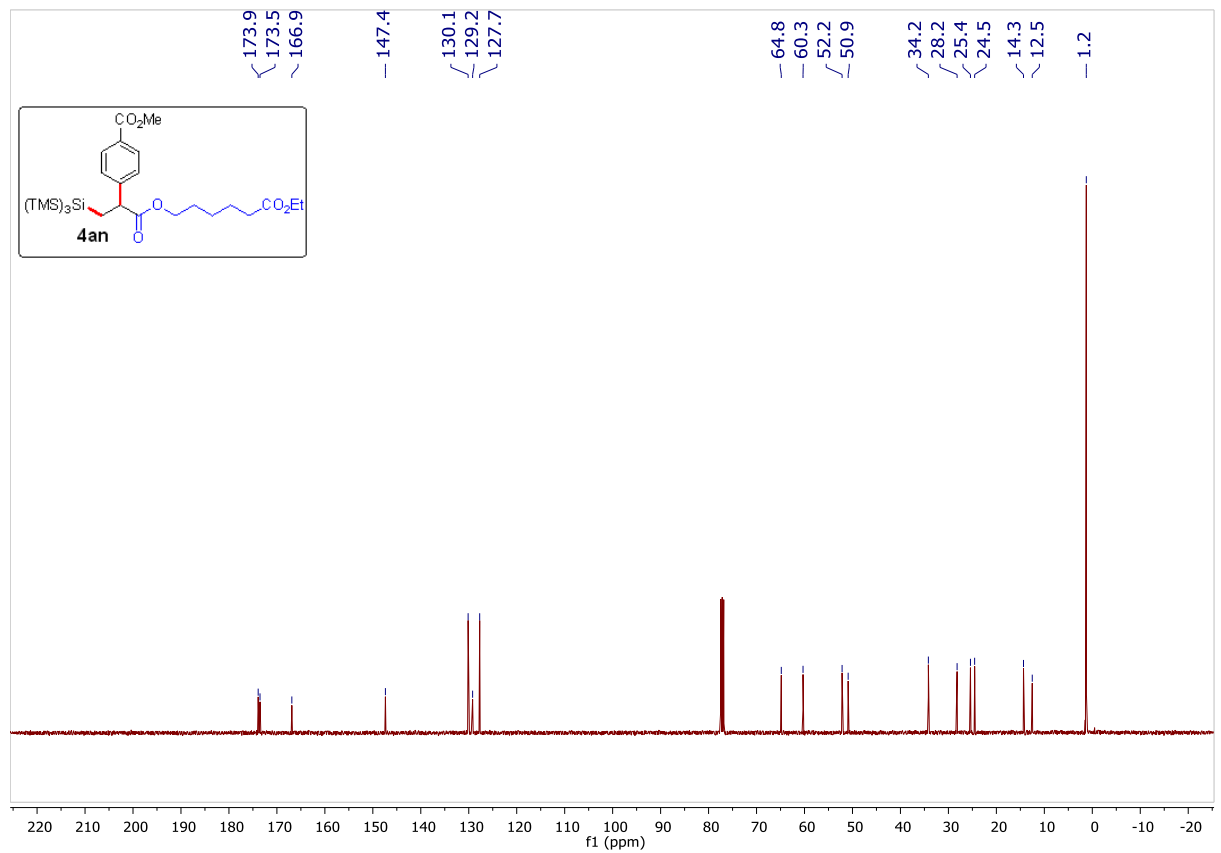
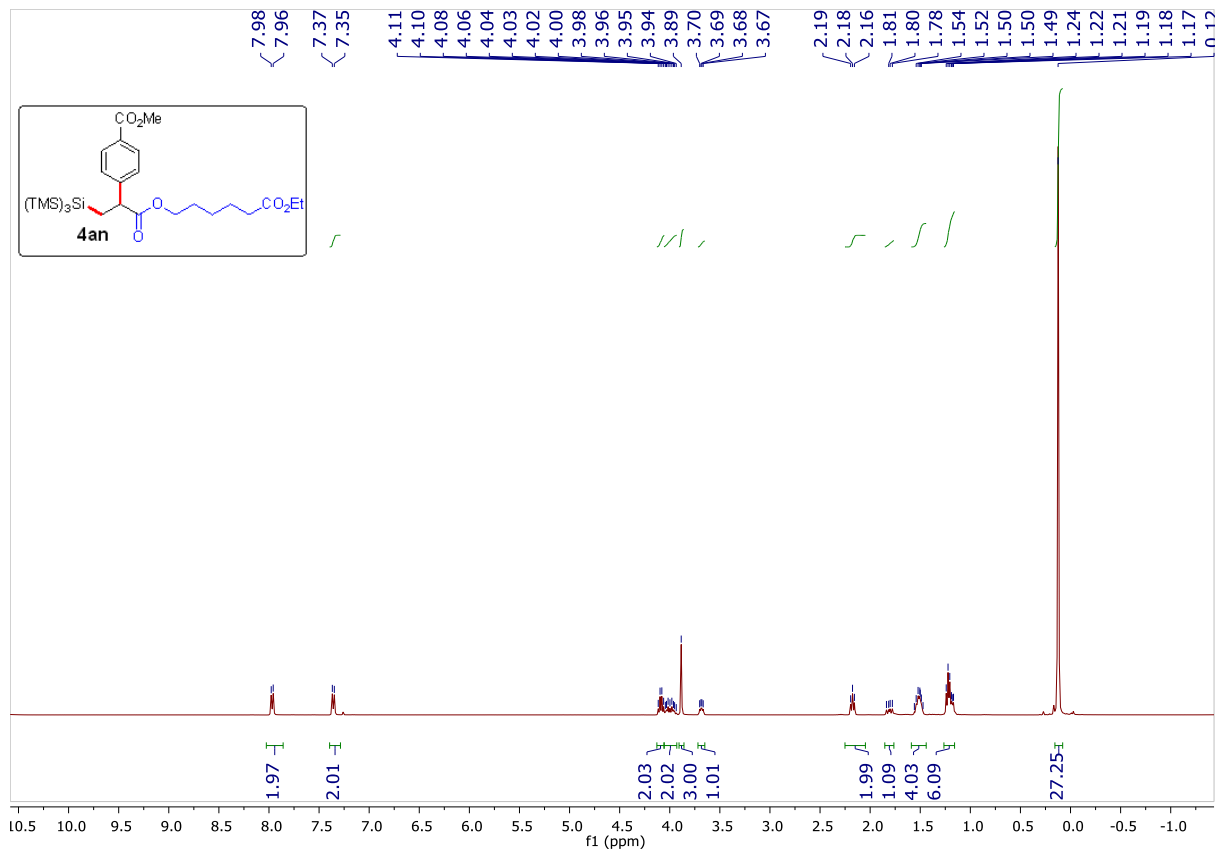


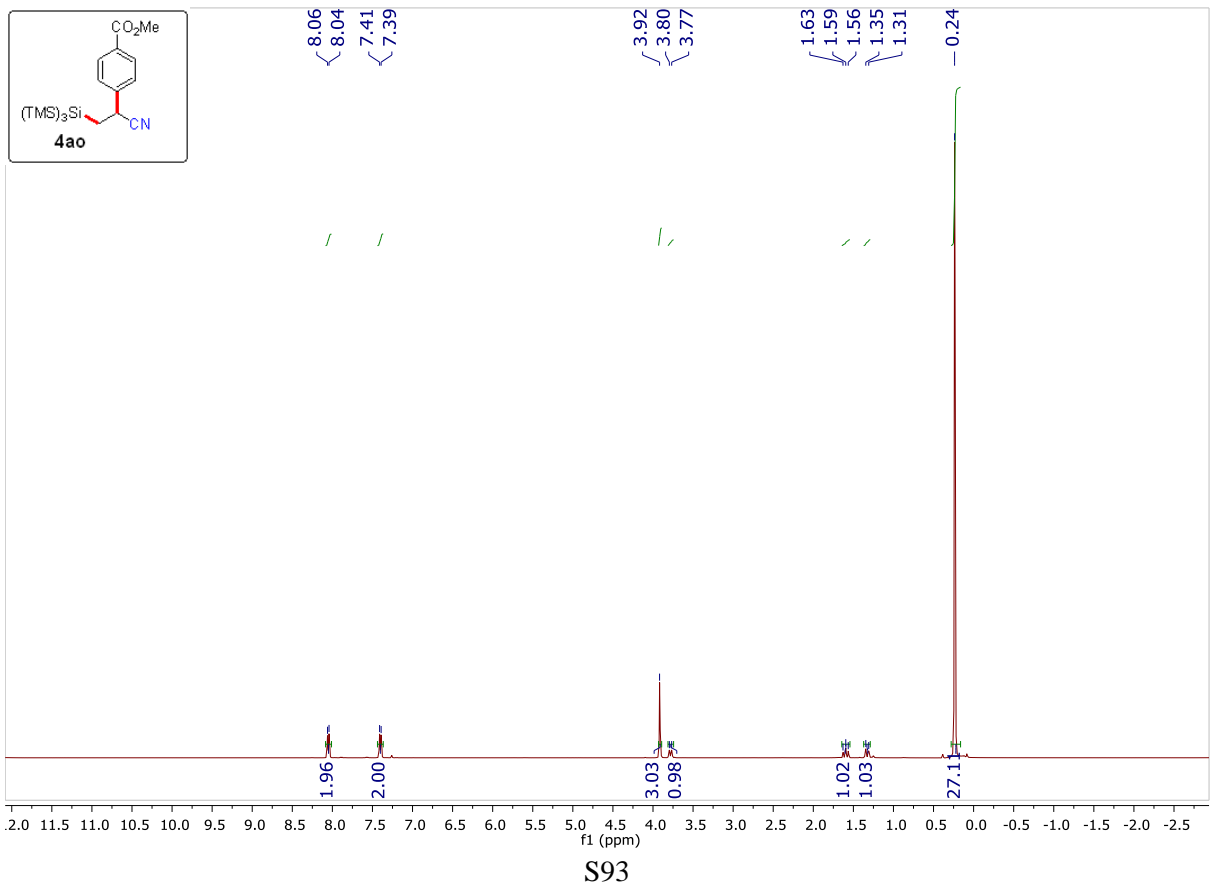
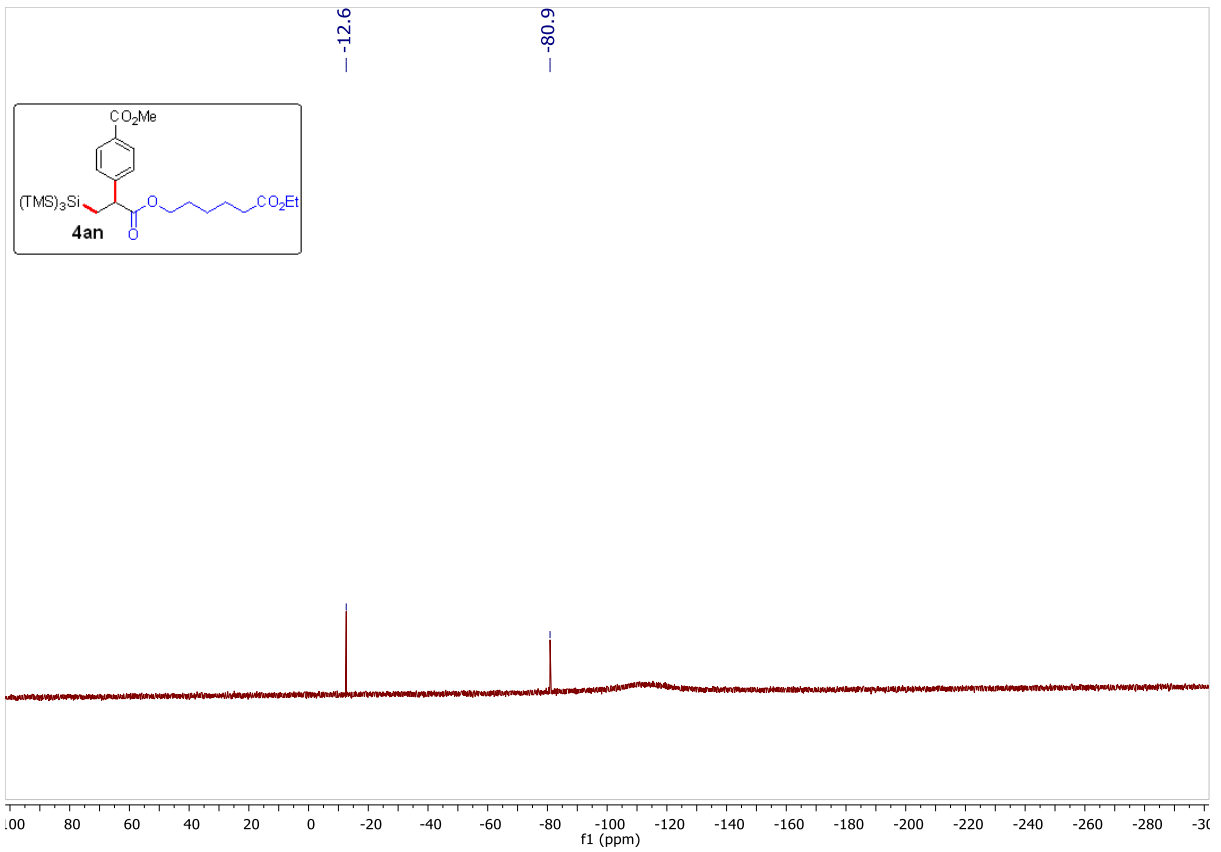


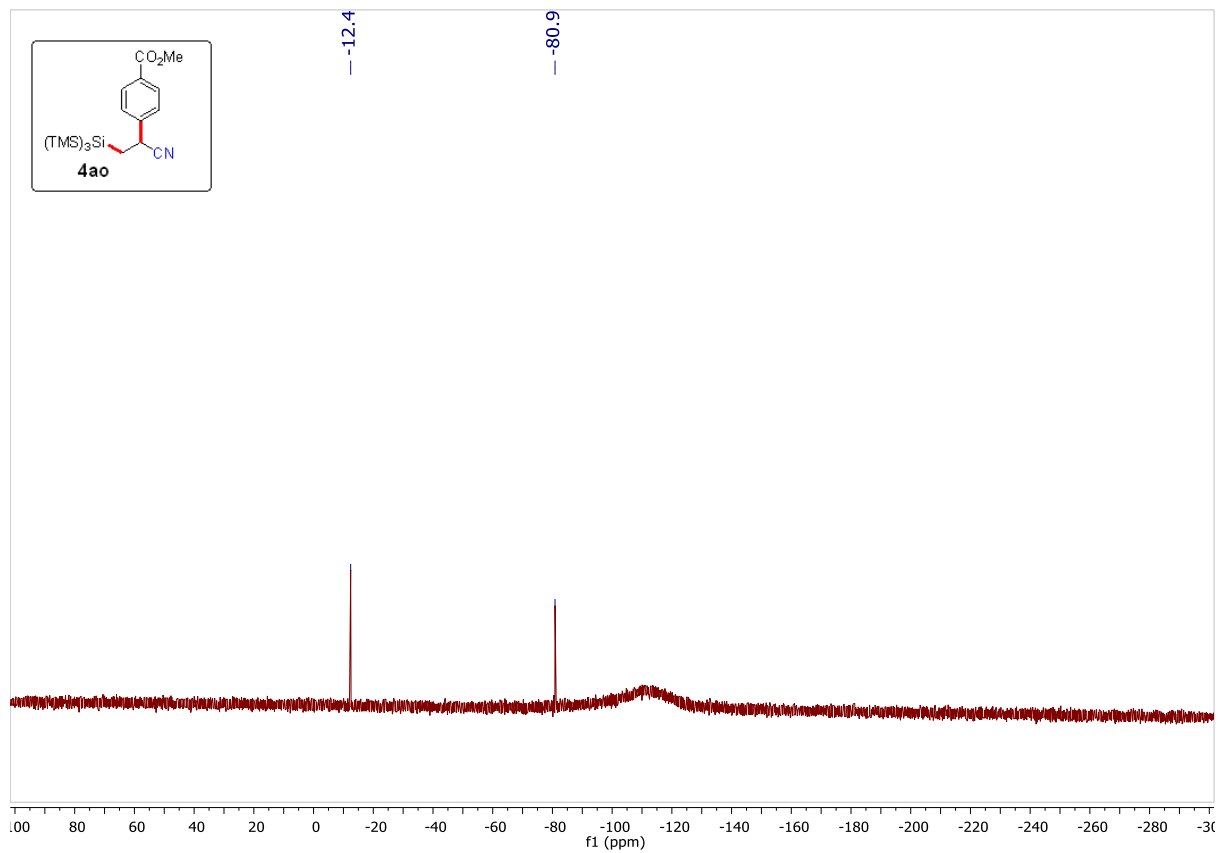
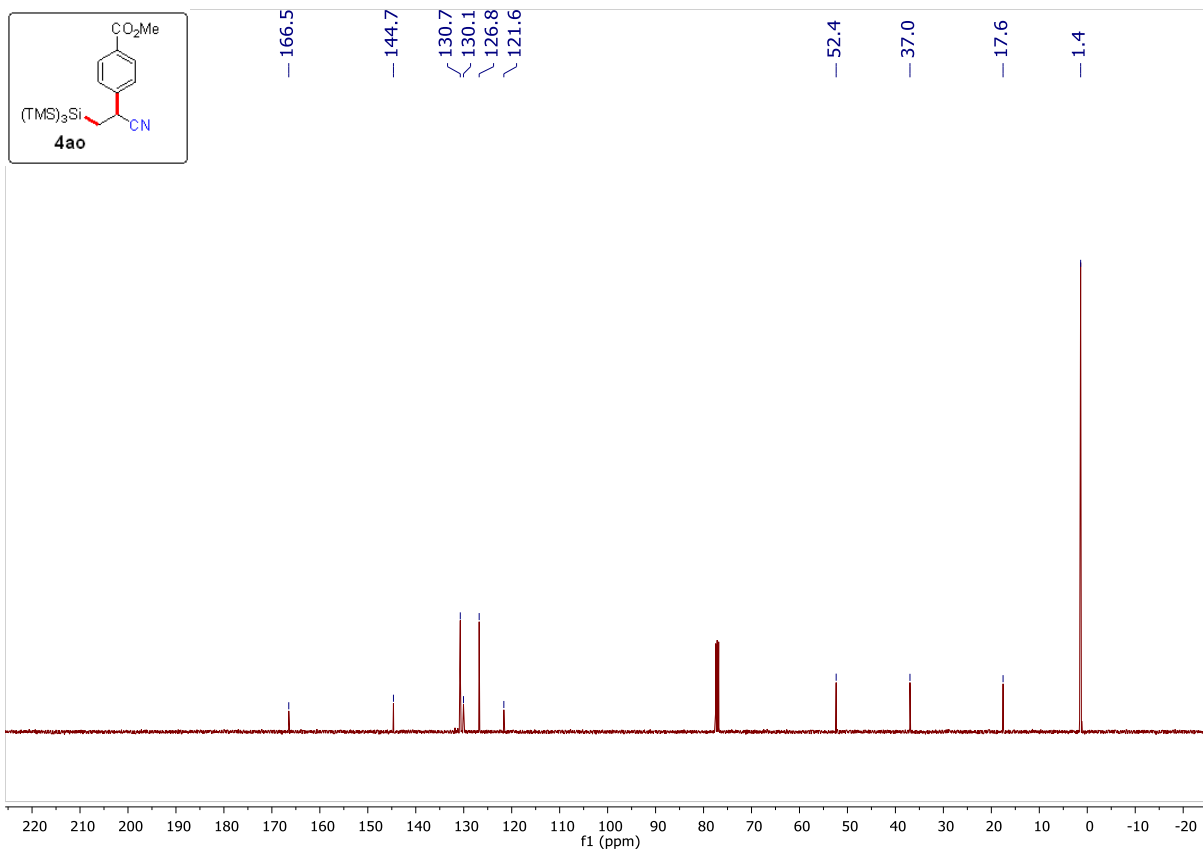




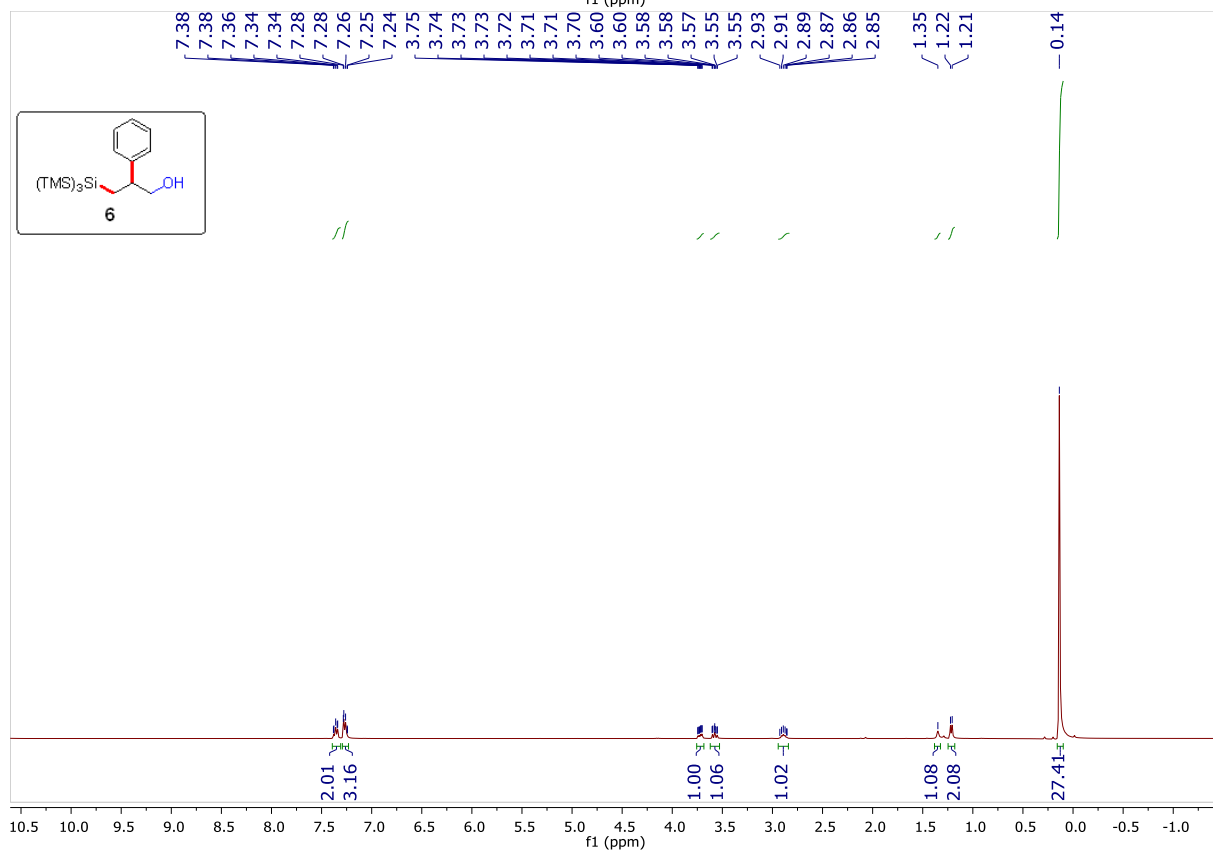
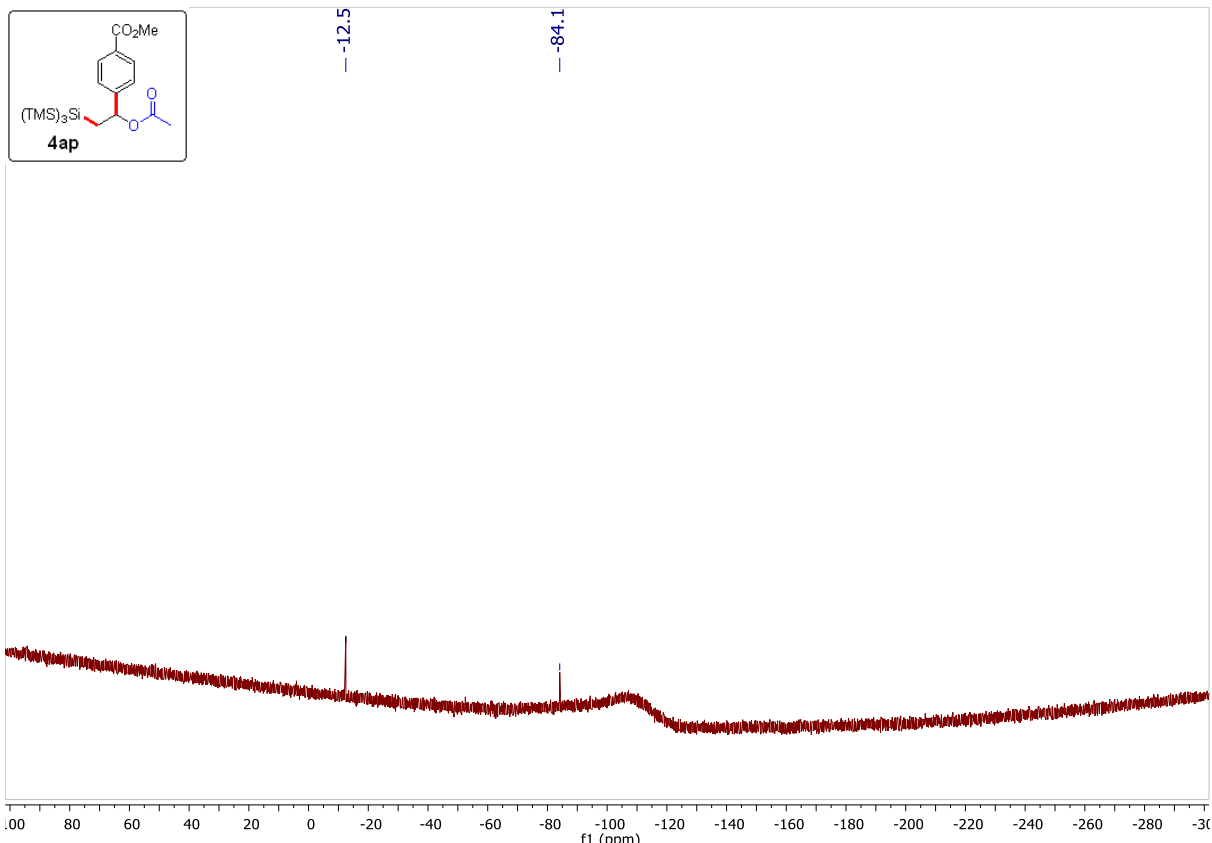
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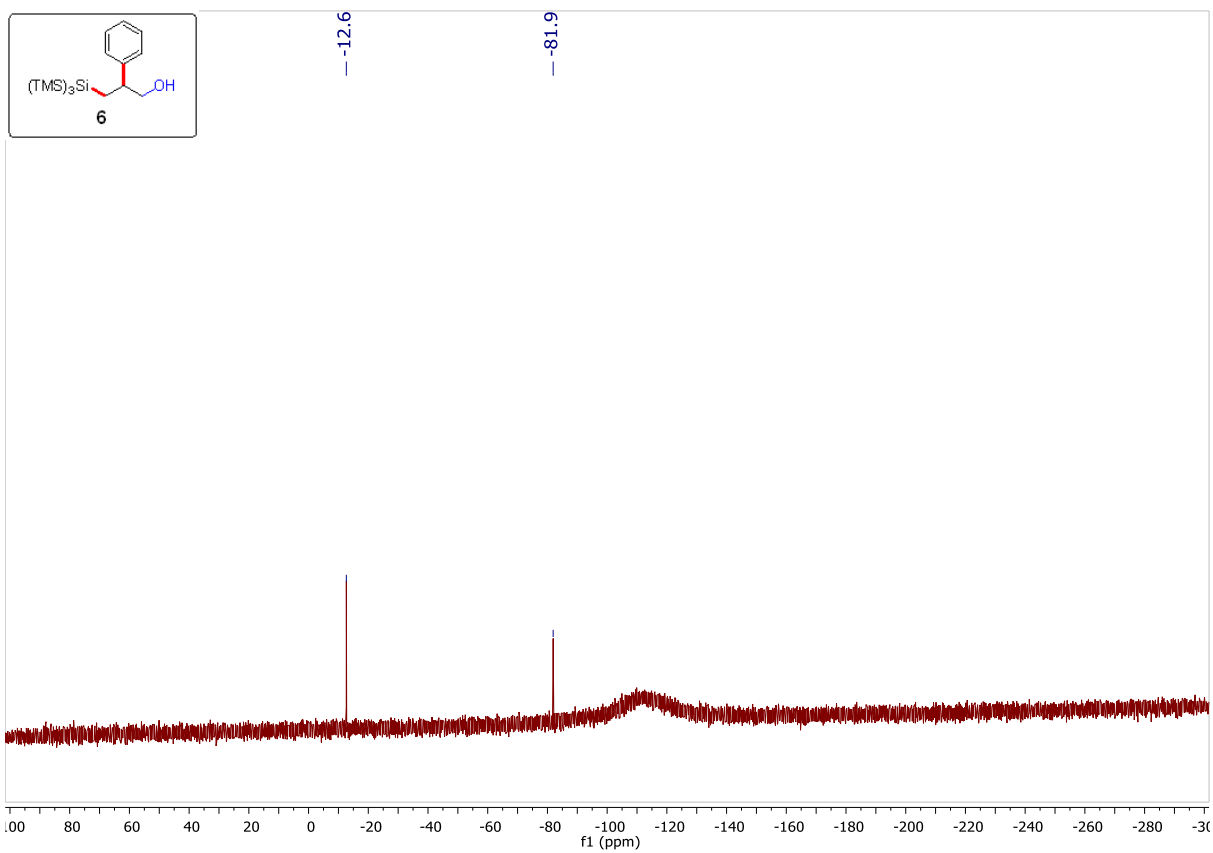
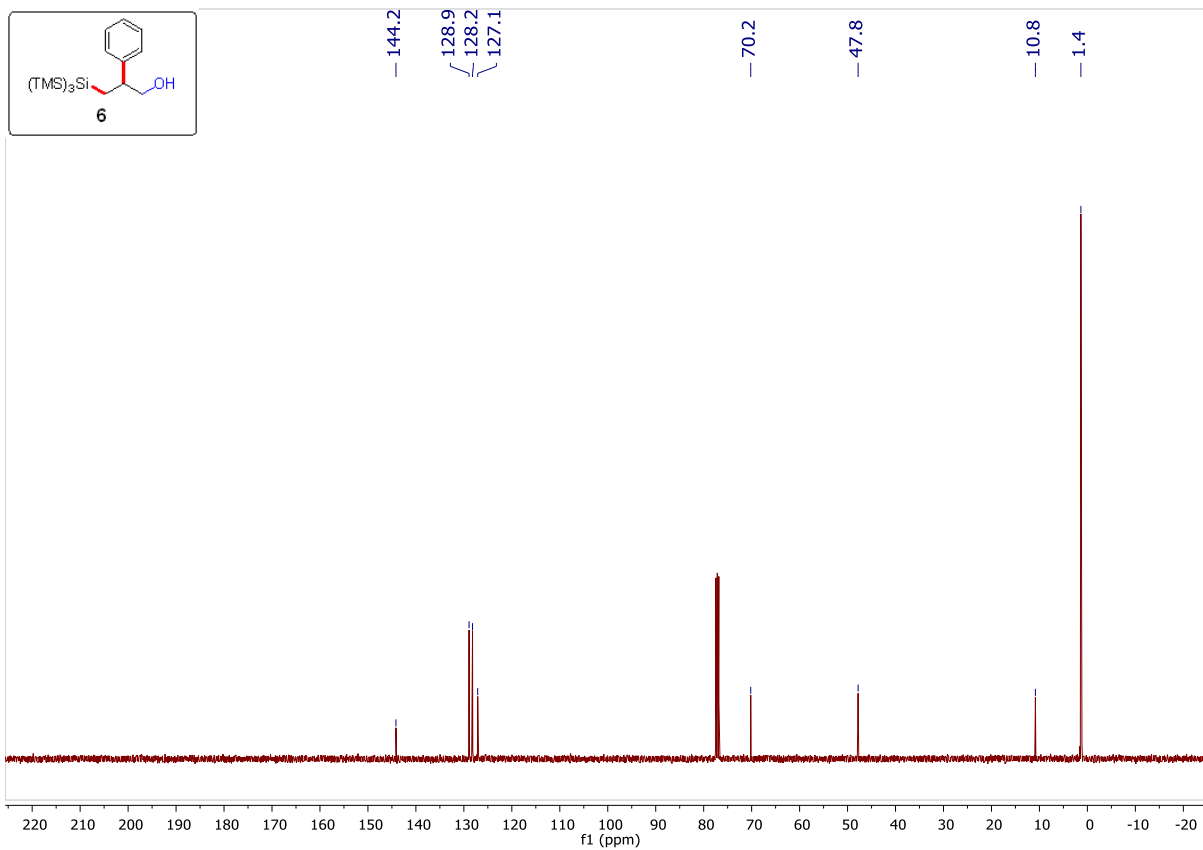




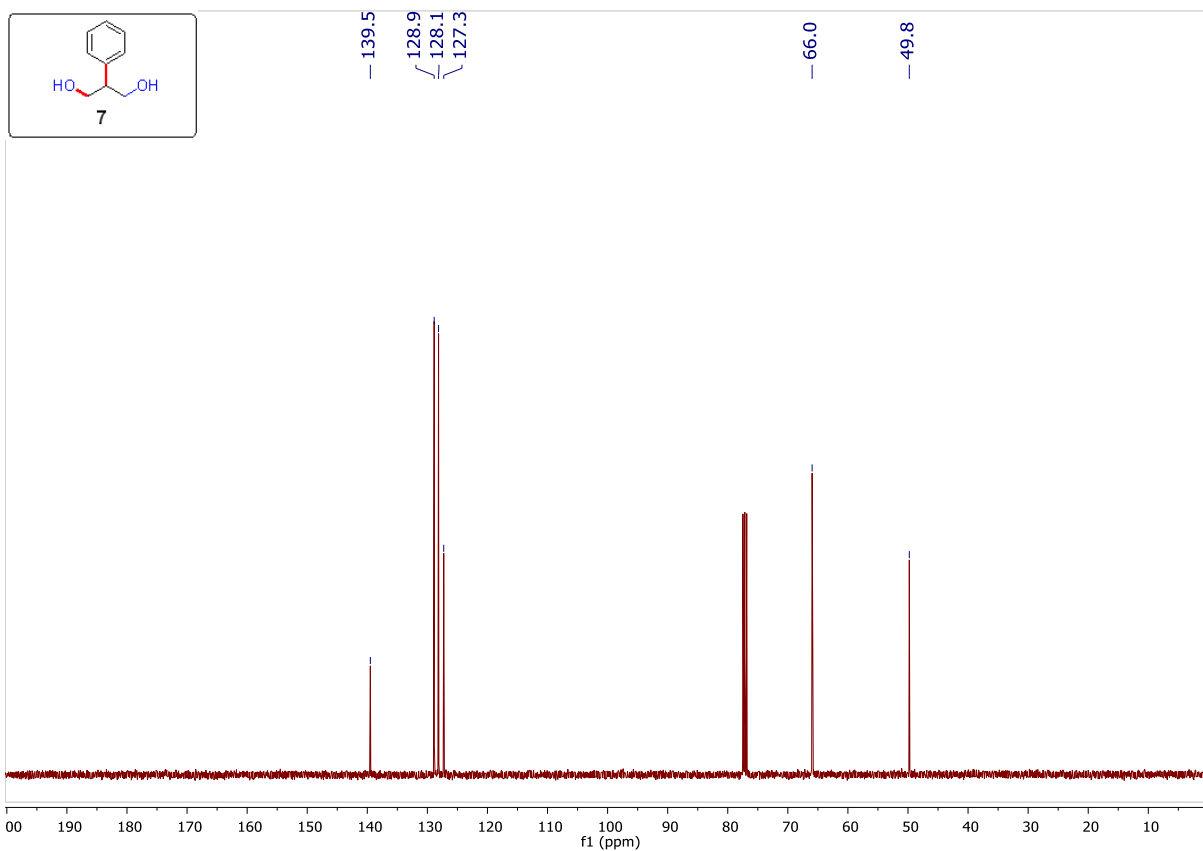
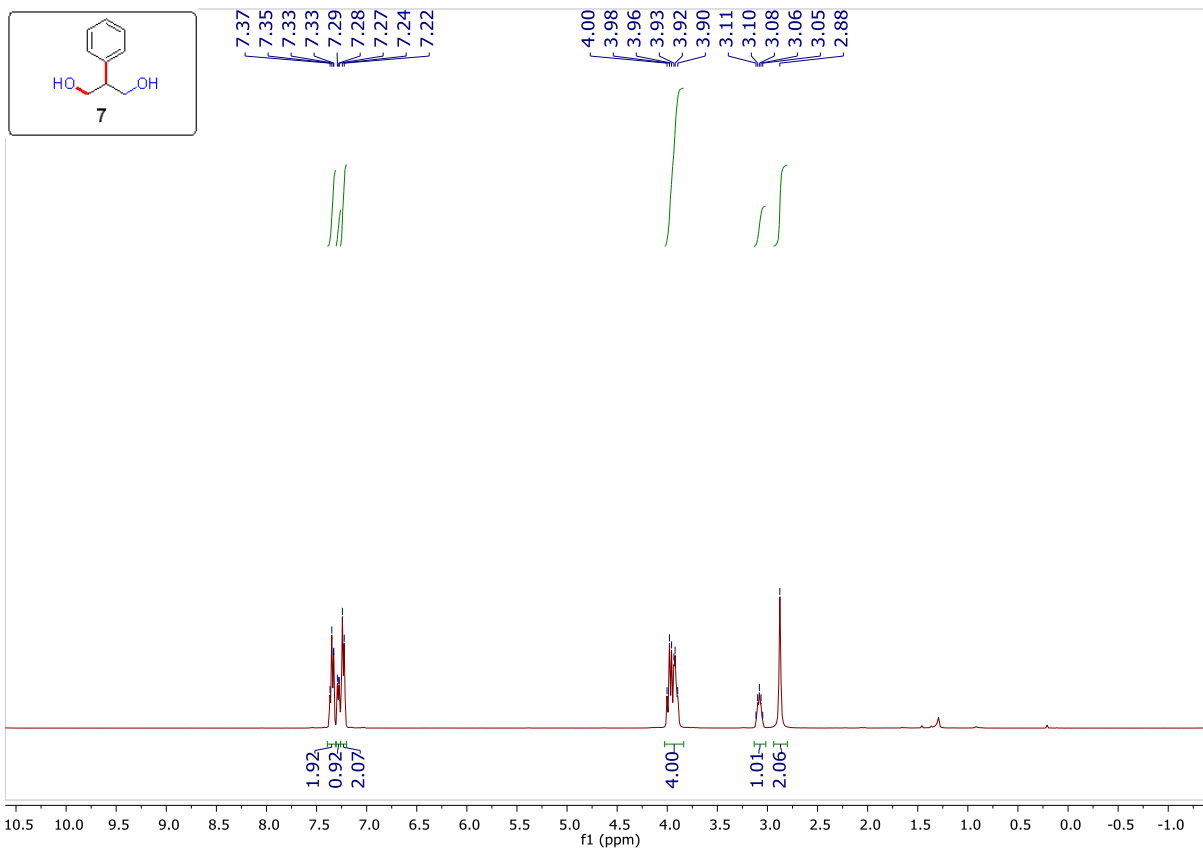


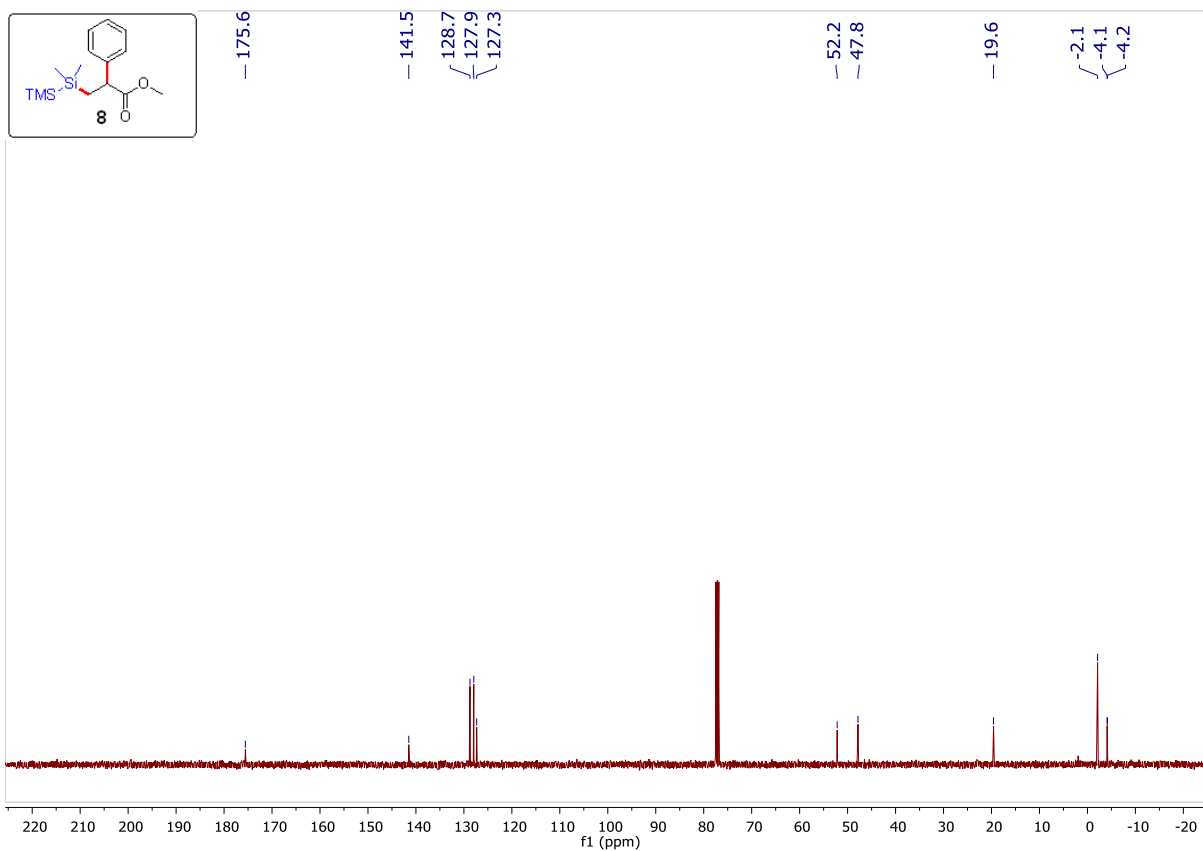
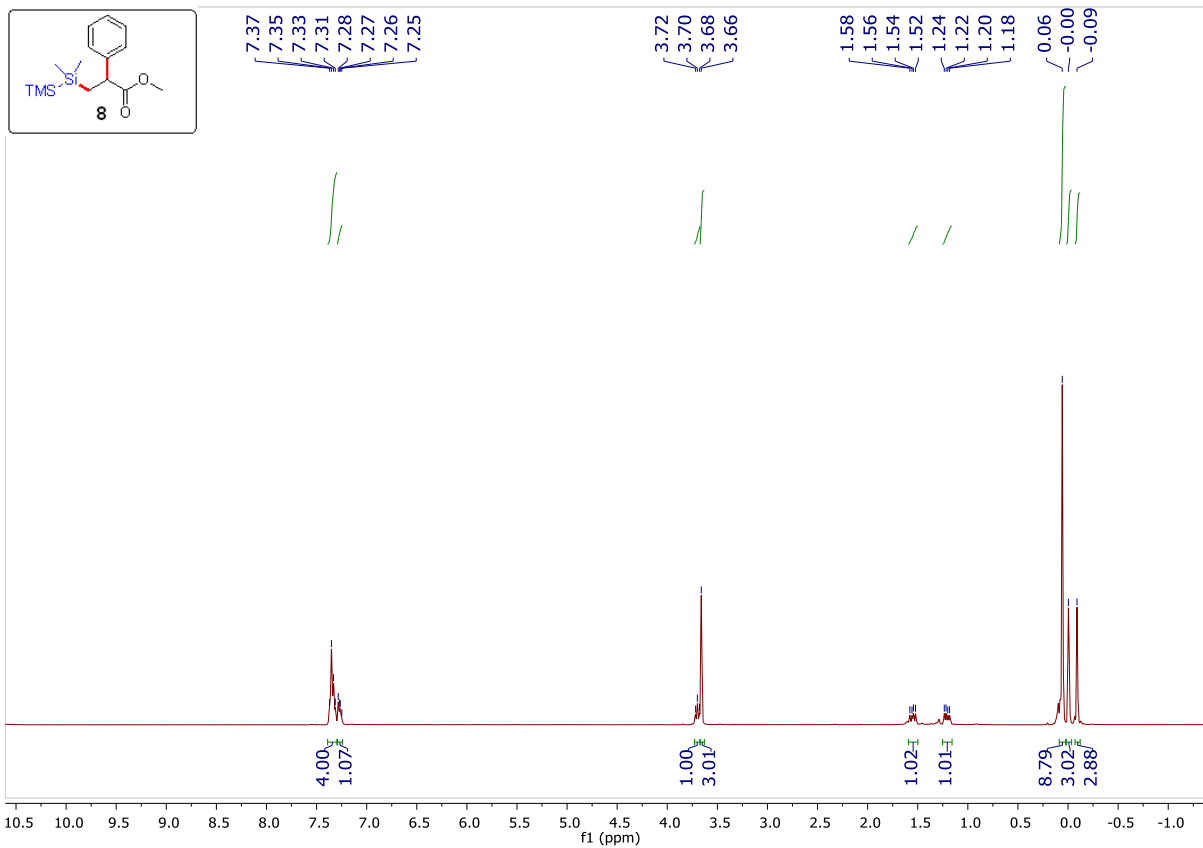
S94

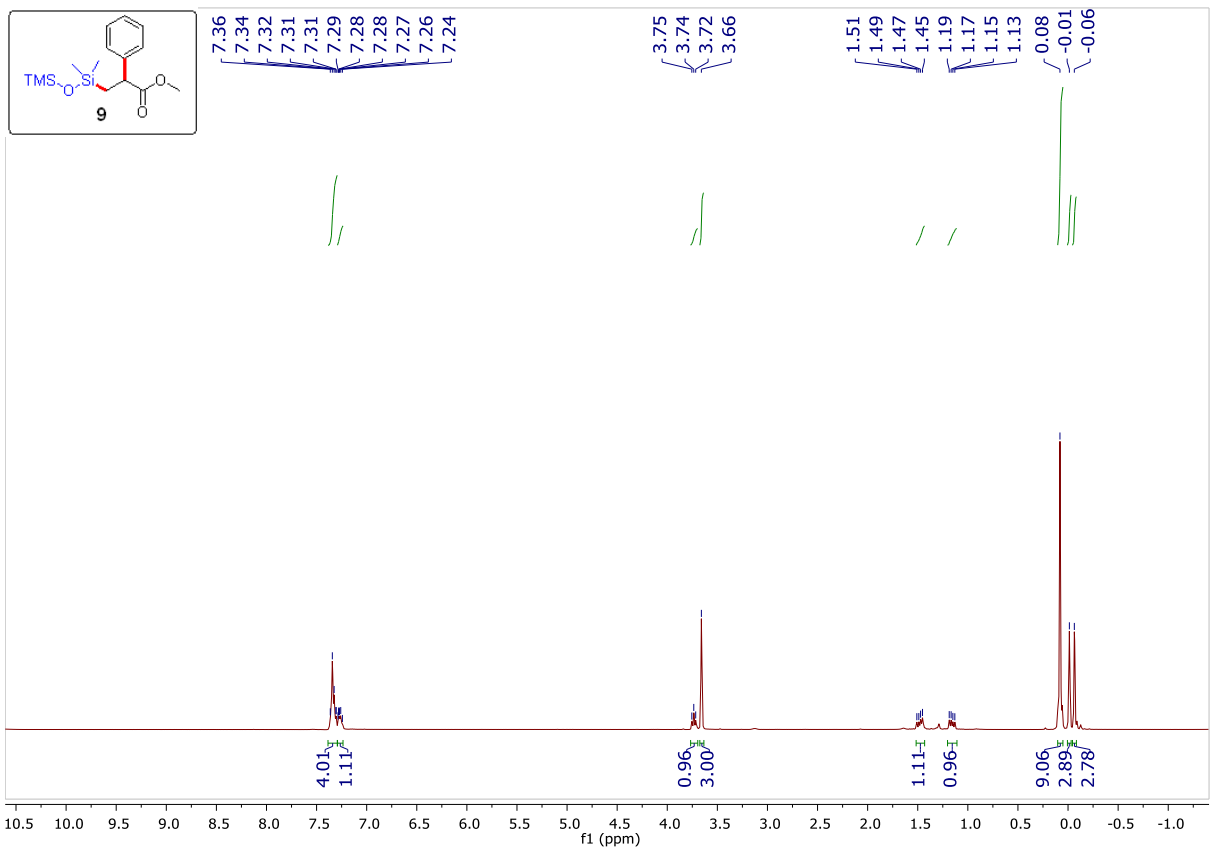
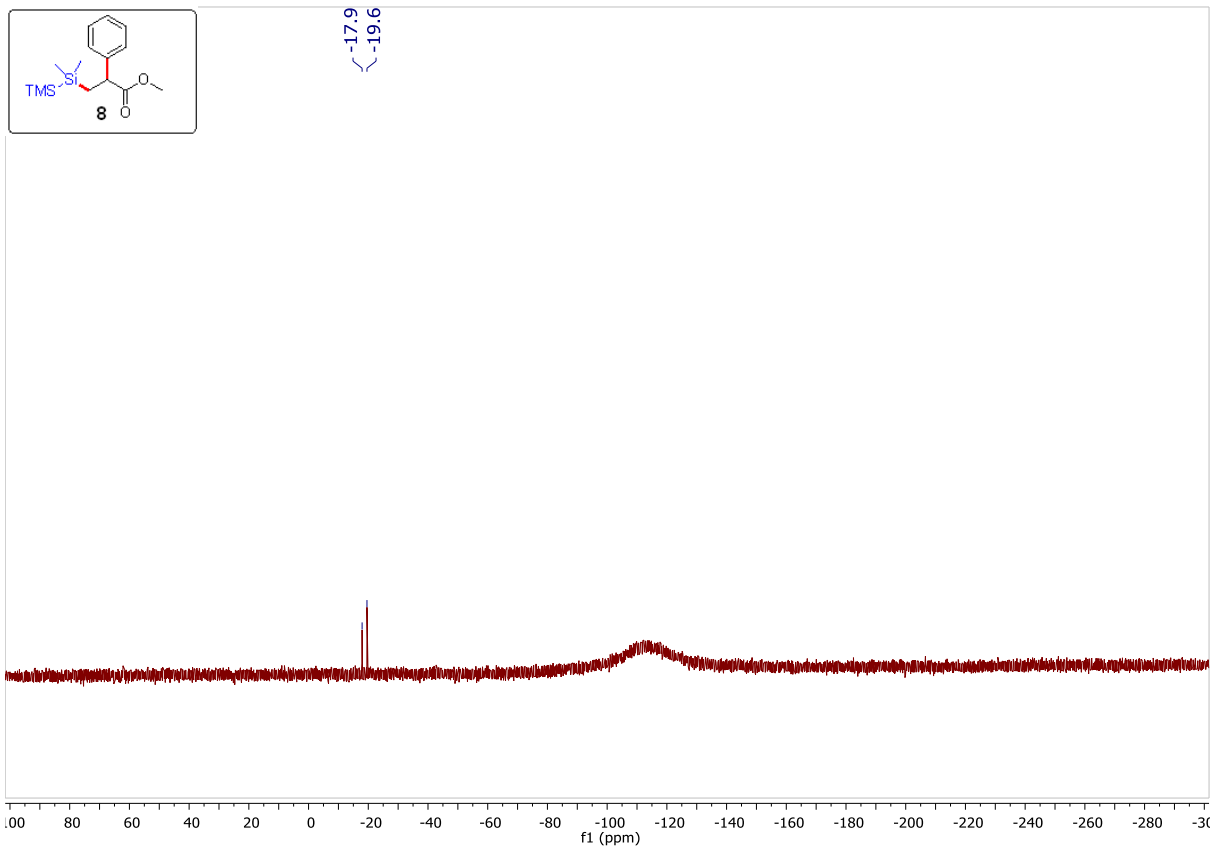




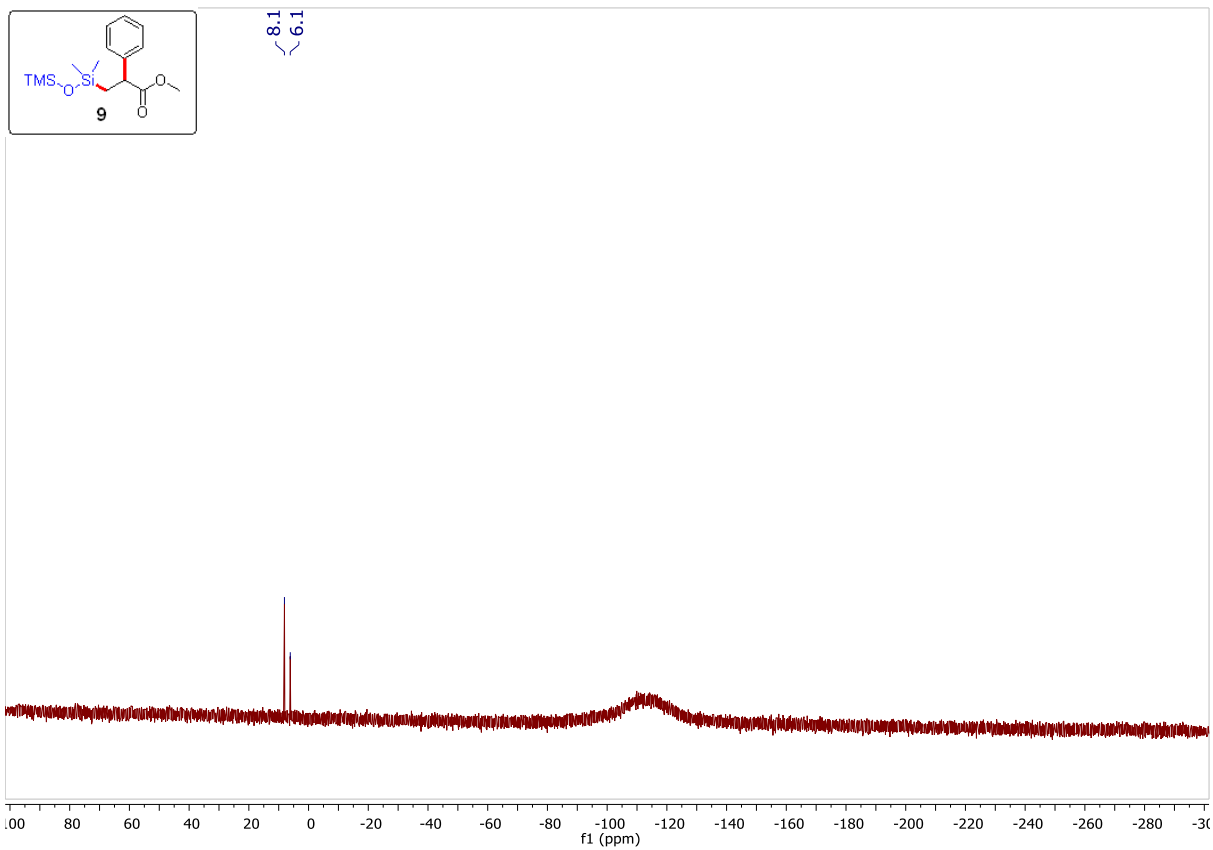
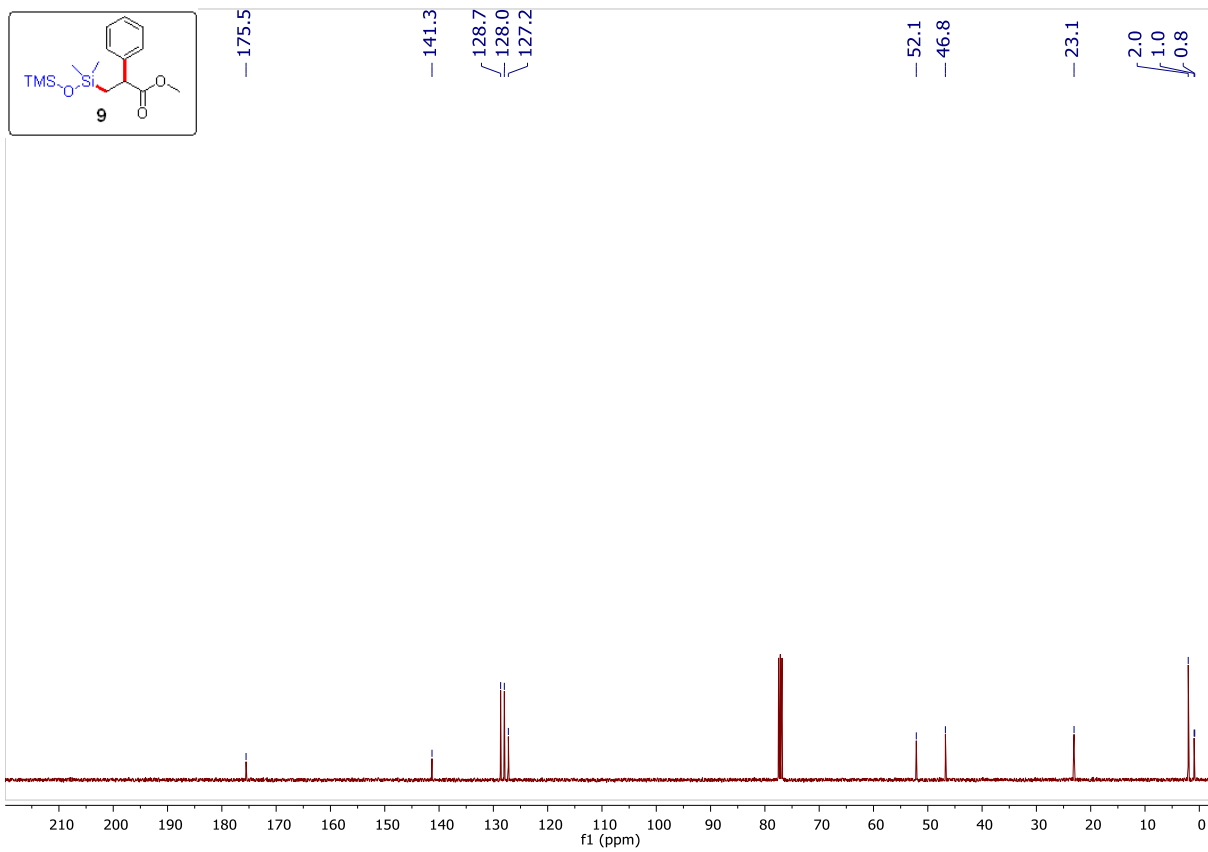
S97







S100



S101