Supporting Information

Visible light-mediated pyridylsilylation of olefins through hydrogen atom transfer

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Appendix I

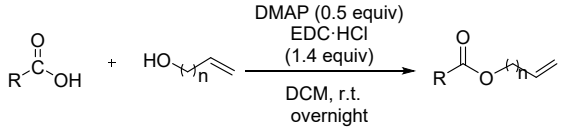
Copies of Relevant ^{1}H-, $^{13}C\{^{1}H\}$- and ^{19}F-NMR Spectra

I. General Methods and Materials.

Unless otherwise specified, proton (^{1}H) and proton-decoupled carbon [$^{13}C\{^{1}H\}$] NMR spectra were recorded at room temperature in base-filtered $CDCl_3$ on a spectrometer operating at 600 and 500 MHz or 300 MHz for proton and 151and 126 MHz or 75 MHz for carbon nuclei. For ^{1}H NMR spectra, signals arising from the residual protio-forms of the solvent were used as the internal standards. ^{1}H NMR data are recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet or combinations of the above. The signal due to residual $CHCl_3$ appearing at δ_H 7.26 and the central resonance of the $CDCl_3$ "triplet" appearing at δ_C 77.0 were used to reference ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, respectively. Infrared spectra were recorded, as thin films or solids, on a Nicolet iS50 FT-IR spectrometer fitted with a Smart iTX sampling module and only major absorptions are reported (in cm^{-1}). High-resolution ESI mass spectra were recorded on a time-of-flight instrument. Melting points were measured on an automated melting point system and are uncorrected. Analytical thin layer chromatography (TLC) was performed with silica gel GF_{254} plates. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included phosphomolybdic acid: ceric sulfate: sulfuric acid (conc.): water (37.5 g: 7.5 g: 37.5 g: 720 mL) or potassium permanganate: potassium carbonate: 5% sodium hydroxide aqueous solution: water (3 g: 20 g: 5 mL: 300 mL). For column chromatography, 200-300 mesh silica gel was employed. Reagents and inorganic salts as well as dried solvents were generally available from commercial sources and used as supplied. Unless indicated otherwise, reactions were performed under a nitrogen atmosphere.

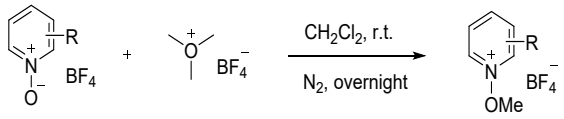
II. Procedures for the Synthesis of Substrates 1a-1al and 2a-2s

General procedure for the synthesis of olefins



Synthesized according to a reported procedure[1]. To a 100 mL round-bottom flask charged with 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoic acid (1.0 equiv) in CH_2Cl_2 (50 ml) were added enol (1.4 equiv. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.4 equiv), and 4-dimethylaminopyridine (0.2 equiv) at 0 °C. After stirring for 24 hours at room temperature, the reaction mixture was diluted with water (100 ml) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were washed with water (1 ✂ 50 mL) and brine (1 ✂ 50 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (petroleum ether/ethyl acetate elution) to afford the relevant olefins.

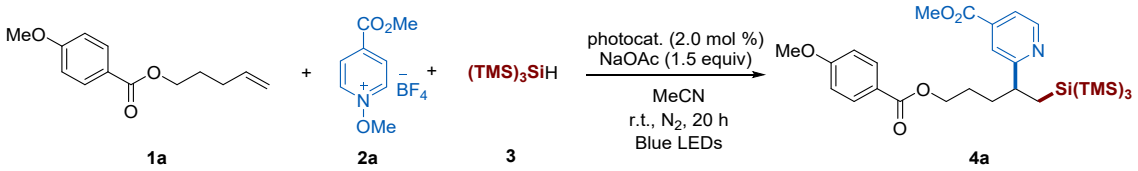
General procedure for the synthesis of *N*-heteroarenium salts



Following a protocol previously reported by our group[2], a solution of the relevant pyridine *N*-oxide (5.0 mmol) and trimethyloxonium tetrafluoroborate (6.0 mmol, 1.2 equiv) in CH_2Cl_2 (25 mL) was stirred for 16 hours while being maintained at room temperature under a nitrogen atmosphere. The resulting mixture was concentrated under reduced pressure and the solid thus obtained was recrystallized (twice) from a mixture of CH_2Cl_2 (6 mL) and diethyl ether (60 mL) stored at -20 °C. Solid compounds were thus obtained.

III. Optimization of the Reaction Conditions

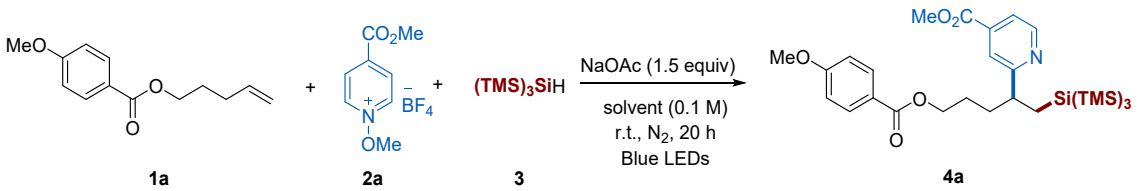
Table S1. Screening of photocatalysts.[a]



Entry	Photocatalyst	Yield (%)[b]
1	Eosin Y	59
2	$RuCl_2(bpy)_3 \cdot 6H_20$	45
3	*fac*-Ir(ppy)$_3$	15
4	$Acr^+ClO_4^-$	33
5	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	trace
6	4CzIPN	0
7	—	71

[a] Unless otherwise noted, reactions were performed using a mixture of **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **3** (0.3 mmol, 3.0 equiv), NaOAc (0.15 mmol, 1.5 equiv), photocatalyst (2.0 mol %) in MeCN (1.0 mL) at room temperature under irradiation with 40W Kessil Blue LEDs 25% intensity, 456 nm) for 20 hours. [b] Yields of isolated products are given.

Table S2. Screening of solvents.[a]



Entry	Solvent	Yield (%)[b]
1	MeCN	71
2	MeOH	53
3	DMSO	31
4	1,2-DCE	29
5	DCM	30
6	1,4-Dioxane	0
7	Toluene	0

[a] Unless otherwise noted, reactions were performed using a mixture of **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **3** (0.3 mmol, 3.0 equiv), NaOAc (0.15 mmol, 1.5 equiv) in solvent (1.0 mL) at room temperature under irradiation with 40W Kessil Blue LEDs (25% intensity, 456 nm) for 20 hours. [b] Yields of isolated products are given.

Table S3. Screening of bases.[a]

Entry	Base	Yield (%)[b]
1	NaOAc	71
2	$NaHCO_3$	78
3	K_2CO_3	59
4	Na_2CO_3	56
5	Na_3PO_4	55
6	Na_2HPO_4	51
7	*t*-BuOK	trace
8	Et_3N	0
9[c]	$NaHCO_3$	32

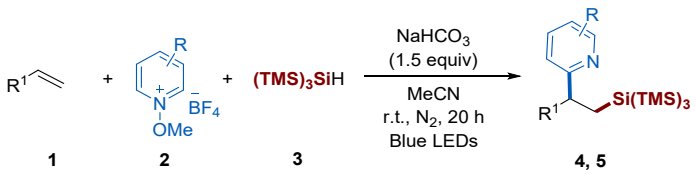
[a] Unless otherwise noted, reactions were performed using a mixture of **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), **3** (0.3 mmol, 3.0 equiv), base (0.15 mmol 1.5 equiv) in MeCN (1.0 mL) at room temperature under airadiation with 40W Kessil Blue LEDs (25% intensity, 456 nm) for 20 hours. [b] Yields of isolated products are given. [c] 20 mol % $NaHCO_3$ was used.

Table S4. Screening of silane sources.[a]

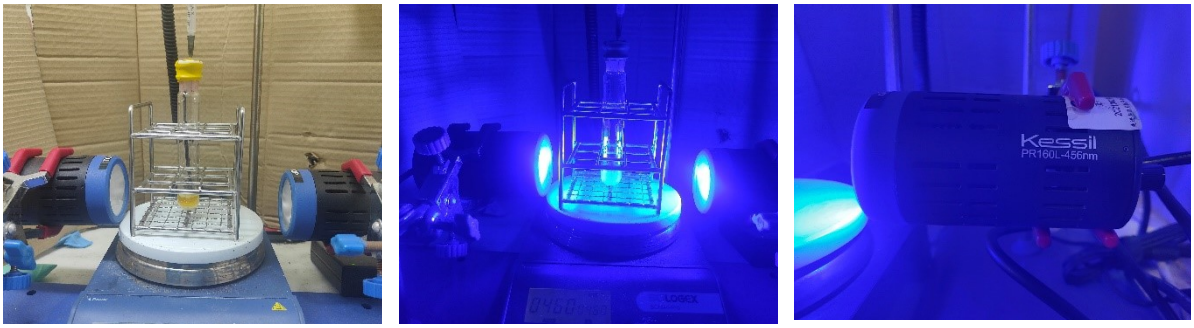
Entry	Silane	Yield (%)[b]
1	$(TMS)_3SiH$	78
2	$(MeO)_3SiH$	ND
3	Et_3SiH	ND
4	$Ph(Me)_2SiH$	ND
5	$Ph_3Si\text{-}H$	ND
6	$Ph_3Si\text{-}S\text{-}H$	ND
7[c]	$(TMS)_3SiH$	trace
8[d]	$(TMS)_3SiH$	0
9[e]	$(TMS)_3SiH$	0

[a] Unless otherwise noted, reactions were performed using a mixture of **1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), silane (0.3 mmol, 3.0 equiv), $NaHCO_3$ (0.15 mmol 1.5 equiv) in MeCN (1.0 mL) at room temperature under irradiation with 40W Kessil Blue LEDs (25% intensity, 456 nm) for 20 hours. [b] Yields of isolated products are given. [c] The reaction was carried out in the dark. [d] The reaction was carried out under air. [e] TEMPO (3.0 equiv) was added. ND = not detected.

IV. General Procedure for the Synthesis of Compound 4a-4z, 4aa-4al, 5a-5r

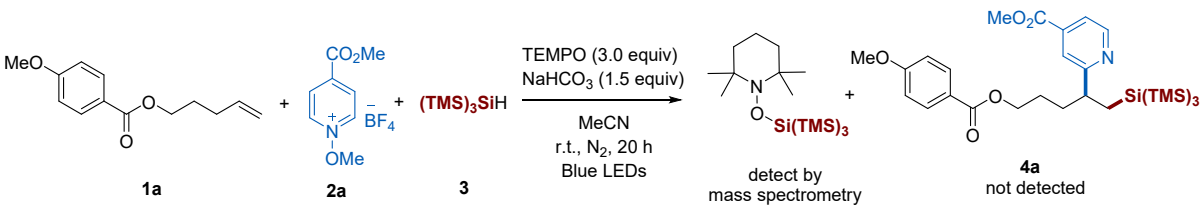


An oven-dried reaction tube equipped with a magnetic stirring bar was charged with the relevant olefins **1** (0.1 mmol, 1.0 equiv), the relevant *N*-methoxyheteroarenium salt **2** (0.15 mmol, 1.5 equiv), $(TMS)_3SiH$ **3** (0.3 mmol, 3.0 equiv), and $NaHCO_3$ (0.15 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen three times. MeCN (1.0 mL) was then added to the reaction mixture via syringe and the resulting solution stirred at room temperature for 20 hours while being irradiated, throughout this time, with two Kessil blue LEDs lamps (456 nm, 10 W, 25% intensity). Thereafter, the entire solvent was removed from the reaction mixture under reduced pressure and the residue thus obtained was purified by column chromatography (petroleum ether/ethyl acetate elution) to afford the relevant product **4a-4z**, **4aa-4al**, and **5a-5r**.



V. Radical Trapping Experiments

Radical trapping experiments using TEMPO



An oven-dried reaction tube equipped with a magnetic stirring bar was charged with the relevant olefin **1a** (0.1 mmol, 1.0 equiv), the relevant *N*-methoxyheteroarenium salt **2a** (0.15

mmol, 1.5 equiv), $(TMS)_3SiH$ **3** (0.3 mmol, 3.0 equiv), TEMPO (0.3 mmol, 3.0 equiv), and $NaHCO_3$ (0.15 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen three times. MeCN (1.0 mL) was then added to the reaction mixture *via* syringe and the resulting solution stirred at room temperature for 20 h while being irradiated, throughout this time, with two Kessil blue LED lamps (456 nm, 10 W, 25% intensity). Thereafter the reaction mixture was treated with water (30 mL) and then extracted with ethyl acetate (3 ✕ 25 mL). The combined organic phases was washed with water (1 ✕ 30 mL) and brine (1 ✕ 30 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was subjected to ESI mass spectral analysis and the spectrum thus obtained (shown immediately below) displayed a molecular-associated ion at *m/z* 404.24 consistent with the presence of the anticipated TEMPO trapping product. No evidence for the formation of pyridine **4a** was obtained.

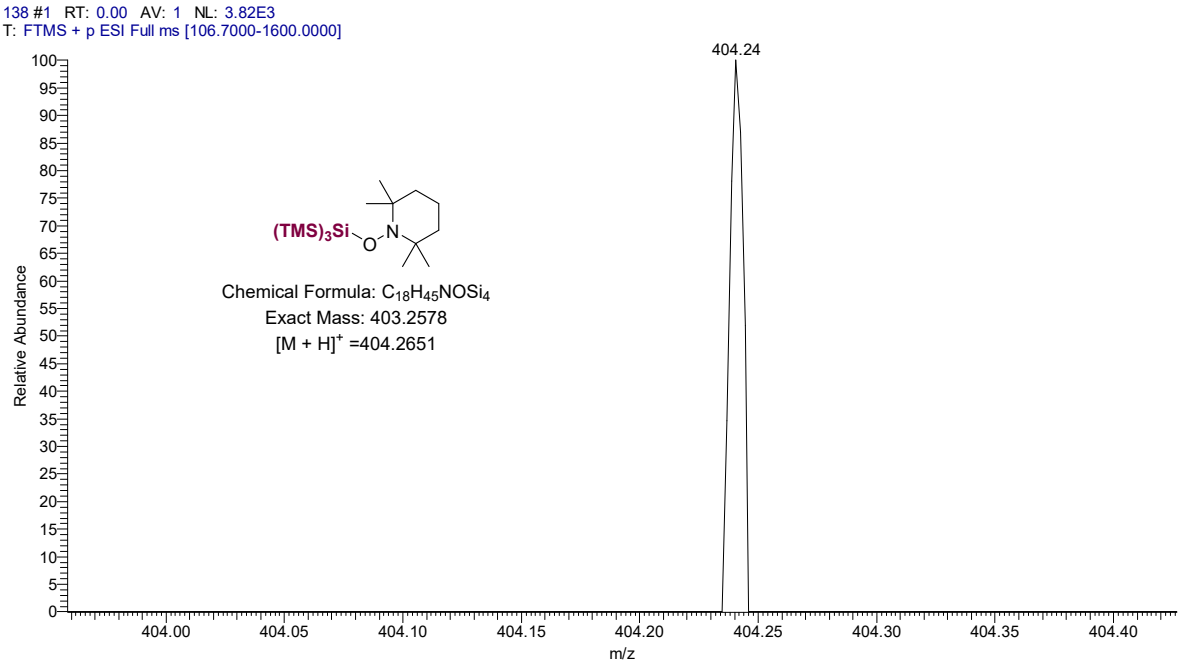
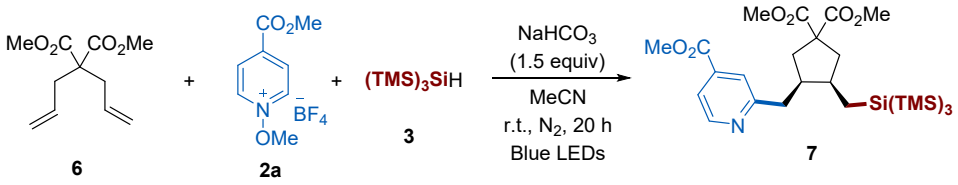


Figure S1. ESI Mass spectrum arising from TEMPO-trapping experiment.

Radical trapping experiments using diene 6



An oven-dried reaction tube equipped with a magnetic stirring bar was charged with the dimethyl 2,2-diallylmalonate **6** (21.2 mg, 0.10 mmol, 1.0 equiv), the relevant *N*-methoxyheteroarenium salt **2a** (0.15 mmol, 1.5 equiv), $(TMS)_3SiH$ **3** (0.3 mmol, 3.0 equiv), and $NaHCO_3$ (0.15 mmol, 1.5 equiv). The tube was evacuated and backfilled with nitrogen three times. MeCN (1.0 mL) was then added to the reaction mixture via syringe and the resulting solution stirred at room temperature for 20 hours while being irradiated, throughout this time, with two Kessil blue LEDs lamps (456 nm, 40 W, 25% intensity). Thereafter, the entire solvent was removed from the reaction mixture under reduced pressure and the residue thus obtained was purified by column chromatography (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) to afford the relevant product **7** (25.1 mg, 42% yield, d.r. = 5:1).

VI. Absorption Spectra

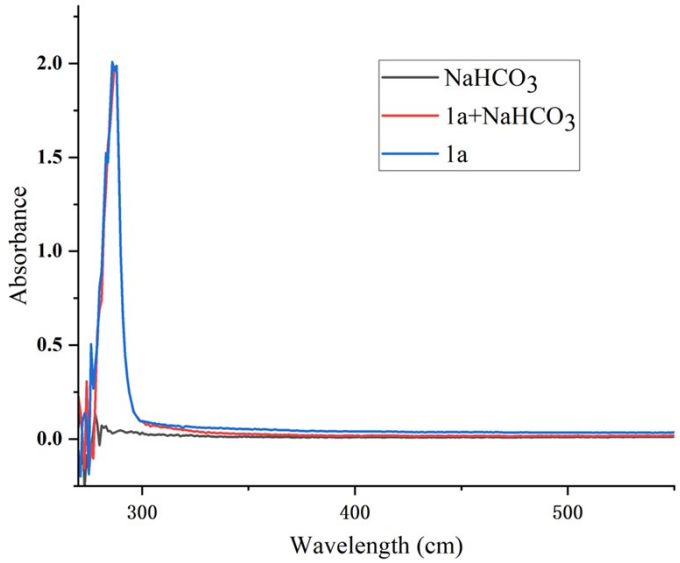


Figure S2. Absorption spectra for **1a** with $NaHCO_3$ (based on 0.025 M of **1a** in MeCN).

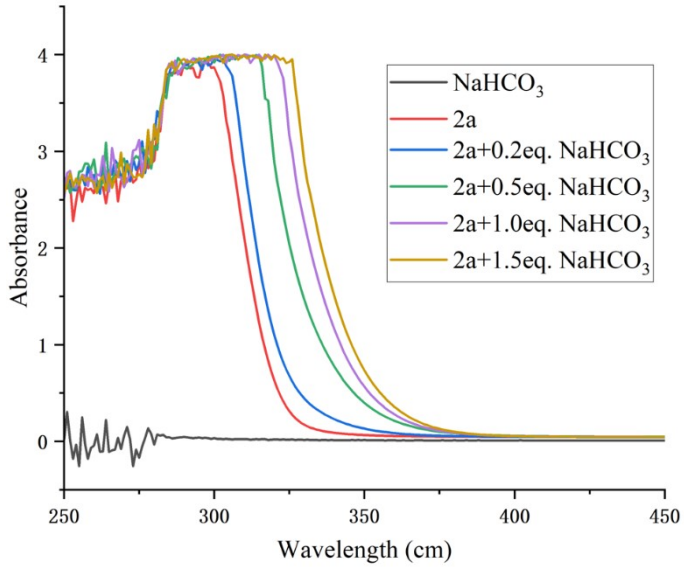


Figure S3. Absorption spectra for **2a** with $NaHCO_3$ (based on 0.025 M of **2a** in MeCN/H_2O = 4/1).

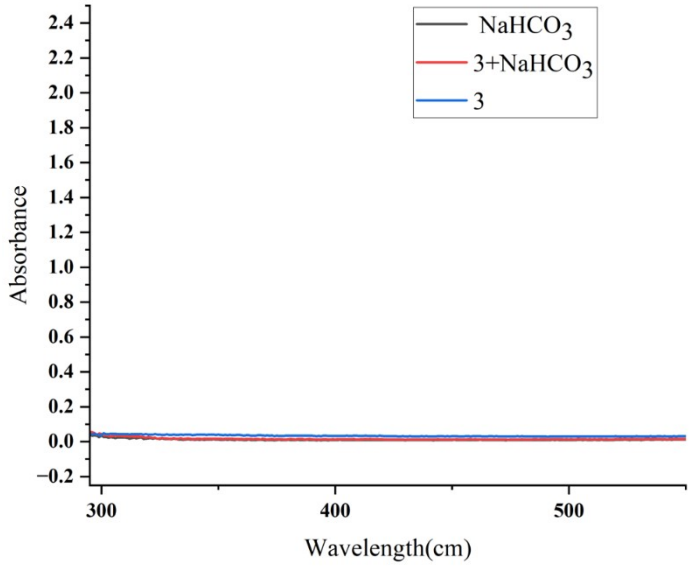


Figure S4. Absorption spectra for **3** with $NaHCO_3$ (based on 0.025 M of **3** in MeCN).

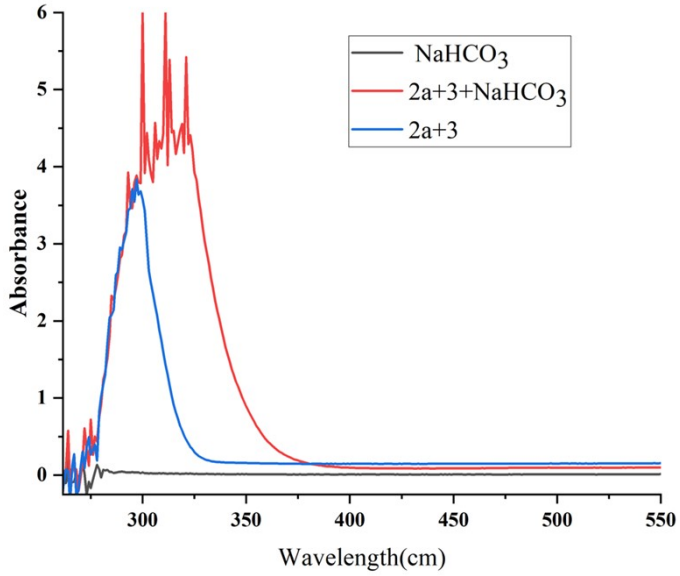


Figure S5. Absorption spectra for **2a+3** with $NaHCO_3$ (based on 0.025 M of **2a+3** in $MeCN/H_2O$ = 4/1).

VII. Quantum Yield Measurements

Determination of the light intensity at 456 nm.

A Kessil LED lamp (λ_{max} = 456 nm) was used at 25% intensity for the measurement of quantum yield. So, following the procedure of Yoon,[3] the photon flux of the LED (λ_{max} = 456 nm) was determined by standard ferrioxalate actinometry. Specifically, a 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (2.211 g) in H_2SO_4 (30 mL of a 0.05 M solution) while a buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (15.0 mg) and sodium acetate (3.38 g) in H_2SO_4 (15.0 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 seconds at λ_{max} = 456 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the resulting mixture was allowed to stir in the dark for 1 h so as to permit the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the resulting solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1

	Non-irrad	Irrad 01	Irrad 02	Irrad 03

A_{510nm}	0.825	2.256	2.639	2.546
		Average $A_{510\ nm}$ of irradiation samples		2.480

$$mol\ of\ Fe^{2+} = \frac{V \cdot \Delta A_{510\ nm}}{l \cdot \epsilon} = \frac{(0.00235\ L) \cdot (1.655)}{(1.00\ cm) \cdot (11{,}100 \frac{L}{mol} \cdot cm)} = 3.50 \times 10^{-7}\ mol \quad (1)$$

V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 $Lmol^{-1}\ cm^{-1}$).[4] The photon flux was calculated using eq 2:

$$Photon\ flux = \frac{mol\ of\ Fe^{2+}}{\emptyset \cdot t \cdot f} = \frac{3.50 \times 10^{-7} mol}{(0.84) \cdot (90\ s) \cdot (0.945)} = 4.9 \times 10^{-9}\ einstein/s \quad (2)$$

where Φ is the quantum yield for the ferrioxalate actinometer,[5] t is the irradiation time (90 s), and f is the fraction of light absorbed at 456 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where $A_{456\ nm}$ is the absorbance of the ferrioxalate solution at 456 nm. An absorption spectrum gave an A_{456} nm value of 1.126 indicating that the fraction of absorbed light (f) is 0.945.

$$f = 1 - 10^{-A_{456nm}} \quad (3)$$

The photon flux was thus calculated to be 4.9×10^{-9} Einsteins s^{-1} (average of three experiments).

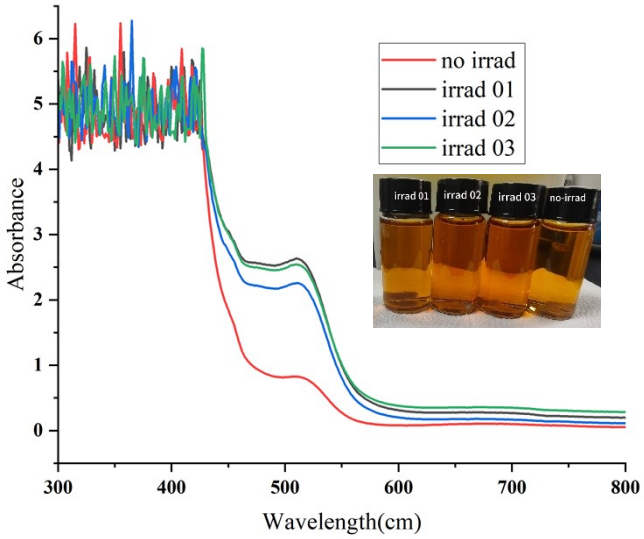


Figure S6. Absorption spectra of three irradiation experiments and non-irradiation experimen t.

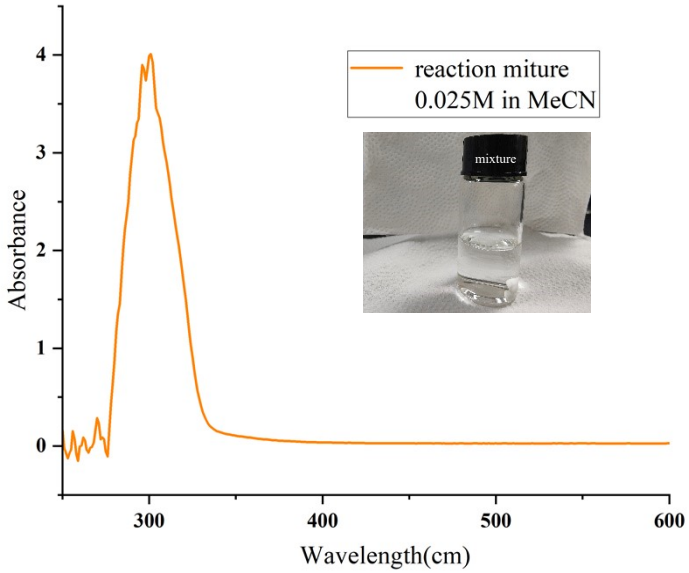
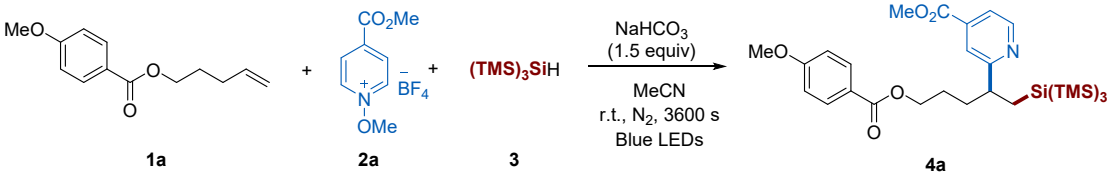


Figure S7. Absorption spectra of 0.025 M solution of Reaction mixture in MeCN.

Determination of the reaction quantum yield.



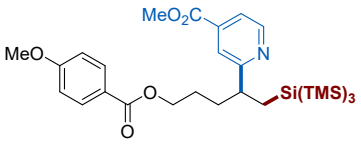
The reaction mixture was stirred and irradiated by Kessil LED (λmax = 456 nm) for 3600 seconds. The yield of product **4a** was determined, by ^{1}H NMR spectroscopic analysis using trimethoxybenzene as an internal standard, to be 20% (0.020×10^{-3} mol of **4a**). The reaction quantum yield (Φ) was determined using eq 4 where the photon flux is 4.9×10^{-9} Einsteins s^{-1} (determined by actinometry as described above), t is the reaction time (3600 s) and f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the reaction mixture (0.025 M) gave an absorbance value of 0.028 at 456 nm (Figure S7), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.062.

$$\Phi = \frac{mol\ of\ product}{flux \cdot t \cdot f} \qquad (4)$$

$$\Phi = \frac{0.020 \times 10^{-3}\ mol}{4.9 \times 10^{-9}\ einstein\ s^{-1} \cdot 3600\ s \cdot 0.062} = 18.3$$

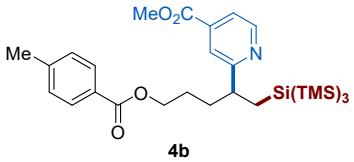
The reaction quantum yield (Φ) was calculated to be 18.3

VIII. Compound Characterization and Related Data



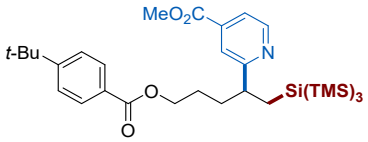
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)-5-((4-methoxy-benzoyl)oxy)pentan-2-yl)isonicotinate (4a). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and

flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4a** (47.1 mg, 78%) as a colorless oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 4.9 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.67 (d, J = 7.2 Hz, 2H), 6.90 – 6.87 (m, 2H), 4.17 (t, J = 6.6 Hz, 2H), 3.95 (s, 3H), 3.84 (s, 3H), 3.00 -2.94 (m, 1H), 1.92 – 1.81 (m, 2H), 1.67 – 1.58 (m, 1H), 1.40 (dd, J = 14.6, 6.2 Hz, 2H), 1.25 (dd, J = 14.5, 7.7 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 166.3, 165.8, 163.2, 150.2, 150.2, 137.8, 131.6, 122.7, 121.5, 120.6, 113.4, 64.6, 55.4, 52.7, 47.0, 35.3, 27.2, 15.4, 1.3; IR (ATR) νmax 3419, 2952, 1731, 1724, 1605, 1253, 834, 618 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{49}NO_5Si_4$: $[M+H]^+$ = 604.2761. Found: 604.2753.



4b

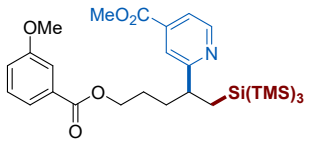
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)-5-((4-meth-ylb-enz-oyl)oxy)pentan-2-yl)isonicotinate (4b). Reaction of pent-4-en-1-yl 4-methylbenzoate **1b** (20. 4 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 7:1 v/v petroleum ether/ethyl acetate) gave compound **4b** (47.6 mg, 81%) as a yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.9, 0.9 Hz, 1H), 7.88 – 7.86 (m, 2H), 7.6 7 – 7.65 (m, 2H), 7.20 (d, J = 7.8 Hz, 2H), 4.18 (t, J = 6.6 Hz, 2H), 3.95 (s, 3H), 2.99 – 2.94 (m, 1H), 2.39 (s, 3H), 1.91 – 1.82 (m, 2H), 1.62 (t, J = 18.3 Hz, 1H), 1.44 – 1.39 (m, 2H), 1.25 (dd, J = 14.6, 7.7 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 166.6, 165.8, 150.3, 143.4, 137.7, 129.6, 128.9, 127.6, 121.5, 120.6, 64.7, 52.6, 47.1, 35.3, 27.2, 21.6, 15.4, 1.3; IR (ATR) νmax 3437, 2952, 1726, 1606, 1441, 1279, 1109, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{49}NO_4Si_4$: $[M+H]^+$ = 587.2811. Found: 588.2817.



4c

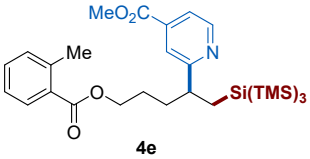
Methyl 2-(5-((4-(tert-butyl)benzoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethyl-lsilyl)-t-risilan-2-yl)pentan-2-yl)isonicotinate (4c). Reaction of pent-4-en-1-yl 4-(tert-butyl)benzoate **1c** (24.6mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15

mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 7:1 v/v petroleum ether/ethyl acetate) gave compound **4c** (46.3 mg, 74%) as a colorle ss oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, J = 4.9, 0.7 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.43 – 7.41 (m, 2H), 4.19 (td, J = 6.6, 2.4 Hz, 2H), 3.95 (s, 3H),3.00 - 2.95 (m, 1H), 1.91 - 1.81(m, 2H), 1.68 – 1.59 (m, 1H), 1.42 (dd, J = 14.6, 6.5 Hz, 2H), 1.33 (s, 9H), 1.25 (dd, J = 14.6, 6.5 Hz, 2H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 166.5, 165.8, 156.4, 150.2, 137.8, 129.4, 127.5, 125.2, 121.5, 120.6, 64.6, 52.6, 47.0, 35.4, 35.0, 31.1, 27.2, 15.3, 1.3; IR (ATR) νmax 3423, 2952, 2897, 1725, 1604, 1441, 1112, 840, 762, 687 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{55}NO_4Si_4$: $[M+H]^+$=630.3281. Found: 630.3269.



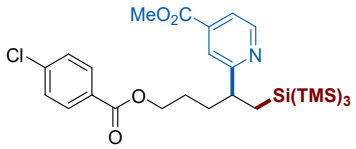
4d

Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-((3-methoxy-benzoyl)oxy)pentan-2-yl)isonicotinate (4d). Reaction of pent-4-en-1-yl 3-methoxybenzoate **1d** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4d** (44.0 mg, 73%) as a colorless oil liquid oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 4.9 Hz, 1H), 7.67 (d, J = 5.3 Hz, 2H), 7.58 (dt, J = 7.7, 1.2 Hz, 1H), 7.50 (dd, J = 2.6, 1.5 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.09 – 7.06 (m, 1H), 4.20 (td, J = 6.6, 1.5 Hz, 2H), 3.95 (s, 3H), 3.83 (s, 3H), 3.00 – 2.94 (m, 1H), 1.92 – 1.81 (m, 2H), 1.67 – 1.61 (m, 1H), 1.43 – 1.39 (m, 2H), 1.25 (dd, J = 14.6, 7.7 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 166.4, 165.8, 159.5, 150.2, 137.8, 131.60, 129.2, 122.0, 121.5, 120.6, 119.3, 114.0, 65.0, 55.4, 52.7, 47.0, 35.2, 27.1, 15.4, 1.3; IR (ATR) νmax 3437, 2950, 2894, 1726, 1595, 1442, 1232, 1105, 830 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{49}NO_5Si_4$: $[M+H]^+$ = 604.2761. Found: 604.2741.



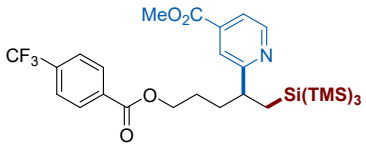
4e

Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)-5-((2-methy-lbenzo-yl)-oxy)pentan-2-yl)isonicotinate (4e). Reaction of pent-4-en-1-yl 2-methylbenzoate **1e** (20.4 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4e** (44.3 mg, 75%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.67 (dd, *J* = 7.1, 2.2 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.21 (dt, *J* = 7.2, 3.4 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.95 (s, 3H), 3.00 – 2.94 (m, 1H), 2.54 (s, 3H), 1.91 – 1.82 (m, 2H), 1.66 – 1.59 (m, 1H), 1.46 – 1.39 (m, 2H), 1.25 (dd, *J* = 14.6, 7.5 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 167.5, 165.8, 150.2, 140.0, 137.7, 131.8, 131.5, 130.5, 129.7, 125.6, 121.5, 120.6, 64.6, 52.6, 47.0, 35.4, 27.1, 21.7, 15.3, 1.2; IR (ATR) νmax 3432, 2948, 2894, 1728, 1595, 1441, 1291, 1082, 836, 685cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{49}NO_4Si_4$: $[M+H]^+$ = 588.2811. Found: 588.2795.



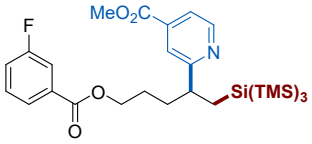
4f

Methyl 2-(5-((4-chlorobenzoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4f). Reaction of pent-4-en-1-yl 4-chlorobenzoate **1f** (22.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 7:1 v/v petroleum ether/ethyl acetate) gave compound **4f** (45.5 mg, 75%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.66 (d, *J* = 5.1 Hz, 2H), 7.39 – 7.36 (m, 2H), 4.20 (t, *J* = 6.5 Hz, 2H), 3.95 (s, 3H), 2.99 -2.93 (m, 1H), 1.91 – 1.82 (m, 2H), 1.66 – 1.59 (m, 1H), 1.42 – 1.38 (m, 2H), 1.24 (dd, *J* = 14.6, 7.8 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) 167.4, 165.8, 165.6, 150.2, 139.2, 137.8, 131, 128.7, 128.6, 121.5, 120.6, 65.1, 52.7, 47.0, 35.2, 27.1, 15.4, 1.3; IR (ATR) νmax 3437, 2950, 2896, 1730, 1595, 1440, 1276, 1107, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{46}ClNO_4Si_4$: $[M+H]^+$ = 608.2265. Found: 608.2249.



4g

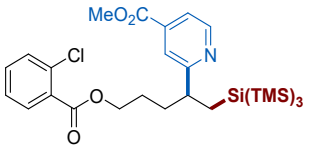
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((4-(trifleoro-methyl)benzoyl)oxy)pentan-2-yl) isonicotinate (4g). Reaction of pent-4-en-1-yl 4-(trifluoromethyl)benzoate **1g** (25.8 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **4g** (48.1 mg, 75%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.9 Hz, 1H), 8.10 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 4H), 4.24 (t, *J* = 6.5 Hz, 2H), 3.96 (s, 3H), 3.04 - 2.94 (m, 1H), 1.92 – 1.85 (m, 2H), 1.69 -1.62 (m, 1H), 1.45 - 1.38 (m, 2H), 1.25 (dd, *J* = 13.9, 8.5 Hz, 1H), 0.14 – 0.10 (m, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.3, 165.7, 165.3, 150.1, 138.0, 134.3 (q, *J* = 32.5 Hz), 133.5, 130.0, 125.3 (q, *J* = 3.7 Hz), 123.6 (d, *J* = 272.6 Hz), 121.6, 120.8 (q, *J* = 26.9 Hz), 65.4, 52.7, 46.9, 35.1, 27.0, 15.5, 1.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.1 (s); IR (ATR) νmax 3722, 2952, 2895, 1730, 1562, 144 1, 1278, 1117, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{46}F_3NO_4Si_4$: $[M+H]^+$ = 642.2529. Found: 642.2508.



4h

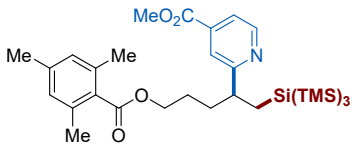
Methyl 2-(5-((3-fluorobenzoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4h). Reaction of pent-4-en-1-yl 3-fluorobenzoate **1h** (20.8 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4h** (48.5 mg, 82%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.8, 1.0 Hz, 1H), 7.78 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.7 – 7.64 (m, 3H), 7.40 – 7.36 (m, 1H), 7.25 – 7.21 (m, 1H), 4.21 (t, *J* = 6.5 Hz, 2H), 3.95 (s, 3H), 2.99 - 2.94 (m, 1H), 1.92 -1.81 (m, 2H), 1.67 – 1.59 (m, 1H), 1.42 - 1.38 (m, 2H), 1.25 (dd, *J* = 14.6, 7.8 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.4, 165.8, 165.4

(d, J = 3.0 Hz), 162.5 (d, J = 246.7 Hz), 150.2, 150.71 – 149.76 (m), 137.8, 132.5 (d, J = 7.5 Hz), 129.9 (d, J = 7.8 Hz), 125.3 (d, J = 2.9 Hz), 121.5, 120.6, 119.9 (d, J = 21.3 Hz), 116.4 (d, J = 23.1 Hz), 65.2, 52.7, 47.0, 35.1, 27.1, 15.4, 1.3; IR (ATR) νmax 3441, 2952, 2897, 1728, 1594, 1440, 1286, 1101, 835, 686 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{46}FNO_4Si_4$: $[M+H]^+$ = 592.2561. Found: 592.2564.



4i

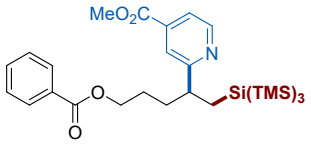
Methyl 2-(5-((2-chlorobenzoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4i). Reaction of pent-4-en-1-yl 2-chlorobenzoate **1i** (22.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4i** (44.7 mg, 74%) as a yellow oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 5.1 Hz, 1H), 7.76 (dd, J = 7.8, 1.7 Hz, 1H), 7.68 (s, 2H), 7.43 – 7.37 (m, 2H), 7.30 – 7.27 (m, 1H), 4.22 (t, J = 6.5 Hz, 2H), 3.95 (s, 3H), 3.02 - 2.95 (m, 1H), 1.92 – 1.83 (m, 2H), 1.67 – 1.60 (m, 1H), 1.44 – 1.39 (m, 2H), 1.25 (dd, J = 14.6, 7.6 Hz, 1H), 0.11 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.4, 165.7, 150.1, 137.8, 133.6, 132.4, 131.3, 131.0, 130.3, 126.5, 121.6, 120.7, 110.9, 65.4, 52.7, 46.9, 35.3, 27.0, 15.4, 1.2; IR (ATR) νmax 3441, 2952, 2896, 1733, 1596, 1440, 1290, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{46}ClNO_4Si_4$: $[M + H]^+$ = 608.2265. Found: 608.2250.



4j

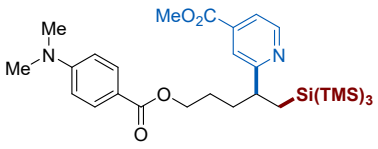
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-((2,4,6-trime-thyl-benzoyl)oxy)pentan-2-yl)isonicotinate (4j). Reaction of pent-4-en-1-yl benzoate **1j** (23.2 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4j** (47.4 mg, 77%) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, J = 5.9 Hz, 1H), 7.66 (d, J = 4.0 Hz, 2H), 6.81 (s, 2H), 4.20

(t, J = 6.6 Hz, 2H), 3.95 (s, 3H), 2.95 (t, J = 7.6 Hz, 1H), 2.26 (s, 3H), 2.22 (s, 6H), 1.86 – 1.79 (m, 2H), 1.64 – 1.59 (m, 1H), 1.44 - 1.39 (m, 2H), 1.24 (dd, J = 14.5, 7.2 Hz, 1H), 0.10 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 167.3, 165.7, 150.2, 139.1, 137.8, 135.0, 131.0, 128.3, 121.5, 120.6, 64.7, 52.7, 47.0, 35.6, 27.1, 21.1, 19.7, 15.0, 1.2; IR (ATR) νmax 3441, 2952, 2896, 1731, 1603, 1441, 1276, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{53}NO_4Si_4$: [M + H]$^+$ = 616.3124. Found: 616.3104.



4k

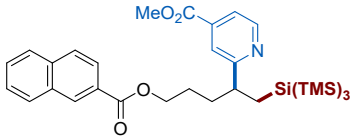
Methyl 2-(5-(benzoyloxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)-pentan-2-yl)isonicotinate (4k). Reaction of pent-4-en-1-yl benzoate **1k** (19.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **4k** (41.8 mg, 73%) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, J = 4.6 Hz, 1H), 7.98 (dd, J = 8.3, 1.3 Hz, 2H), 7.68 – 7.66 (m, 2H), 7.54 – 7.51 (m, 1H), 7.40 (t, J = 7.8 Hz, 2H), 4.21 (t, J = 6.6 Hz, 2H), 3.95 (s, 3H), 3.00 - 2.95 (m, 1H),1.93 - 1.82 (m, 2H), 1.68 – 1.60 (m, 1H), 1.45 – 1.38 (m, 2H), 1.27 – 1.23 (m, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 166.5, 165.8, 150.2, 137.8, 132.8, 130.3, 129.5, 128.2, 121.5, 120.6, 64.8, 52.6, 47.0, 35.6, 27.1, 15.4, 1.3; IR (ATR) νmax 2952, 2897, 1727, 1602, 1441, 1275, 1112, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{47}NO_4Si_4$: [M + H]$^+$ = 574.2655 . Found: 574.2637.



4l

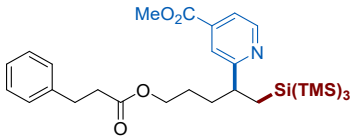
Methyl 2-(5-((4-(dimethylamino)benzoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4l). Reaction of pent-4-en-1-yl 4-(dimethylamino)benzoate **1l** (23.3 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 5:1 v/v petroleum ether/ethyl acetate) gave

compound **4l** (31.4 mg, 51%) as a light yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.0 Hz, 1H), 7.86 – 7.83 (m, 2H), 7.67 – 7.65 (m, 2H), 6.61 (d, *J* = 9.1 Hz, 2H), 4.15 (td, *J* = 6.6, 2.4 Hz, 2H), 3.95 (s, 3H), 3.02 (s, 6H), 2.98 – 2.93 (m, 1H), 1.92 – 1.79 (m, 2H), 1.64 – 1.57 (m, 1H), 1.41 (dd, *J* = 14.5, 6.4 Hz, 2H), 1.25 (dd, *J* = 14.6, 7.5 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.6, 166.9, 165.9, 153.2, 150.3, 137.6, 131.2, 121.5, 120.5, 117.2, 110.5, 64.1, 52.6, 47.1, 40.0, 35.4, 27.3, 15.3, 1.3; IR (ATR) νmax 3390. 2, 2950, 2896, 1730, 1707, 14441, 1283, 1180, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{52}N_2O_4Si_4$: $[M+H]^+$ = 617.3077. Found: 617.3066.



4m

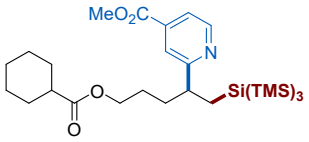
Methyl 2-(5-((2-naphthoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4m). Reaction of pent-4-en-1-yl 2-naphthoate **1m** (23.3 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4m** (50.5 mg, 81%) as a yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.0 Hz, 1H), 8.56 (s, 1H), 8.02 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.86 (t, 2H), 7.69 (t, 2H), 7.59 – 7.52 (m, 2H), 4.28 (t, *J* = 6.6 Hz, 2H), 3.94 (s, 3H), 3.04 – 2.98 (m, 1H), 1.99 – 1.86 (m, 2H), 1.75 – 1.66 (m, 1H), 1.51 – 1.41 (m, 2H), 1.28 (dd, *J* = 14.6, 7.8 Hz, 1H), 0.14 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5, 166.7, 165.778, 150.2, 137.8, 135.5, 132.4, 131.0, 129.3, 128.1, 128.0, 127.7, 127.5, 126.5, 125.3, 121.5, 120.6, 65.0, 52.6, 47.0, 35.2, 27.2, 15.5, 1.3; IR (ATR) νmax 3430, 2953, 2894, 1725, 1281, 1099, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{49}NO_4Si_4$: $[M + Na]^+$ = 646.2 631. Found: 646.2611.



4n

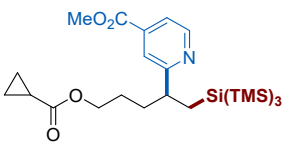
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-((3-phen-ylprop-ano-yl)oxy)pentan-2-yl)isonicotinate (4n). Reaction of pent-4-en-1-yl 3-phenylpropanoate **1n** (21.8 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15

mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 6:1 v/v petroleum ether/ethyl acetate) gave compound **4n** (49.7 mg, 83%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.67 – 7.65 (m, 2H), 7.28 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H),4.01 - 3.91 (m, 5H), 2.91 (t, *J* = 7.9 Hz, 3H), 2.59 – 2.56 (m, 2H), 1.85 – 1.78 (m, 1H), 1.77 – 1.69 (m, 1H), 1.51 - 1.54 (m, 1H), 1.38 (dd, *J* = 14.5, 6.0 Hz, 1H), 1.30 – 1.25 (m, 1H), 1.24 – 1.21 (m, 1H), 0.14 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.8, 167.5, 165.8, 150.2, 140.5, 137.8, 128.4, 128.2, 126.2, 121.5, 120.6, 64.4, 52.7, 47.0, 35.8, 35.1, 30.9, 27.0, 15.4, 1.3; IR (ATR) νmax 3451, 2953, 2891. 1735, 15 97, 1442, 1293, 836, 689 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{51}NO_4Si_4$: $[M + H]^+$ = 602.2968. Found: 602.2952.



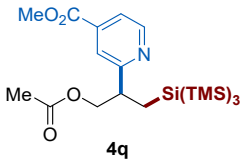
4o

Methyl 2-(5-((cyclohexanecarbonyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)pentan-2-yl)isonicotinate (4o). Reaction of pent-4-en-1-yl cyclohexane carboxylate **1o** (19.6 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 9:1 v/v petroleum ether/ethyl acetate) gave compound **4o** (35.3 mg, 61%) as a colorle ss oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.1 Hz, 1H), 7.66 (d, *J* = 9.4 Hz, 2H), 3.96 – 3.91 (m, 5H), 2.96 – 2.89 (s, 1H), 2.25 – 2.20 (m, 1H), 1.84 (d, *J* = 11.6 Hz, 2H), 1.80 – 1.75 (m, 2H), 1.73 - 1.71(m, 2H), 1.63 – 1.60 (m, 1H), 1.49 – 1.44 (m, 1H), 1.40 – 1.37(m, 3H), 1.26 – 1.20 (m, 5H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 176.1, 167.5, 165.8, 150.1, 137.7, 121.5, 120.6, 64.0, 52.7, 47.0, 43.2, 35.2, 29.0, 29.0, 27.1, 25.7, 25.4, 25.4, 154, 1.3; IR (ATR) νmax 3446, 2938, 2862, 1735, 1597, 1477, 1291, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{53}NO_4Si_4$: $[M + H]^+$ = 580.3124 Found: 580.3110.



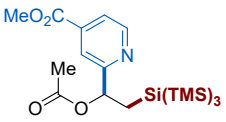
4p

Methyl 2-(5-((cyclopropanecarbonyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4p). Reaction of pent-4-en-1-yl cyclopropanecarboxylate **1p** (15.4 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 9:1 v/v petroleum ether/ethyl acetate) gave compound **4p** (27.5 mg, 51%) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.67 (s, 2H), 4.01 – 3.93 (m, 5H),2.98 – 2.94 (m, 1H), 1.89 – 1.83 (m, 1H), 1.79 – 1.72 (m, 1H),1.57 - 1.54 (m, 1H), 1.51 – 1.47 (m, 1H), 1.38 (dd, *J* = 14.5, 5.9 Hz, 1H),1.28 - 1.24 (m, 2H), 0.95 – 0.93 (m, 2H), 0.83 – 0.80 (m, 2H), 0.14 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 193.8, 174.9, 167.6, 165.7, 150.10, 121.6, 120.7, 120.6, 64.4, 52.7, 46.9, 35.0, 27.1, 15.6, 12.8, 8.4, 1.2; IR (ATR) νmax 3442, 2952, 1733, 1597, 1444, 1291, 1108, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{47}NO_4Si_4$: [M + H] $^+$ = 538.2655. Found: 538.2640.



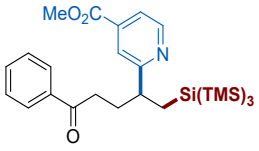
4q

Methyl 2-(1-acetoxy-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) propan-2-yl) isonicotinate (4q). Reaction of allyl acetate **1q** (10.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4q** (41.0 mg, 85%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.71 (s, 1H), 7.69 (dd, *J* = 5.0, 1.5 Hz, 1H), 4.24 – 4.16 (m, 2H), 3.95 (s, 3H), 3.31 – 3.25 (m, 1H), 1.92 (s, 3H), 1.45 (dd, *J* = 14.6, 8.3 Hz, 1H), 1.21 (dd, *J* = 14.7, 5.5 Hz, 1H), 0.09 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.7, 165.7, 164.0 150.3, 137.6, 122.4, 121.1, 69.7, 52.7, 46.0, 20.8, 9.7, 1.1; IR (ATR) νmax 3454, 2950, 2897, 1739, 1600, 1438, 1239, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{41}NO_4Si_4$: [M + H]$^+$ = 484.2185. Found: 484.2171.



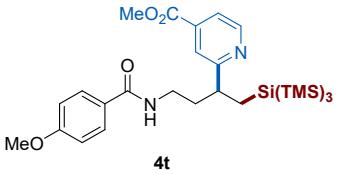
4r

Methyl 2-(1-acetoxy-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) ethyl) isonicotinate (4r). Reaction of vinyl acetate **1r** (8.6 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4r** (40.8 mg, 87%) as a light-yellow oil solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.78 (s, 1H), 7.72 (dd, *J* = 5.0, 1.5 Hz, 1H), 5.78 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.95 (s, 3H), 2.09 (s, 3H), 1.52 – 1.51 (m, 2H), 0.16 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5, 165.5, 162.9, 150.2, 138.2, 121.9, 119.9, 77.7, 52.7, 21.5, 15.3, 1.1; IR (ATR) νmax 3447, 2952, 2894, 1739, 1601, 1440, 1294, 1053, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{39}NO_4Si_4$: $[M + H]^+$ = 470.2029. Found: 470.2021.



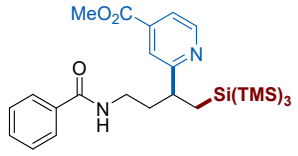
4s

Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-oxo-5-phenylpentan-2-yl)isonicotinate (4s). Reaction of 1-phenylpent-4-en-1-one **1s** (16.1 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4s** (42.4 mg, 78%) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.1 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 2H), 7.72 (s, 1H), 7.68 (d, *J* = 4.7 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 3.95 (s, 3H), 3.07 – 3.06 (m, 1H), 2.81 – 2.76 (m, 1H), 2.70 – 2.65 (m, 1H), 2.24 – 2.19 (m, 1H), 2.15 – 2.08 (m, 1H), 1.47 (dd, *J* = 14.5, 6.7 Hz, 1H), 1.27 (dd, *J* = 14.6, 7.3 Hz, 1H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 199.5, 167.2, 165.7, 150.1, 138.0, 136.8, 132.8, 128.4, 1288.0, 121.6, 120.7, 52.7, 46.6, 36.6, 33.3, 15.4, 1.2; IR (ATR) νmax 3443, 2950, 2894, 1735, 1592, 1442, 1293, 1111, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{45}NO_4Si_4$: $[M + H]^+$ = 544.2549. Found: 544.2533.



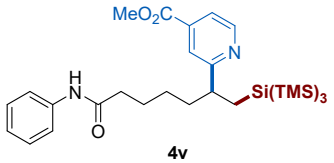
4t

Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-(4-methoxybenzamido) butan-2-yl) isonicotinate (4t). Reaction of N-(but-3-en-1-yl)-4-methoxybenzamide **1t** (20.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 1:1 v/v petroleum ether/ethyl acetate) gave compound **4t** (45.3 mg, 77%) as a yellow oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.74 (s, 1H), 7.65 – 7.62 (m, 3H), 6.88 – 6.85 (m, 2H), 6.38 (s, 1H), 3.94 (s, 3H), 3.82 (s, 3H), 3.42 – 3.37 (m, 1H), 3.14 - 3.09 (m, 1H),3.03 - 2.98 (m, 1H), 2.13 – 2.08 (m, 1H), 1.95 – 1.89 (m, 1H), 1.42 (dd, *J* = 14.6, 7.1 Hz, 1H), 1.23 (dd, *J* = 14.6, 7.0 Hz, 1H), 0.09 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.3, 166.5, 165.6, 161.9, 150.0, 138.1, 128.5, 126.9, 121.2, 120.8, 113.5, 55.3, 52.6, 45.0, 38.7, 38.0, 15.2, 1.2; IR (ATR) νmax 3330, 2948, 2893, 1733, 1635, 1298, 11881112, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{48}N_2O_4Si_4$: $[M+H]^+$ = 589.2764. Found: 589.2744.



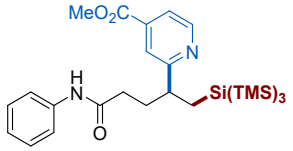
4u

Methyl 2-(4-benzamido-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) butan-2-yl) isonicotinate (4u). Reaction of N-(but-3-en-1-yl)benzamide **1u** (17.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4u** (40.2 mg, 72%) as a yellow oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.1 Hz, 1H), 7.75 (s, 1H), 7.68 – 7.65 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 6.49 (s, 1H), 3.95 (s, 3H), 3.45 – 3.39 (m, 1H), 3.16 – 3.11 (m, 1H), 3.07 – 3.01 (m, 1H), 2.16 – 2.10 (m, 1H), 1.97 - 1.91 (m, 1H), 1.43 (dd, *J* = 14.6, 7.0 Hz, 1H), 1.26 – 1.23 (m, 1H), 0.10 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.3, 167.0, 165.6, 149.9, 138.2, 134.6, 131.2, 128.4, 126.8, 121.3, 120.9, 52.7, 45.0, 38.6, 38.1, 15.3, 1.2; IR (ATR) νmax 3315, 2952, 2892, 1732, 1644, 1543, 1440, 1295, 1106, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{46}N_2O_3Si_4$: $[M+H]^+$ = 559.2658. Found: 559.2636.



4v

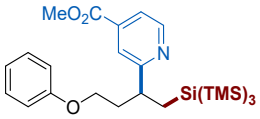
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-7-oxo-7-(phenylamino)heptan-2-yl)isonicotinate (4v). Reaction of *N*-phenylhex-5-enamide **1v** (18.9 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4v** (41.5 mg, 71%) as a light yellow oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.0 Hz, 1H), 7.66 (s, 1H), 7.63 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.21 (s, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 3H), 2.94 - 2.90 (m, 1H), 2.24 (t, *J* = 7.5 Hz, 2H), 1.77 (q, *J* = 7.7 Hz, 2H), 1.73 - 1.69 (m, 1H), 1.64 – 1.57 (m, 1H), 1.36 (dd, *J* = 14.5, 6.2 Hz, 1H), 1.23 (dd, *J* = 15.2, 8.5 Hz, 2H), 1.05 - 0.97 (m, 1H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 171, 167.8, 165.7, 149.8, 137.9, 129.0, 124.1, 121.6, 120.6, 119.8, 52.7, 47.1, 38.5, 37.5, 27.5, 25.6, 15.4, 1.3; IR (ATR) vmax 3308, 2950, 1735, 1665, 1546, 1441, 1298, 1112, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{48}N_2O_3Si_4$: $[M + Na]^+$ = 609.2791. Found: 609.2778.



4w

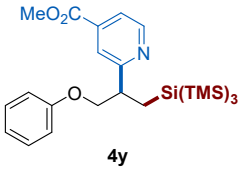
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-oxo-5-(phenylamino) pentan-2-yl) isonicotinate (4w). Reaction of N-phenylpent-4-enamide **1w** (17.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4w** (41.3 mg, 74%) as a white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.0 Hz, 1H), 8.32 (s, 1H), 7.81 (s, 1H), 7.72 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 3.96 (s, 3H), 3.19 – 3.14 (m, 1H), 2.28 – 2.22 (m, 1H), 2.11 (dd, *J* = 14.0, 5.7 Hz, 1H), 2.02 (dd, *J* = 14.1, 8.5 Hz, 1H), 1.97 – 1.93 (m, 1H), 1.46 (dd, *J* = 14.6, 7.3 Hz, 1H), 1.26 – 1.22 (m, 1H), 0.08 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.67, 167.2, 165.5, 149.5, 138.5, 138.3, 128.8,

123.8, 121.3, 121.0, 119.5, 52.8, 45.7, 36.0, 35.8, 14.8, 1.1; IR (ATR) vmax 3418, 2951, 1733, 1597, 1441, 1108, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{46}N_2O_3Si_4$: $[M + H]^+$ = 559.2658. Found: 559.2640.



4x

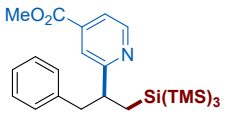
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-phenoxybutan-2-yl) isonicotinate (4x). Reaction of (but-3-en-1-yloxy)benzene **1x** (14.8 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3=10:1 v/v petroleum ether/ethyl acetate) gave compound **4x** (40.9 mg, 77%) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.1 Hz, 1H), 7.75 (s, 1H), 7.68 – 7.65 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 6.49 (s, 1H), 3.95 (s, 3H), 3.45 – 3.39 (m, 1H), 3.16 – 3.11 (m, 1H), 3.07 – 3.01 (m, 1H), 2.16 – 2.10 (m, 1H), 1.97 - 1.01 (m, 1H), 1.43 (dd, *J* = 14.6, 7.0 Hz, 1H), 1.26 – 1.23 (m, 1H), 0.10 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.3, 167.0, 165.6, 149.9, 138.2, 134.6, 131.2, 128.4, 126.8, 121.3, 120.9, 52.7, 45.0, 38.6, 38.1, 15.3, 1.2; IR (ATR) vmax 3453, 2953, 1737, 1597, 1293, 1106, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{45}NO_3Si_4$: $[M + H]^+$ = 532.2549. Found: 532.2534.



4y

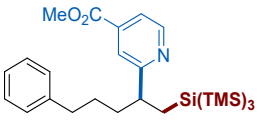
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-3-phenoxypropan-2-yl) isonicotinate (4y). Reaction of (allyloxy)benzene **1y** (14.4 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **4y** (40.8 mg, 79%) as an light-yellow oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 5.0 Hz, 1H), 7.83 (s, 1H), 7.70 (d, *J* = 3.5 Hz, 1H), 7.23 – 7.21 (m, 2H), 6.91 – 6.88 (m, 1H), 6.80 (dd, *J* = 8.7, 1.0 Hz, 2H), 4.14 (t, *J* = 8.3 Hz, 1H), 4.06 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.97 (s, 3H),3.47 - 3.44 (m, 1H), 1.52 (dd, *J* = 14.7, 8.1 Hz, 1H), 1.41 (dd, *J* =

14.7, 5.6 Hz, 1H), 0.11 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.8, 164.5, 158.7, 150.2, 150.2, 137.5, 129.3, 122.9, 121.1, 120.7, 114.6, 73.4, 52.7, 46.8, 9.5, 1.2; IR (ATR) νmax 3448, 2948, 2894, 2468, 2076, 1735, 1597, 1293, 1107, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{43}NO_3Si_4$: $[M+H]^+$ = 518.2393. Found: 518.2380.



4z

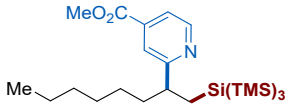
Methyl 2-(1-azido-4-benzamidobutan-2-yl) isonicotinate (4z). Reaction of allylbenzene **1z** (20.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **4z** (27.0 mg, 54%) as a yello w oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.6 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.49 (s, 1H), 7.18 – 7.15 (m, 2H), 7.10 (t, *J* = 6.7 Hz, 1H), 6.98 (d, *J* = 6.9 Hz, 2H), 3.91 (s, 3H), 3.25 – 3.20 (m, 1H), 2.99 (dd, *J* = 13.2, 8.2 Hz, 1H), 2.91 (dd, *J* = 13.2, 7.1 Hz, 1H), 1.52 (dd, *J* = 14.6, 8.6 Hz, 1H), 1.34 (dd, *J* = 14.6, 5.1 Hz, 1H), 0.06 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.7, 165.7, 150.1, 140.1, 137.4, 129.1, 128.2, 126.0, 122.2, 120.6, 52.6, 49.2, 46.1, 13.4, 1.2; IR (ATR) νmax 2941, 2854, 1737, 1561, 1438, 1113, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{43}NO_2Si_4$: $[M + H]^+$ = 502.2444. Found: 502.2430.



4aa

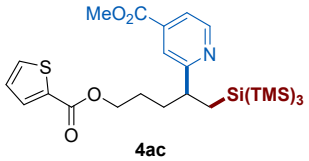
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) octan-2-yl) isonicotinate (4aa). Reaction of pent-4-en-1-ylbenzene **1aa** (14.6 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **4aa** (29.0 mg, 55%) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.0 Hz, 1H), 7.65 (d, *J* = 16.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.14 – 7.12 (m, 1H), 7.06 (d, *J* = 6.8 Hz, 2H), 3.96 (s, 3H), 2.98 – 2.94 (m, 1H), 2.58 – 2.48 (m, 2H), 1.81 – 1.73 (m, 2H), 1.51 – 1.45 (m, 1H), 1.35 (dd, *J* = 14.5, 5.9 Hz, 1H), 1.28 – 1.22 (m, 2H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.9, 165.8, 149.9, 142.2, 137.8, 137.8,

128.3, 128.2, 125.7, 121.6, 120.5, 52.7, 47.2, 38.5, 36.0, 30.0, 15.4, 1.3; IR (ATR) vmax 3439, 2948, 1738, 1595, 1442, 1291, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{46}N_2O_3Si_4$: $[M + H]^+$= 530.2757. Found: 530.2743.



4ab

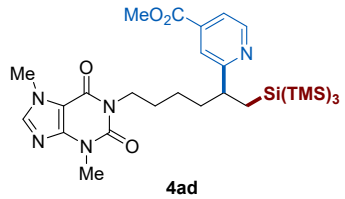
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) octan-2-yl) isonicotinate (4ab). Reaction of oct-1-ene **1ab** (11.2 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (1:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 1:1 v/v petroleum ether/ethyl acetate) gave compound **4ab** (25.6 mg, 52%) as a yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.7 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 2H), 3.95 (s, 3H),2.92 – 2.86 (m, 1H), 1.72 – 1.64 (m, 2H), 1.35 (dd, *J* = 14.5, 6.1 Hz, 1H), 1.25 – 1.13 (m, 8H), 0.96 – 0.89 (m, 1H), 0.81 (t, *J* = 7.0 Hz, 3H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.4, 166.0, 150.1, 137.5, 121.5, 120.3, 52.6, 47.4, 39.0, 31.7, 29.4, 27.9, 22.5, 15.3, 14.0, 1.3; IR (ATR) vmax 2941, 2854, 1738, 1561, 1438, 1288, 1112, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{49}NO_2Si_4$: $[M + H]^+$= 496.2913. Found: 496.2900.



4ac

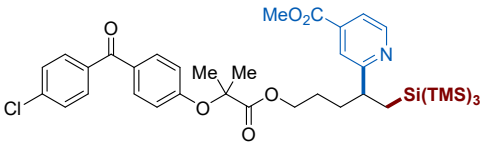
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((thiophene-2-carbonyl) oxy) pentan-2-yl) isonicotinate (4ac). Reaction of pent-4-en-1-yl thiophene-2-carboxylate **1ac** (19.6 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4ac** (42.1 mg, 73%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.8 Hz, 1H), 7.74 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.68 (s, 2H), 7.52 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.07 (t, 1H), 4.18 (td, *J* = 6.6, 1.3 Hz, 2H), 3.95 (s, 3H), 3.01 – 2.94 (m, 1H), 1.89 – 1.80 (m, 2H), 1.65 – 1.59 (m, 1H), 1.40 (dd, *J* = 14.5, 6.2 Hz, 2H), 1.25 (dd, *J* = 14.5, 7.8 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 167.4, 165.7, 162.2, 150.0, 137.9, 133.9, 133.3, 132.2, 127.6, 121.6, 120.7, 65.0,

52.7, 46.9, 35.1, 27.1, 15.4, 1.3; IR (ATR) νmax 3450, 2952, 1726, 1431, 1268, 1096, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{45}NO_4SSi_4$: $[M + Na]^+$ = 602.2039. Found: 602.2020.



4ad

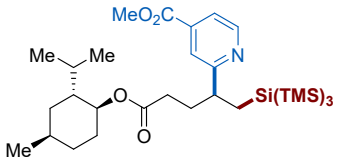
Methyl 2-(6-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) hexan-2-yl) isonicotinate (4ad). Reaction of 1-(hex-5-en-1-yl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione **1ad** (26.2 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (100% ethyl acetate elution, R_f = 0.5 in 100% ethyl acetate) gave compound **4ad** (46.9 mg, 73%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.9 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.46 (s, 1H), 3.94 (dd, *J* = 4.2, 1.5 Hz, 6H), 3.89 – 3.80 (m, 2H), 3.51 (s, 3H), 2.92 – 2.86 (m, 1H), 1.73 – 1.70 (m, 2H), 1.58 – 1.50 (m, 2H), 1.39 (dd, *J* = 15.1, 6.5 Hz, 1H), 1.21 (dd, *J* = 14.5, 7.0 Hz, 2H), 1.05 – 0.97 (m, 1H), 0.08 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.8, 165.9, 155.1, 151.3, 150.0, 148.6, 141.3, 137.6, 121.5, 120.4, 107.6, 52.6, 47.4, 41.2, 39.2, 33.5, 29.6, 28.1, 25.3, 14.8, 1.2; IR (ATR) νmax 3429, 3110, 2945, 1706, 1658, 1552, 1292, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{51}N_5O_4Si_4$: $[M + H]^+$ = 646.3091. Found: 646.3071.



4ae

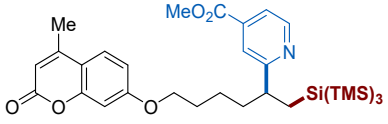
Methyl 2-(5-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4ae). Reaction of pent-4-en-1-yl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate **1ae** (38.6 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4ae** (58.2 mg, 76%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 5.0 Hz, 1H), 7.70 – 7.67 (m, 4H), 7.64 (s, 2H), 7.45 – 7.43 (m, 2H), 6.81 – 6.79 (m, 2H), 4.09 – 4.01 (m, 2H), 3.95 (s, 3H), 2.95 – 2.89 (s, 1H), 1.74

– 1.69 (m, 2H), 1.61 (s, 6H), 1.51 – 1.44 (s, 1H), 1.38 (dd, J = 14.6, 6.6 Hz, 1H), 1.31 – 1.25 (m, 1H), 1.19 (dd, J = 14.6, 7.3 Hz, 1H), 0.10 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 194.1, 173.5, 167.0, 165.6, 159.5, 150.0, 138.3, 136.4, 131.9, 131.1, 130.3, 128.5, 121.6, 120.8, 117.4, 79.3, 65.5, 52.7, 46.8, 35.1, 26.8, 25.4, 25.3, 15.1, 1.2; IR (ATR) νmax 2952, 2894, 1735, 1657, 1599, 1436, 1138, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{56}ClNO_6Si_4$: $[M + H]^+$ = 770.2946. Found: 770.2923.



4af

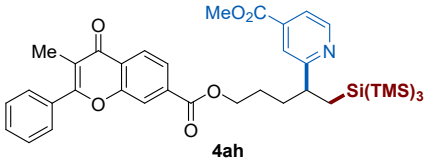
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-(((1R,2S,4S)-2-isopropyl-4-methylcyclohexyl)oxy)-5-oxopentan-2-yl)isonicotinate (4af). Reaction of (1R,2S,4S)-2-isopropyl-4-methylcyclohexyl pent-4-enoate **1af** (23.8 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **4af** (44.6 mg, 72%, d.r. = 1:1) as colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 4.1 Hz, 1H), 7.65 (s, 2H), 4.66 – 4.60 (m, 1H), 3.95 (s, 3H), 2.97 – 2.91 (m, 1H), 2.12 – 2.05 (m, 2H), 2.00 – 1.87 (m, 3H), 1.81 – 1.74 (m, 1H), 1.67 – 1.60 (m, 2H), 1.48 – 1.39 (m, 2H), 1.32 – 1.21 (m, 2H), 1.05 – 0.97 (m, 1H), 0.92 – 0.83 (m, 8H), 0.70 (dd, J = 10.1, 7.0 Hz, 3H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.6 (172.5), 167.0 (166.9), 165.7, 150.3, 137.8, 121.7 (121.6), 120.7, 74.0 (74.0), 52.7, 47.0 (46.9), 46.6, 40.9, 34.2 (34.2), 33.9 (33.7), 33.0 (32.9), 31.3, 26.2 (26.1), 23.3 (23.3), 22.0 (22.0), 20.7 (20.7), 16.2, 15.2 (15.0), 1.2; IR (ATR) νmax 2952, 2897, 1733, 1642, 1446, 1291, 1127, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{59}NO_4Si_4$: $[M + H]^+$ = 622.3594. Found: 622.3578.



4ag

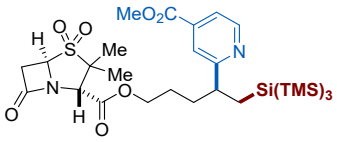
Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-6-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)hexan-2-yl)isonicotinate (4ag). Reaction of 7-(hex-5-en-1-yloxy)-4-methyl-2H-chromen-2-one **1ag** (25.8 mg, 0.10 mmol) with the *N*-methoxypyridinium

tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4ag** (43.5 mg, 68%) as a light-yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.7 Hz, 1H), 7.65 (s, 2H), 7.43 (dd, *J* = 8.8, 1.8 Hz, 1H), 6.75 (dd, *J* = 8.8, 1.9 Hz, 1H), 6.70 (t, *J* = 2.1 Hz, 1H), 6.09 (s, 1H), 3.94 (s, 3H), 3.89 (t, 2H), 2.94 – 2.91 (m, 1H), 2.37 (s, 3H), 1.79 – 1.70 (m, 4H), 1.38 – 1.31 (m, 2H), 1.24 (dd, *J* = 15.2, 8.9 Hz, 1H), 1.16 – 1.08 (m, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.8, 165.8, 162.0, 161.3, 155.2, 152.5, 150.1, 137.7, 125.4, 121.4, 120.5, 113.4, 112.5, 111.8, 101.3, 68.1, 52.6, 47.3, 38.5, 29.0, 24.2, 18.6, 15.3, 1.3; IR (ATR) νmax 2948, 2895, 1732, 1616, 1391, 1286, 1146, 832 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{51}NO_5Si_4$: $[M + H]^+$ = 642.2917. Found: 642.2902.



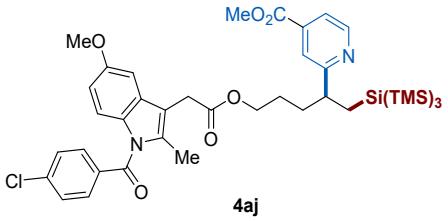
4ah

Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-((3-methyl-4-oxo-2-phenyl-4H-chromene-7-carbonyl)oxy)pentan-2-yl)isonicotinate (4ah). Reaction of hex-5-en-1-yl 3-methyl-4-oxo-2-phenyl-4H-chromene-7-carboxylate **1ah** (36.2 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4ah** (52.1 mg, 71%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.0 Hz, 1H), 8.45 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.16 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.76 – 7.75 (m, 2H), 7.65 (s, 2H), 7.51 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.41 (t, *J* = 7.7 Hz, 1H), 4.25 – 4.22 (m, 2H), 3.94 (s, 3H), 2.97 – 2.88 (m, 1H), 2.24 (s, 3H), 1.76 – 1.69 (m, 2H), 1.66 – 1.63 (m, 2H), 1.35 (dd, *J* = 11.7, 6.6 Hz, 1H), 1.23 (dd, *J* = 13.5, 7.2 Hz, 2H), 1.05 – 0.99 (m, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 178.2, 165.5, 164.4, 162.1, 160.9, 154.4, 150.6, 137.8, 136.1, 133.0, 130.8, 130.5, 129.3, 128.4, 124.0, 123.3, 122.7, 121.4, 120.6, 117.7, 65.1, 55.4, 52.7, 47.2, 31.9, 28.7, 26.3, 23.5, 11.7; IR (ATR) νmax 3443, 2948, 1738, 1441, 1291, 1249, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{38}H_{53}NO_6Si_4$: $[M + H]^+$ = 732.3023. Found: 732.2998.



4ai

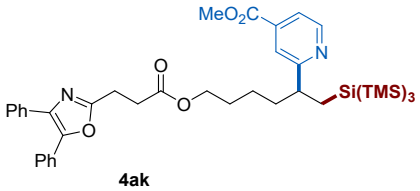
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-(4-(methoxycarbonyl) pyridin-2-yl) pentyl (2R,5S)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo [3.2.0] heptane-2-carboxylate 4,4-dioxide (4ai). Reaction of pent-4-en-1-yl (2R,5S)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide **1ai** (30.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4ai** (43.7 mg, 64%, d.r. = 1:1) light-yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (t, 1H), 7.68 (d, *J* = 12.2 Hz, 2H), 4.58 (dt, *J* = 4.3, 2.3 Hz, 1H), 4.32 (s, 1H), 4.15 – 4.09 (m, 1H), 4.07 – 4.01 (m, 1H), 3.96 (s, 3H), 3.47 (dd, *J* = 16.2, 4.2 Hz, 1H), 3.41 (d, *J* = 16.2 Hz, 1H), 2.97 – 2.91 (m, 1H), 1.79 (q, *J* = 7.9 Hz, 2H), 1.55 (d, *J* = 4.6 Hz, 3H), 1.42 – 1.37 (m, 1H), 1.33 (d, *J* = 6.2 Hz, 3H), 1.21 (dd, *J* = 14.5, 7.6 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.6, 166.9, 166.9 (166.8), 165.6, 150.0, 138.0, 121.5 (121.0), 120.8, 66.3 (66.2), 63.2, 62.6, 61.1, 52.8, 46.8, 38.3, 35.0 (35.0), 26.9 (26.8), 20.3 (20.3), 18.6 (18.6), 15.4 (15.3), 1.2; IR (ATR) νmax 2948, 2901, 1800, 1739, 1601, 1445, 1193, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{52}N_2O_7SSi_4$: $[M + H]^+$ = 685.2645. Found: 685.2623.



4aj

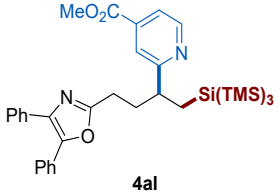
Methyl 2-(5-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)-1-(1,1-,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4aj). Reaction of pent-4-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate **1aj** (42.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 4:1 v/v petroleum ether/ethyl acetate) gave compound **4aj** (41.9 mg, 52%) as a yellow-

green oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.1 Hz, 1H), 7.69 (s, 2H), 7.66 – 7.64 (m, 2H), 7.47 – 7.45 (m, 2H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.00 (t, *J* = 6.9 Hz, 2H), 3.97 (s, 3H), 3.80 (s, 3H), 3.61 (s, 2H), 3.01 – 2.91 (m, 1H), 2.34 (s, 3H), 1.86 – 1.80 (m, 1H), 1.77 (dd, *J* = 10.5, 4.2 Hz, 1H), 1.56 – 1.48 (m, 1H), 1.38 (dd, *J* = 14.5, 6.1 Hz, 1H), 1.33 – 1.28 (m, 1H), 1.26 – 1.21 (m, 1H), 0.14 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.8, 168.2, 167.1, 165.5, 156.0, 139.2, 135.9, 133.9, 131.2, 130.8, 130.6, 129.1, 121.7, 120.8, 114.9, 112.5, 111.6, 101.2, 64.9, 55.7, 52.8, 46.7, 35.0, 30.2, 27.1, 1545, 13.3, 1.3; IR (ATR) νmax 2948, 1738, 1685, 1478, 1300, 1157, 835cm^{-1}; HRMS (ESI) Calcd for $C_{40}H_{57}ClN_2O_6Si_4$: $[M + H]^+$ = 809.3055 Found: 809.3035.



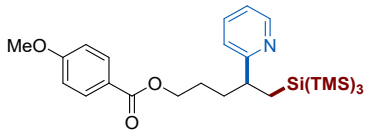
4ak

Methyl 2-(6-((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)hexan-2-yl)isonicotinate (4ak). Reaction of hex-5-en-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate **1ak** (37.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4ak** (44.6 mg, 59%) as a light-yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 – 8.70 (m, 1H), 7.65 (d, *J* = 3.9 Hz, 2H), 7.62 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.57 – 7.55 (m, 2H), 7.37 – 7.33 (m, 6H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.94 (s, 3H), 3.13 (t, 2H), 2.94 – 2.88 (m, 1H), 2.86 – 2.83 (m, 2H), 1.73 (q, *J* = 7.2, 6.0 Hz, 2H), 1.62 – 1.51 (m, 2H), 1.37 (dd, *J* = 14.5, 6.3 Hz, 1H), 1.23 (dd, *J* = 14.5, 7.7 Hz, 2H), 1.06 – 0.97 (m, 1H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.9, 167.8, 165.8, 161.7, 150.2, 145.4, 137.7, 135.1, 132.4, 129.0, 128.6, 128.5, 128.4, 128.0, 127.9, 126.4, 121.5, 120.5, 64.58, 52.6, 47.2, 38.5, 31.1, 28.64, 24.2, 23.5, 15.3, 1.3; IR (ATR) νmax 3443, 2948, 1738, 1592, 1441, 1291, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{40}H_{58}N_2O_5Si_4$: $[M + Na]^+$ = 781.3315. Found: 781.3288.



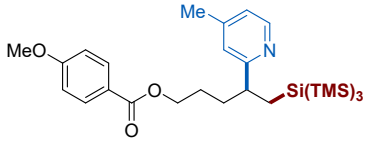
4al

Methyl 2-(4-(4,5-diphenyloxazol-2-yl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)butan-2-yl)isonicotinate (4al). Reaction of 2-(but-3-en-1-yl)-4,5-diphenyloxazole **1al** (27.5 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4al** (42.6 mg, 65%) as a orange-yellow oil liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 1H), 7.73 (s, 1H), 7.63 – 7.57 (m, 3H), 7.52 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.36 – 7.29 (m, 6H), 3.89 (s, 3H), 3.11 – 3.03 (m, 1H), 2.66 (dt, *J* = 8.2, 4.1 Hz, 2H), 2.34 – 2.26 (m, 2H), 1.50 (dd, *J* = 14.5, 6.9 Hz, 1H), 1.29 (d, *J* = 7.5 Hz, 1H), 0.11 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.5, 165.6, 162.8, 150.1, 145.1, 137.8, 134.9, 132.5, 130.0, 129.0, 128.9, 128.5, 128.4, 128.3, 127.9, 127.8, 126.4, 122.1, 120., 52.6, 46.6, 36.0, 26.5, 15.3, 1.2; IR (ATR) νmax 2947, 1731, 1437, 1289, 837, 7 59 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{50}N_2O_3Si_4$: $[M + H]^+$ = 659.2971 Found: 659.2949.



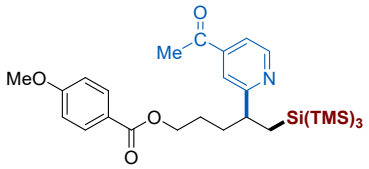
5a

5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(pyridin-2-yl)pentyl 4-methoxybenzoate (5a). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2b** (29.6 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **5a** (28.8 mg, 53%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.5 Hz, 1H), 7.94 (d, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.06 (m, 2H), 6.90 – 6.87 (m, 2H), 4.20 – 4.15 (m, 2H), 3.85 (s, 3H), 2.96 – 2.83 (m, 1H), 1.90 – 1.80 (m, 2H), 1.67 – 1.58 (m, 1H), 1.42 (dt, *J* = 13.8, 6.9 Hz, 2H), 1.24 (dd, *J* = 14.5, 7.6 Hz, 1H), 0.12 (s, 28H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.3, 165.9, 163.2, 149.1, 136.9, 131.6, 122.8, 122.7, 121.5, 113.5, 64.7, 55.4, 46.7, 35.4, 27.2, 15.3, 1.3;IR (ATR) νmax 3434, 2951, 1716, 1602, 1257, 1111, 838 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{47}NO_3Si_4$: $[M + H]^+$ = 546.2706. Found: 546.2691.



5b

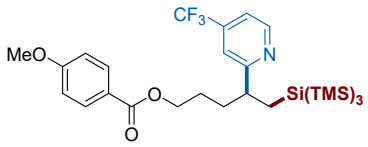
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (5b). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2c** (31.7 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5b** (31.7 mg, 57 %) as a colorless oil liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.1 Hz, 1H), 7.97 – 7.94 (m, 2H), 6.98 (s, 2H), 6.91 – 6.87 (m, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.85 (s, 3H), 2.95 – 2.81 (m, 1H), 2.36 (s, 3H), 1.89 – 1.81 (m, 2H), 1.69 – 1.51 (m, 2H), 1.43 – 1.36 (m, 2H), 1.27 (dd, *J* = 8.6, 3.0 Hz, 1H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.2, 163.3, 131.6, 124.4, 123.7, 122.6, 113.5, 64.3, 55.4, 44.9, 34.5, 27.2, 21.8, 15.8, 1.3; IR (ATR) νmax 2952, 2891, 1702, 1602, 1508, 1445, 1250, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{49}NO_3Si_4$: $[M + H]^+$ = 560.2862. Found: 560.2846.



5c

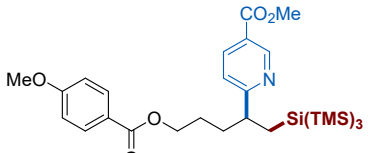
4-(4-Acetylpyridin-2-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5c). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2d** (35.9 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5c** (35.6 mg, 61%) as a yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.56 (d, *J* = 5.2 Hz, 2H), 6.90 – 6.87 (m, 2H), 4.20 – 4.15 (m, 2H), 3.85 (s, 3H), 3.04 – 2.95 (m, 1H), 2.61 (s, 3H), 1.93– 1.83 (m, 2H), 1.67 – 1.59 (m, 1H), 1.44 – 1.38 (m, 2H), 1.29 – 1.24 (m, 1H), 0.12 (s, 29H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 197.5, 167.8, 166.3, 163.3, 150.4, 143.5, 131.6, 122.7, 119.9, 119.3, 113.5, 64.5, 55.4, 47.0, 35.3, 27.2, 26.7, 15.5, 1.3; IR (ATR) νmax 2948, 2

897, 1708, 1605, 1258, 1108, 838cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{49}NO_4Si_4$: $[M + Na]^+$ = 610.2631. Found: 610.2614.



5d

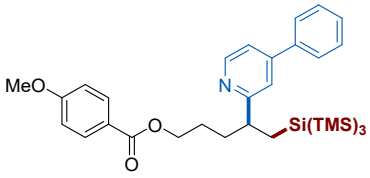
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-(trifluoromethyl)pyridin-2-yl)pentyl 4-methoxybenzoate (5d). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2e** (39.8 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **5d** (43.3 mg, 71 %) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.1 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.35 (s, 1H), 6.90 – 6.88 (m, 2H), 4.19 (td, *J* = 6.5, 2.5 Hz, 2H), 3.84 (s, 3H), 3.02 – 2.97 (m, 1H), 1.94 – 1.88 (m, 1H), 1.86 (dd, *J* = 12.5, 8.2 Hz, 1H), 1.68 – 1.60 (m, 1H), 1.41 (dd, *J* = 14.6, 6.3 Hz, 2H), 1.26 (dd, *J* = 14.6, 7.6 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.8, 166.2, 163.3, 149.9, 139.2 (q, *J* = 34.4 Hz), 131.6, 122.7 (q, *J* = 273.4 Hz), 122.7, 118.1 (q, *J* = 3.7 Hz), 117.4 (q, *J* = 3.42 Hz), 113.5, 64.4, 55.5, 47.0, 35.2, 27.1, 15.4, 1.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.8 (s); IR (ATR) νmax 3729, 2950, 2900, 1714, 1608, 1410, 1168, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{46}F_3NO_3Si_4$: $[M + Na]^+$ = 636.2399. Found: 636.2380.



5e

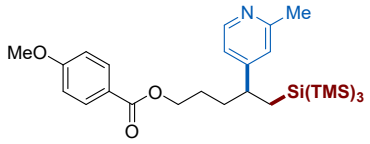
Methyl 6-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)-5-((4-methoxy-benzoyl)oxy)pentan-2-yl)nicotinate (5e). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2f** (38.3 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5e** (43.2 mg, 72 %) as a colorless oil liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 6.89 – 6.87 (m, 2H), 4.19 – 4.15 (m, 2H), 3.93 (s, 3H), 3.84 (s,

3H), 2.96 – 2.91 (m, 1H), 1.91 – 1.81 (m, 2H), 1.64 – 1.57 (m, 1H), 1.40 (dt, J = 14.6, 6.7 Hz, 2H), 1.23 (dd, J = 14.6, 7.7 Hz, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.9, 166.2, 165.8, 163.2, 150.8, 137.6, 131.5, 123.9, 122.7, 122.1, 113.5, 64.5, 55.4, 52.2, 47.1, 35.1, 27.2, 15.3, 1.3; IR (ATR) νmax 3412, 2948, 1721, 1595, 1266, 1110, 832 cm^{-1}; HRMS (ESI) Calcd for $C_{29}H_{49}NO_5Si_4$: $[M + Na]^+$ = 626.2580. Found: 626.2564.



5f

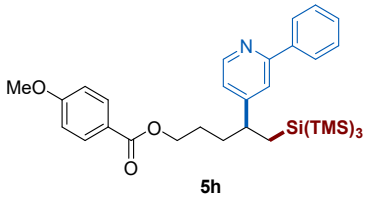
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-phenylpyridin-2-yl)pentyl 4-methoxybenzoate (5f). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2g** (41.0 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 5:1 v/v petroleum ether/ethyl acetate elution, *R*f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5f** (39.0mg, 63%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 5.3 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.63 (dd, J = 8.2, 1.5 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.41 (d, J = 22.7 Hz, 2H), 6.88 – 6.85 (m, 2H), 4.24 – 4.17 (m, 2H), 3.84 (s, 3H), 3.08 – 2.96 (m, 1H), 1.94 (q, J = 9.3 Hz, 2H), 1.74 – 1.65 (m, 1H), 1.53 – 1.48 (m, 2H), 1.33 (dd, J = 14.6, 7.8 Hz, 1H), 0.15 (s, 28H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.3, 165.8, 163.2, 148.6, 144.0, 137.8, 131.6, 129.5, 129.2, 127.2, 122.7, 120.8, 120.0, 113.5, 64.5, 55.4, 46.5, 35.2, 27.3, 15.5, 1.3; IR (ATR) νmax 2951, 2899, 1713, 1608, 1255, 1105, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{51}NO_3Si_4$: $[M+H]^+$ = 622.3019. Found: 622.3002.



5g

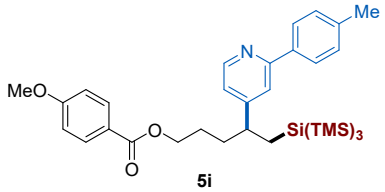
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-methylpyridin-4-yl)pentyl 4-methoxybenzoate (5g). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2h** (31.7 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 5:1 v/v petroleum ether/ethyl acetate elution, *R*f = 0.2 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5g** (30.7 mg, 55 %) as a colorless oil liquid; ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.43 (d, J = 5.3 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.10 (d, J = 6.4 Hz, 2H), 6.93 – 6.89 (m, 2H), 4.21 – 4.17 (m, 2H), 3.86 (s, 3H), 2.72 – 2.62 (m, 4H), 2.00 – 1.86 (m, 1H), 1.63 – 1.53 (m, 1H), 1.46 – 1.37 (m, 1H), 1.18 (d, J = 6.8 Hz, 2H), 0.13 (s, 27H); ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 166.2, 163.7, 163.4, 155.7, 144.1, 131.6, 124.3, 122.4, 121.4, 113.6, 64.0, 55.4, 45.5, 34.9, 27.3, 21.6, 17.2, 1.3; IR (ATR) νmax 3439, 2951, 2892, 1713, 1606, 1510, 1168, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{49}NO_3Si_4$: $[M + H]^+$ = 560.2862. Found: 560.2844.



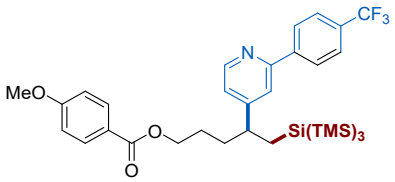
5h

5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-phenylpyridin-4-yl)pentyl 4-methoxybenzoate (5h). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2i** (41.0 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5h** (32.8 mg, 53 %) as a coloeless oil liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, J = 4.7 Hz, 1H), 8.04 (d, J = 7.9 Hz, 2H), 7.92 (d, J = 7.0 Hz, 2H), 7.61 (s, 1H), 7.58 – 7.50 (m, 3H), 7.29 (s, 1H), 6.90 – 6.85 (m, 2H), 4.22 (t, J = 5.6 Hz, 2H), 3.85 (s, 3H), 2.84 – 2.73 (m, 1H), 2.03 – 1.97 (m, 1H), 1.64 (dd, J = 15.8, 7.2 Hz, 2H), 1.51 – 1.40 (m, 1H), 1.25 (d, J = 6.2 Hz, 2H), 0.15 (s, 27H); ^{13}C {^1H} NMR (151 MHz, $CDCl_3$) δ 166.2, 163.4, 156.0, 147.6, 141.1, 137.4, 131.6, 130.2, 129.1, 128.9, 127.5, 122.5, 121.8, 120.7, 113.6, 64.2, 55.4, 45.5, 35.3, 27.3, 17.1, 1.3; IR (ATR) νmax 3414, 2939, 1714, 1603, 1254, 1106, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{51}NO_3Si_4$: $[M + H]^+$ = 622.3019. Found: 622.3004.



5i

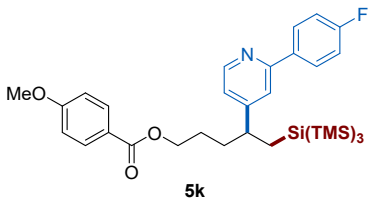
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)-trisilan-2-yl)-4-(2-(p-tolyl)pyridin-4-yl)-pentyl 4-methoxybenzoate (5i). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2j** (43.1mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5i** (34.2 mg, 54%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.1 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.51 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 5.2 Hz, 1H), 6.88 – 6.85 (m, 2H), 4.21 (td, *J* = 6.3, 2.8 Hz, 2H), 3.84 (s, 3H), 2.73 – 2.68 (m, 1H), 2.41 (s, 3H), 1.98 – 1.92 (m, 1H), 1.69 – 1.60 (m, 2H), 1.52 – 1.46 (m, 1H), 1.29 – 1.22 (m, 2H), 0.14 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.3 163.3, 158.0 157.5, 149.4, 139.1 136.2, 131.6, 129.5, 127.0, 122.6, 120.9, 119.5, 113.5, 64.4, 55.4, 45.2, 35.7, 27.3, 21.3, 16.9, 1.3; IR (ATR) νmax 2953, 1713, 1604, 1508, 1111, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{53}NO_3Si_4$: [M + H] $^+$ = 636.3175. Found: 636.3153.



5j

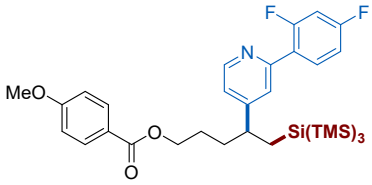
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-(4-(trifluoro-methyl)-phenyl)pyridin-4-yl)pentyl 4-methoxybenzoate (5j). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2k** (51.2 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5j** (39.8 mg, 58%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.1 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.94 – 7.91 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.55 (s, 1H), 7.15 (dd, *J* = 5.1, 1.6 Hz, 1H), 6.88 – 6.85 (m, 2H), 4.25 – 4.19 (m, 2H), 3.84 (s, 3H), 2.77 – 2.71 (m, 1H), 2.00 – 1.94 (m, 1H), 1.72 – 1.59 (m, 2H), 1.53 – 1.46 (m, 1H), 1.27 – 1.5 (m, 2H), 0.15 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.2, 163.3, 158.3, 156.0, 149.8, 142.4, 131.5, 130.9 (q, *J* = 32.4 Hz), 127.4, 125.7 (q, *J* = 3.8 Hz), 125.2, 122.6, 122.1, 120.1, 113.5, 64.3, 55.4, 45.2, 35.7, 27.3, 17.0, 1.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.6 (s); IR (ATR) νmax

2951, 2897, 1712, 1510, 1326, 1260, 1167, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{34}H_{50}F_3NO_3Si_4$: $[M + H]^+$ = 690.2893. Found: 690.2869.



5k

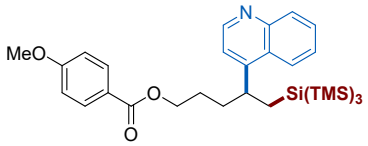
4-(2-(4-Fluorophenyl)pyridin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5k). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2l** (43.7 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5k** (39.2 mg, 61%) as a colorless oil liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.1 Hz, 1H), 7.98 – 7.92 (m, 4H), 7.47 (s, 1H), 7.15 (t, *J* = 8.7 Hz, 2H), 7.08 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.88 – 6.85 (m, 2H), 4.20 (d, *J* = 6.1 Hz, 2H), 3.84 (s, 3H), 2.74 – 2.68 (m, 1H), 1.98 – 1.85 (m, 1H), 1.71 – 1.59 (m, 2H), 1.55 – 1.46 (m, 1H), 1.29 – 1.21 (m, 2H), 0.14 (s, 27H);^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 166.2, 164.5, 163.3, 162.5, 158.0, 156.6, 149.6, 135.3 (d, *J* = 3.0 Hz), 131.5, 128.9 (d, *J* = 8.3 Hz), 122.6, 121.2, 119.4, 115.6 (d, *J* = 21.6 Hz), 113.5, 64.3, 55.4, 45.2, 35.7, 27.3, 16.9, 1.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.9 (s); IR (ATR) νmax 3425, 2950, 2897, 1712, 1604, 1513, 1257, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{50}FNO_3Si_4$: $[M + H]^+$ = 640.2925. Found: 640.2903.



5l

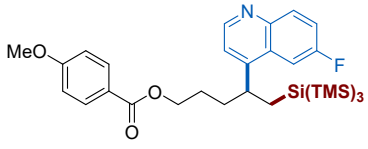
4-(2-(2,4-Difluorophenyl)pyridin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trim-ethylsilyl)-trisilan-2-yl)pentyl 4-methoxybenzoate (5l). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2m** (46.4 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5l** (42.6 mg, 65%) as a colorless oil liquid; ^1H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.1 Hz, 1H), 8.00 (dd, *J* = 8.8, 6.7 Hz, 1H), 7.95 – 7.92 (m, 2H), 7.57 (s, 1H), 7.13 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.94

– 6.91 (m, 1H), 6.89 – 6.87 (m, 2H), 4.21 (dt, J = 8.5, 4.2 Hz, 2H), 3.85 (s, 3H), 2.74 – 2.69 (m, 1H), 1.98 – 1.92 (m, 1H), 1.70 – 1.59 (m, 2H), 1.53 – 1.46 (m, 1H), 1.27 (dd, J = 9.6 Hz, 1H), 1.21 (dd, J = 14.6, 8.1 Hz, 1H), 0.14 (s, 28H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.3, 164.3 (d, J = 11.7 Hz), 163.3, 162.3 (d, J = 12.3 Hz), 161.5 (d, J = 12.1 Hz), 159.5 (d, J = 11.9 Hz), 152.3, 149.3, 132.3 (dd, J = 9.8, 4.3 Hz), 131.6, 123.5 (d, J = 9.0 Hz), 122.6, 121.6, 113.5, 112.0 (dd, J = 21.1, 3.6 Hz), 104.6 – 104.2 (m), 64.3, 55.4, 45.1, 35.6, 27.3, 16.9, 1.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -108.7 (s), -112.3 (s); IR (ATR) νmax 3403, 2951, 2901, 1714, 1605, 1261, 1106, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{33}H_{49}F_2NO_3Si_4$: $[M + H]^+$ = 658.2830. Found: 658.2809.



5m

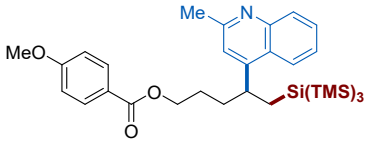
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(quinolin-4-yl)pentyl 4-methoxybenzoate (5m). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2n** (37.1 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5m** (35.0 mg, 59 %) as a colorless oil liquid; ^{1}H NMR (600MHz, $CDCl_3$) δ 8.87 (d, J = 4.6 Hz, 1H), 8.18 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.6 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.74 – 7.71 (m, 1H), 7.59 – 7.56 (m, 1H), 7.35 (s, 1H), 6.89 – 6.86 (m, 2H), 4.18 (t, J = 6.5 Hz, 2H), 3.84 (s, 3H), 3.70 – 3.58 (m, 1H), 2.10 – 2.04 (m, 1H), 1.91 – 1.83 (m, 1H), 1.66 – 1.59 (m, 1H), 1.54 – 1.48 (m, 1H), 1.41 – 1.38 (m, 1H), 1.30 – 1.25 (m, 1H), 0.15 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.2, 163.3, 154.4, 149.9, 148.1, 131.5, 130.2, 129.3, 127.3, 126.6, 122.5, 117.5, 113.5, 64.4, 55.4, 40.6, 34.7, 27.0, 16.6, 1.3; IR (ATR) ν_{max} 2948, 2895, 2100, 1713, 1604, 1510, 1254, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{31}H_{49}NO_3Si_4$: $[M + H]^+$ = 596.2862. Found: 596.2843.



5n

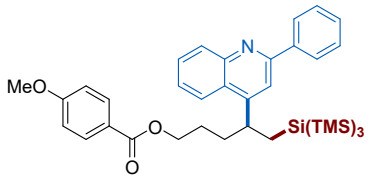
4-(6-Fluoroquinolin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5n). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10

mmol) with the *N*-methoxypyridinium tetrafluoroborate **2o** (39.8mg; 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5j** (32.4 mg, 53%) as a colorless oil liquid; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.6 Hz, 1H), 8.16 (dd, *J* = 9.2, 5.8 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.34 (d, *J* = 4.4 Hz, 1H), 6.90 – 6.86 (m, 2H), 4.19 (t, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 3.49 – 3.40 (m, 1H), 2.14 – 2.00 (m, 1H), 1.91 – 1.77 (m, 2H), 1.67 – 1.49 (m, 2H), 1.31 (dd, *J* = 27.4, 9.6 Hz, 2H), 0.15 (s, 27H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.2, 163.3, 161.7, 156.0, 149.3 (d, *J* = 1.3 Hz), 145.2, 138.6, 132.7 (d, *J* = 8.5 Hz), 131.6, 128.2, 122.5, 119.7 (d, *J* = 2.4 Hz), 113.5, 106.5(d, *J* = 2.4 Hz), 64.4, 55.4, 40.6, 34.5, 27.0, 16.6, 1.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.0 (s); IR (ATR) νmax 3464, 2948, 1724, 1603, 1258, 1111, 835 cm^{-1}; HRMS (ESI) Calcd for : $C_{31}H_{48}FNO_3Si_4$: $[M + H]^+$ = 614.2768. Found: 614.2752.



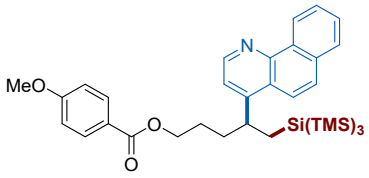
5o

5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-methylquinolin-4-yl)pentyl 4-methoxybenzoate (5o). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2p** (39.2 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 4:1 v/v petroleum ether/ethyl acetate) gave compound **5o** (41.9 mg, 69 %) as a colorless oil liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.72 – 7.67 (m, 1H), 7.51 (t, *J* = 8.2 Hz, 1H), 7.21 (s, 1H), 6.90 – 6.85 (m, 2H), 4.19 (t, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.68– 3.52 (m, 1H), 2.77 (s, 3H), 2.09 – 2.00 (m, 1H), 1.85 (s, 1H), 1.69 – 1.55 (m, 1H), 1.54 – 1.49 (m, 1H), 1.42 – 1.29 (m, 2H), 0.13 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.3, 163.2, 144.2, 131.6, 129.8 128.8, 127.1, 125.4, 123.5, 122.8, 121.0, 113.5, 64.7, 55.4, 47.5, 35.3, 27.2, 18.8, 15.0, 1.3.; IR (ATR) νmax 3447, 2948, 2895, 1714, 1600, 1254, 1107, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{51}NO_3Si_4$: $[M + H]^+$ = 610.3019. Found: 610.3001.



5p

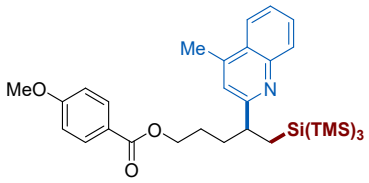
5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-phenylquinolin-4-yl)pentyl 4-methoxybenzoatee (5p). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2q** (48.5mg; 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **5p** (40.9 mg, 61 %) as a colorless oil liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.18 – 8.15 (m, 2H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.78 (t, *J* = 7.2 Hz, 2H), 7.59 – 7.50 (m, 4H), 6.86 – 6.82 (m, 2H), 4.22 (t, *J* = 6.2 Hz, 2H), 3.84 (s, 3H), 3.76 – 3.66 (m, 1H), 2.20 – 2.10 (m, 1H), 2.00 – 1.92 (m, 1H), 1.76 – 1.58 (m, 2H), 1.45 (d, *J* = 14.0 Hz, 1H), 1.32 (d, *J* = 9.1 Hz, 1H), 0.17 (s, 31H); ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.2, 163.3, 156.7, 147.0, 138.2, 131.5, 130.2, 129.9, 129.6, 129.0, 128.0, 126.7, 126.3, 122.5, 115.5, 113.5, 64.3, 55.4, 38.3, 34.6, 27.11, 17.12, 1.4; IR (ATR) νmax 3457, 2948, 1712, 1598, 1257, 1106, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{37}H_{53}NO_3Si_4$: $[M + H]^+$=672.3175. Found: 672.3152.



5q

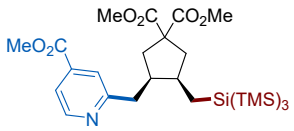
4-(Benzo[h]quinolin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5q). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2r** (44.6 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel 10:1 v/v petroleum ether/ethyl acetate elution, *R*f = 0.3 in 8:1 v/v petroleum ether/ethyl acetate) gave compound **5q** (30.2mg, 47%) as a colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (d, *J* = 7.8 Hz, 1H), 8.98 (d, *J* = 4.8 Hz, 1H), 7.98 – 7.83 (m, 5H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 4.6 Hz, 1H), 6.86 – 6.81 (m, 2H), 4.20 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 3H), 3.75 – 3.64 (m, 1H), 2.15 – 2.05 (m, 1H), 1.89 (d, *J* = 8.1 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.58 – 1.52 (m, 1H), 1.44 (dd, *J* = 14.5, 4.9 Hz, 1H), 1.34 – 1.26 (m, 1H), 0.17

(s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.2, 163.2, 153.8, 148.5, 146.6, 133.1, 132.0, 131.5, 129.3, 128.2, 127.7, 127.6, 127.1, 125.0, 122.6, 121.8, 113.4, 103.9, 64.4, 55.4, 38.0, 34.8, 26.9, 16.6, 1.4; IR (ATR) vmax 2951, 2896, 1716, 1605, 1258, 1107, 1031, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{35}H_{51}NO_3Si_4$: $[M + H]^+$ = 646.3019. Found: 646.3000.



5r

5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-methylquinolin-2-yl)pentyl 4-methoxybenzoate (5r). Reaction of pent-4-en-1-yl 4-methoxybenzoate **1a** (22.0 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2s** (39.2 mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (10:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 10:1 v/v petroleum ether/ethyl acetate) gave compound **5r** (41.1 mg, 67%) as a yellow oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.39, 1H), 7.95 – 7.92 (m, 3H), 7.67 (s, 1H), 7.50 (s, 1H), 7.11 (s, 1H), 6.89 – 6.87 (m, 2H), 4.20 (td, J = 6.5, 2.2 Hz, 2H), 3.85 (s, 3H), 3.09 – 2.99 (m, 1H), 2.69 (s, 3H), 1.94 (s, 2H), 1.73 – 1.66 (m, 1H), 1.52 (dd, J = 14.3, 6.4 Hz, 2H), 1.29 – 1.23 (m, 1H), 0.12 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.2, 163.3, 158.4, 154.8, 147.3, 131.5, 129.5, 129.0, 125.9, 122.5, 118.2, 113.5, 64.4, 55.4, 37.8, 34.8, 27.0, 25.0, 16.3, 1.3; IR (ATR) vmax 3441, 2951, 2895, 1713, 1603, 1254, 837cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{51}NO_3Si_4$: $[M + H]^+$ = 610.3019. Found: 610.3001.



7

Dimethyl (3R,4R)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-4-((4-(methoxycarbonyl)pyridin-2-yl)methyl)cyclopentane-1,1-dicarboxylate (7). Reaction of dimethyl 2,2-diallylmalonate **6** (21.2 mg, 0.10 mmol) with the *N*-methoxypyridinium tetrafluoroborate **2a** (38.3mg, 0.15 mmol) and tris(trimethylsilyl)silane **3** (93 uL, 0.30 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **7** (25.1 mg, 42%) as a light yellow oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, J = 5.0 Hz, 1H), 7.70 (s, 1H), 7.65 (dd, J = 5.0, 1.4 Hz, 1H), 3.94 (s, 3H), 3.73 (s, 3H), 3.68

(s, 3H), 3.01 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.68 (dd, *J* = 13.5, 10.1 Hz, 1H), 2.63 – 2.59 (m, 1H), 2.55 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.24 (dd, *J* = 13.8, 6.6 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.05 (dd, *J* = 14.0, 2.3 Hz, 1H), 0.69 (dd, *J* = 13.9, 12.3 Hz, 1H), 0.15 (s, 27H); ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1 (173.0), 173.1 (172.9), 165.8 (165.8), 162.5 (162.2), 150.2 (150.2), 137.7 (137.6), 122.6 (122.4), 120.4 (120.3), 58.7 (57.9), 52.7 (52.7), 52.6 (52.6), 44.2 (49.0), 41.4 (45.2), 41.1 (43.3), 38.0 (42.2), 37.7 (39.6), 14.1 (22.7), 8.1 (11.6), 1.3 (1.4); IR (ATR) νmax 2949, 2890, 1732, 1562, 1436, 1244, 830, 732cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{49}NO_6Si_4$: $[M + H]^+$ = 596.2710. Found: 596.2718.

IX. References

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[2] Y. Chen, G.-Y. Zhang, C. Guo, P. Lan, M. G. Banwell, Y.-T. He, *Chem. Eur. J.* **2022**, *28*, e202104627.

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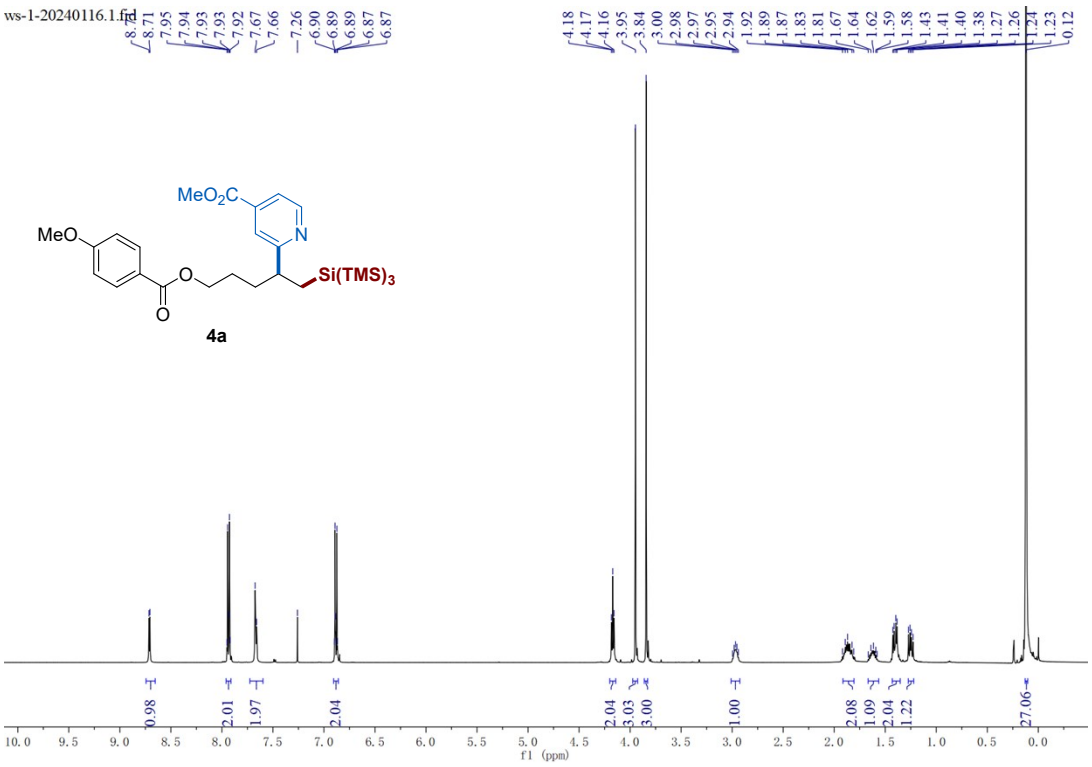
Appendix I

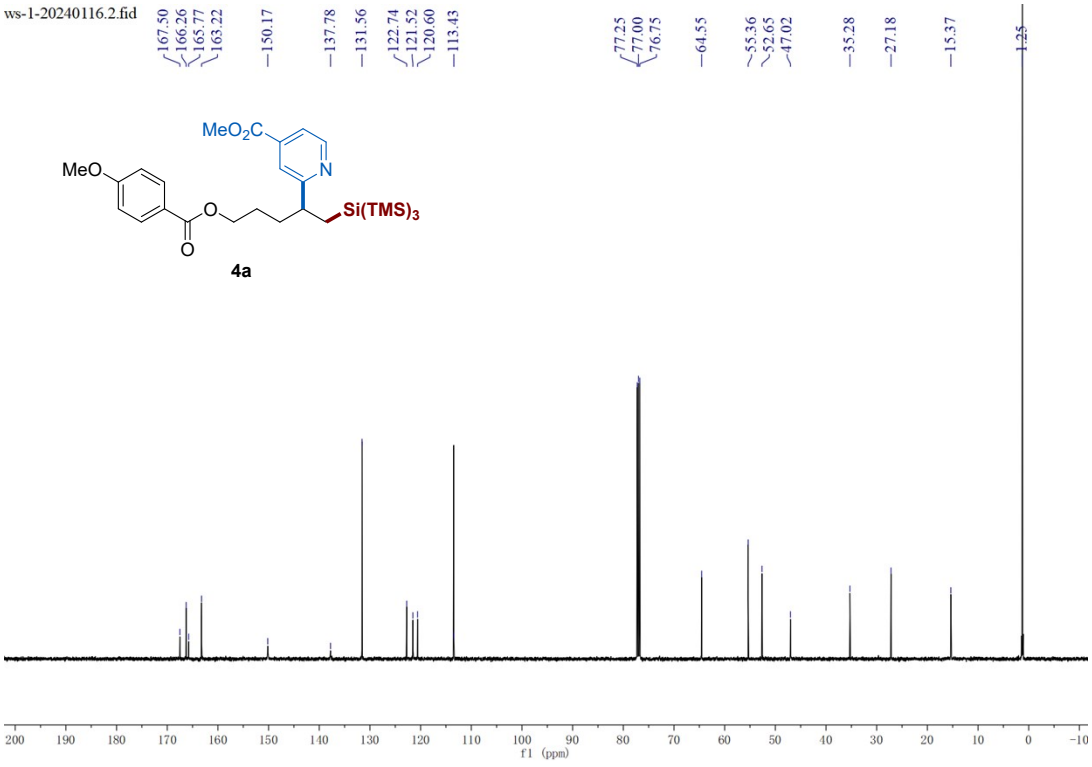
Copies of Relevant ^{1}H-, $^{13}C\{^{1}H\}$- and ^{19}F-NMR Spectra

Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((4-methoxybenzoyl) oxy) pentan-2-yl) isonicotinate (4a)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

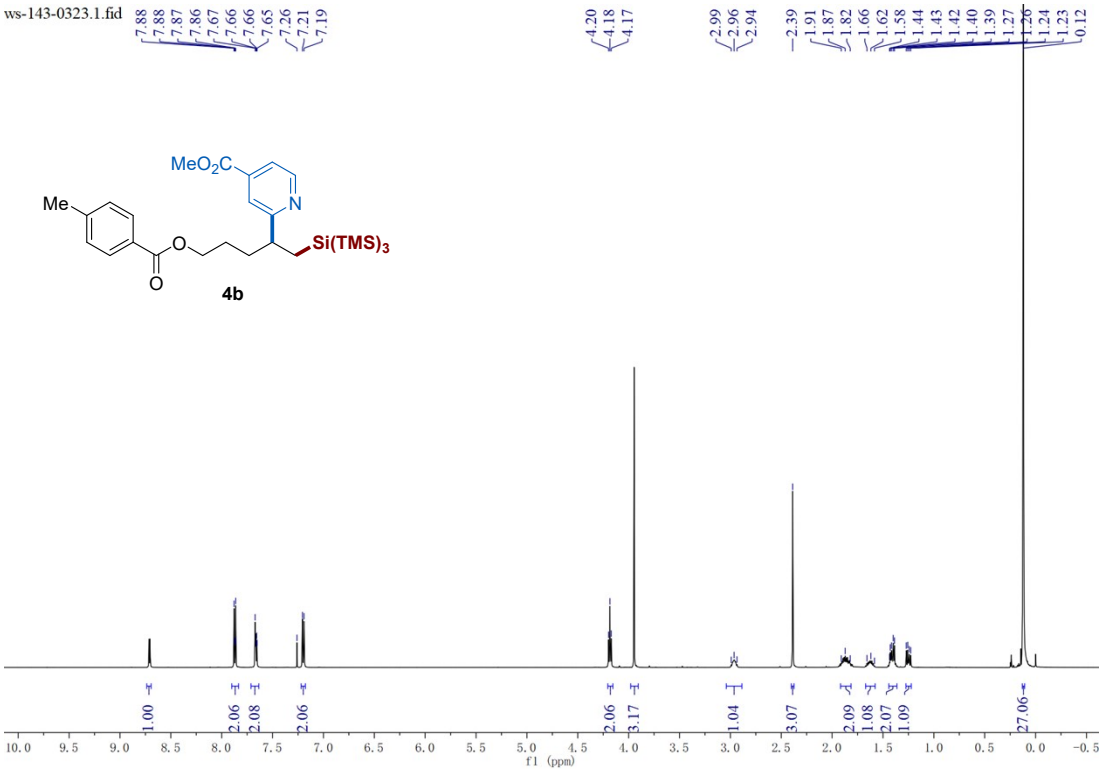


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

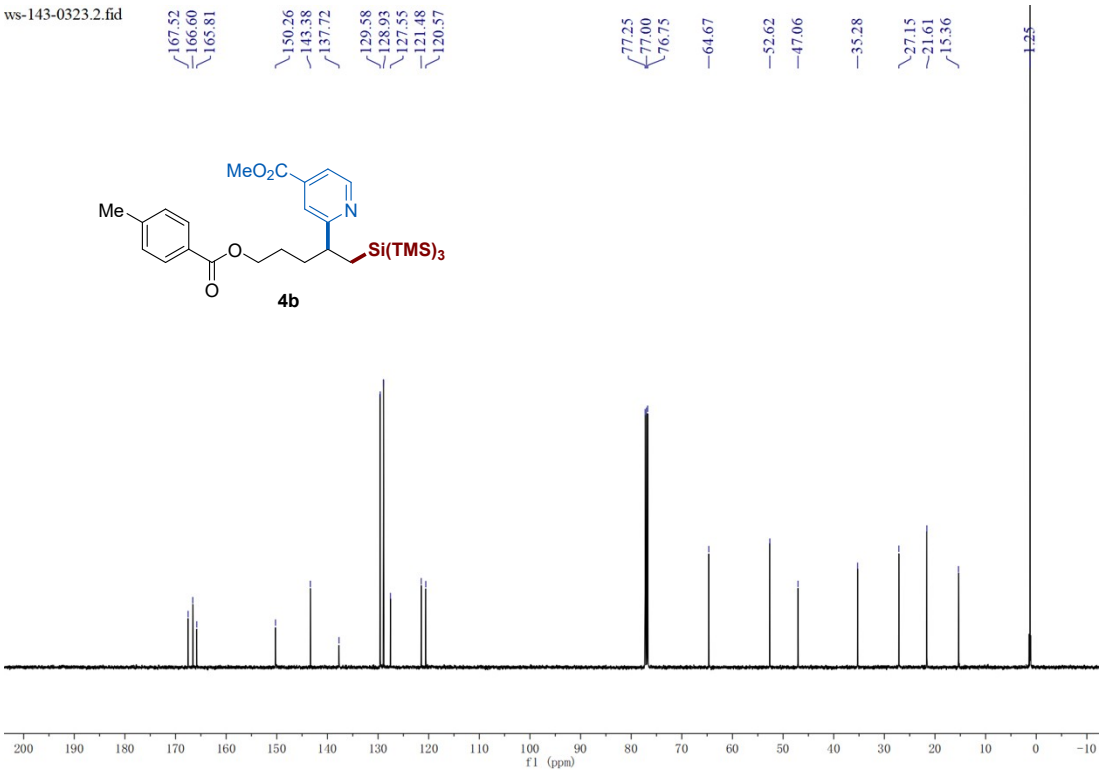


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((4-methylbenzoyl) oxy) pentan-2-yl) isonicotinate (4b).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

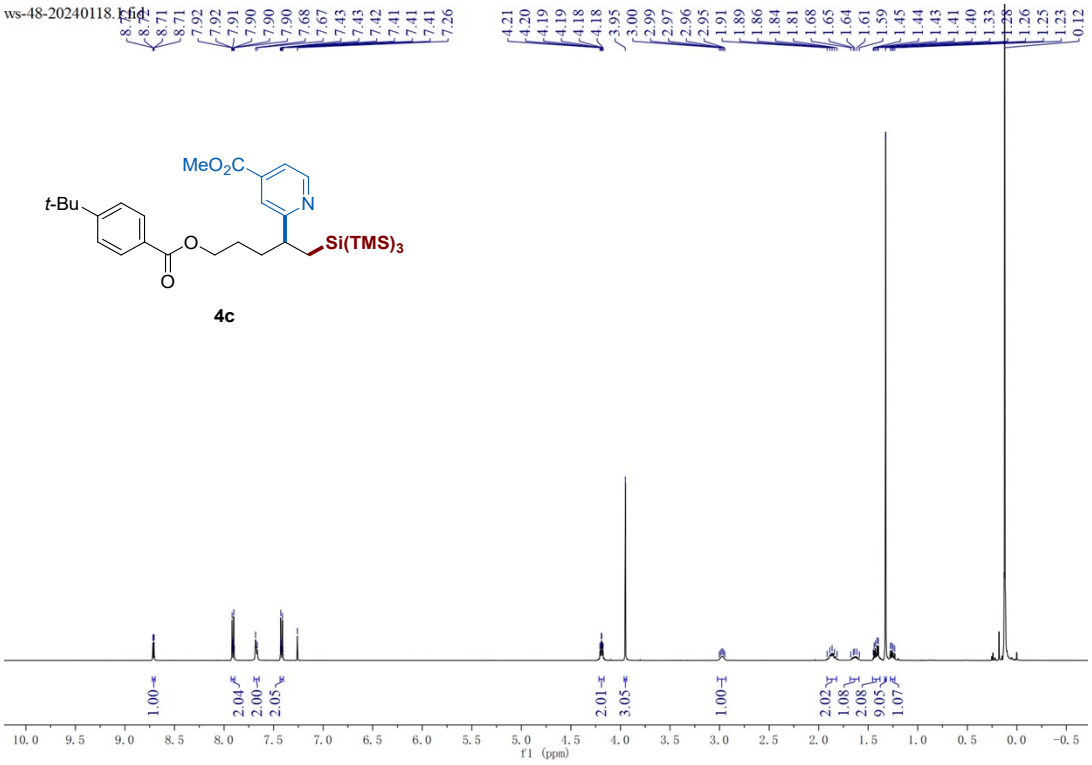


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

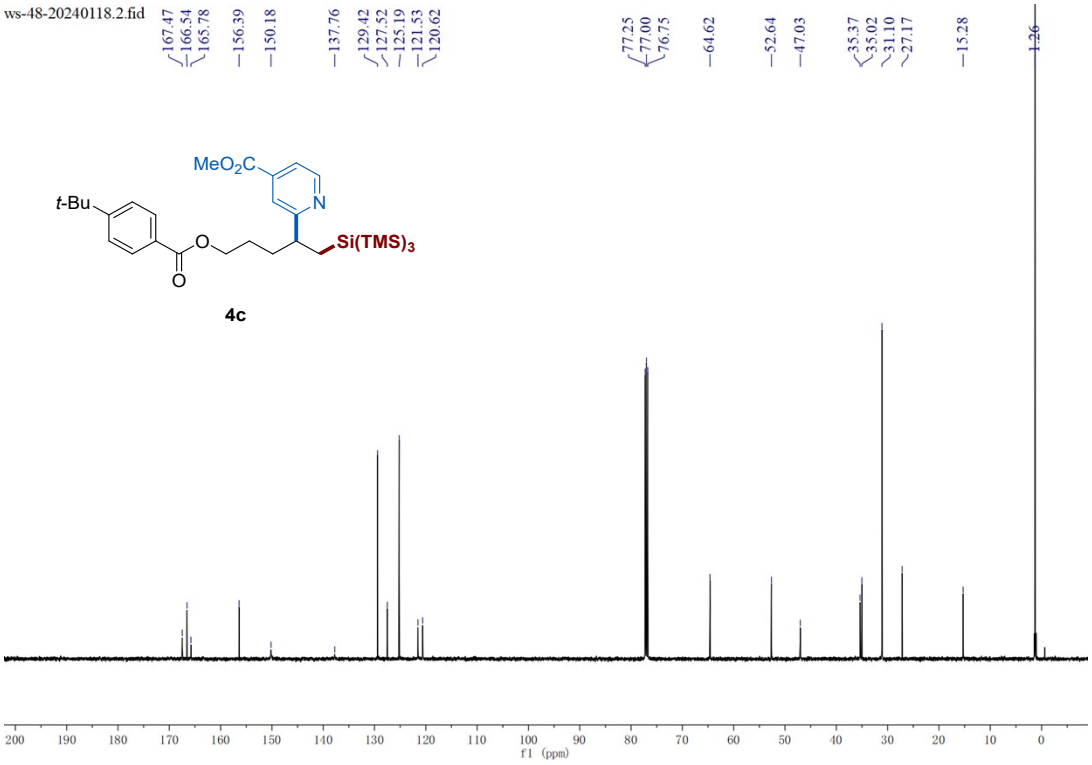


Methyl 2-(5-((4-(tert-butyl) benzoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4c).

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

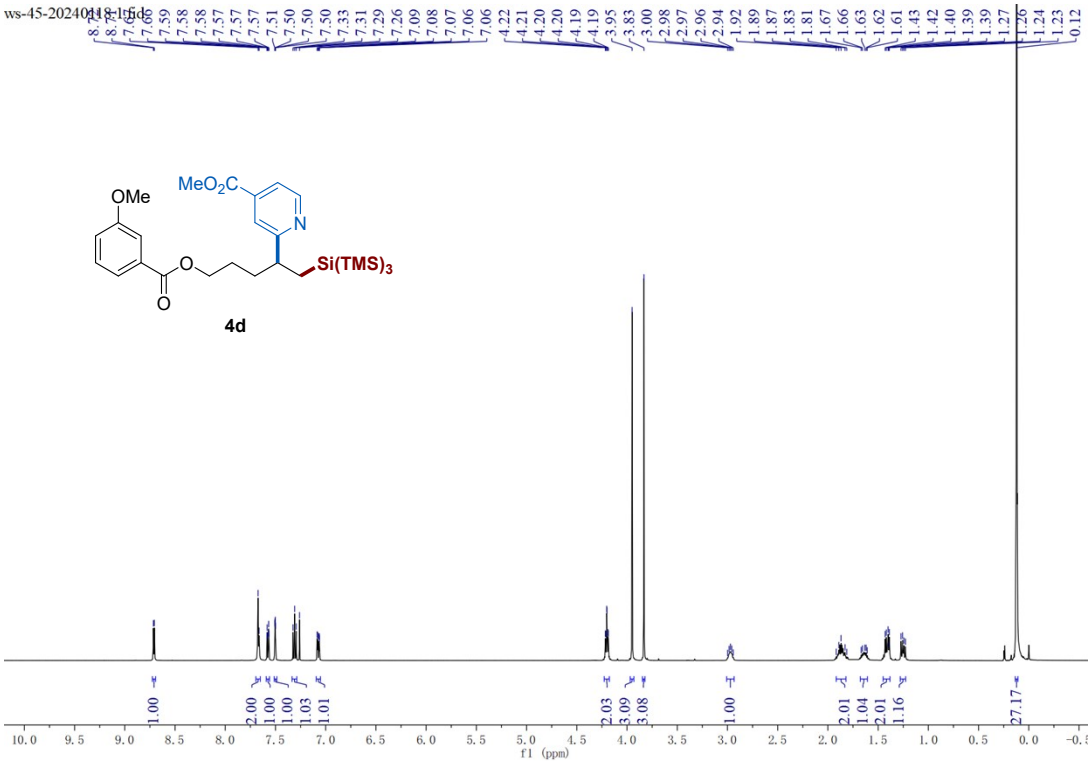


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

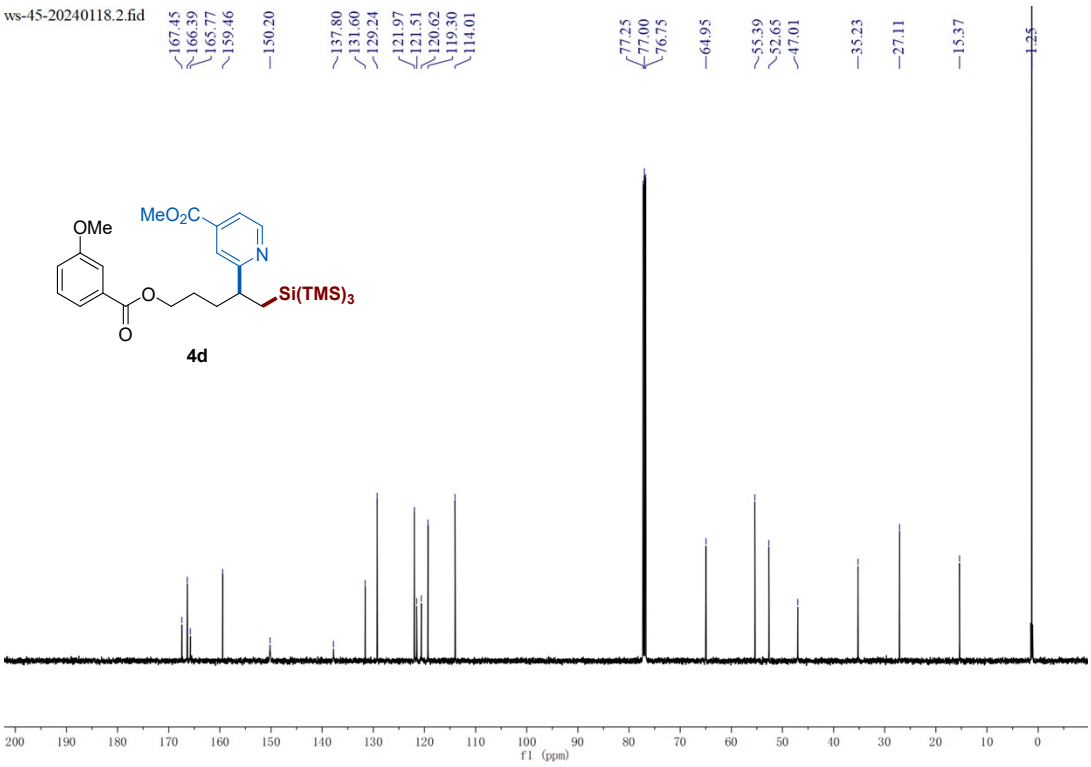


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((3-methoxybenzoyl) oxy) pentan-2-yl) isonicotinate (4d).

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

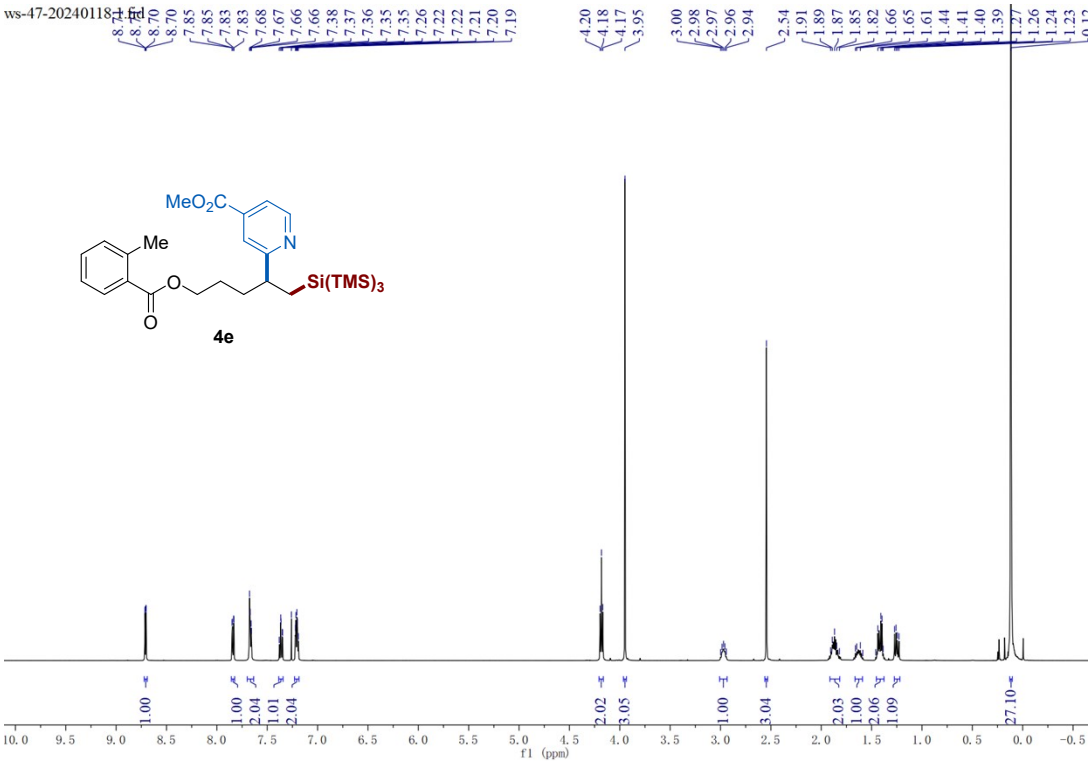


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

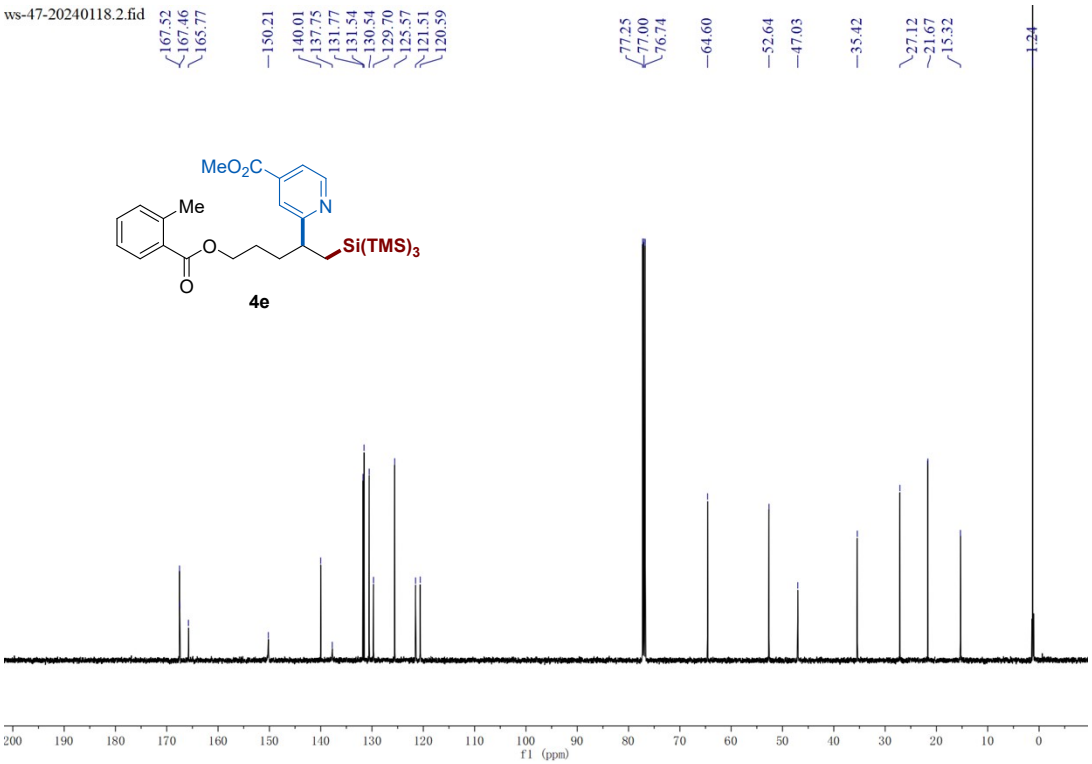


Methyl 2-(1-azido-5-((2-methylbenzoyl) oxy) pentan-2-yl) isonicotinate (4e).

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

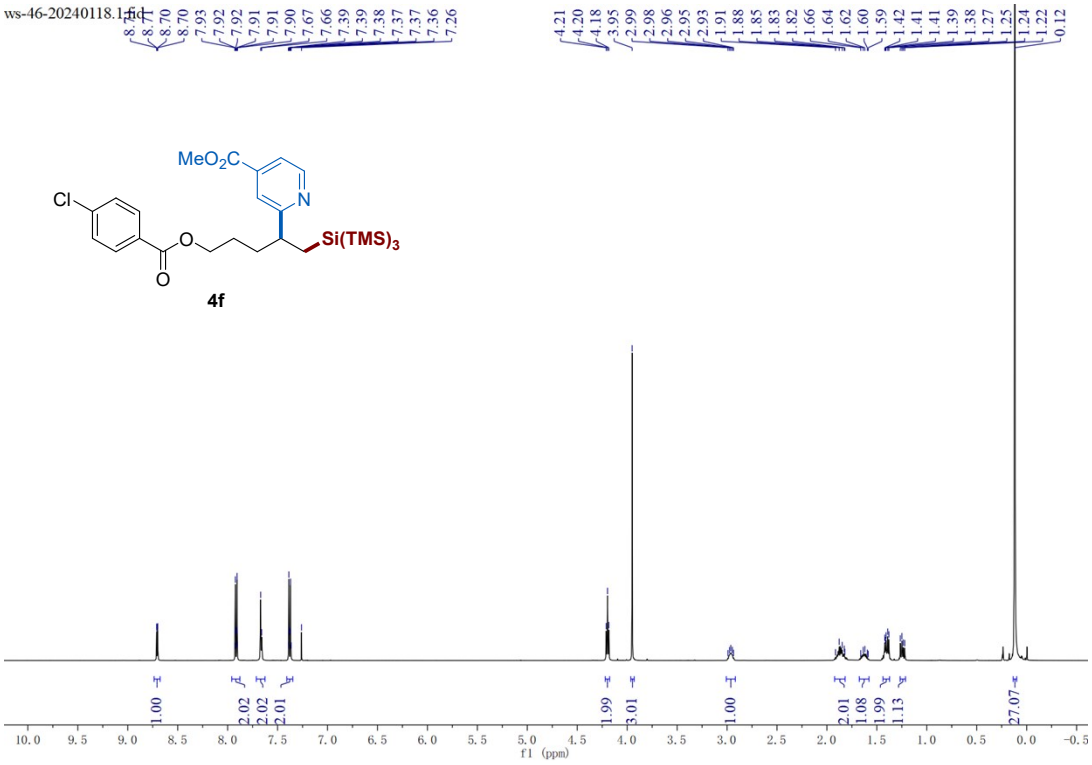


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

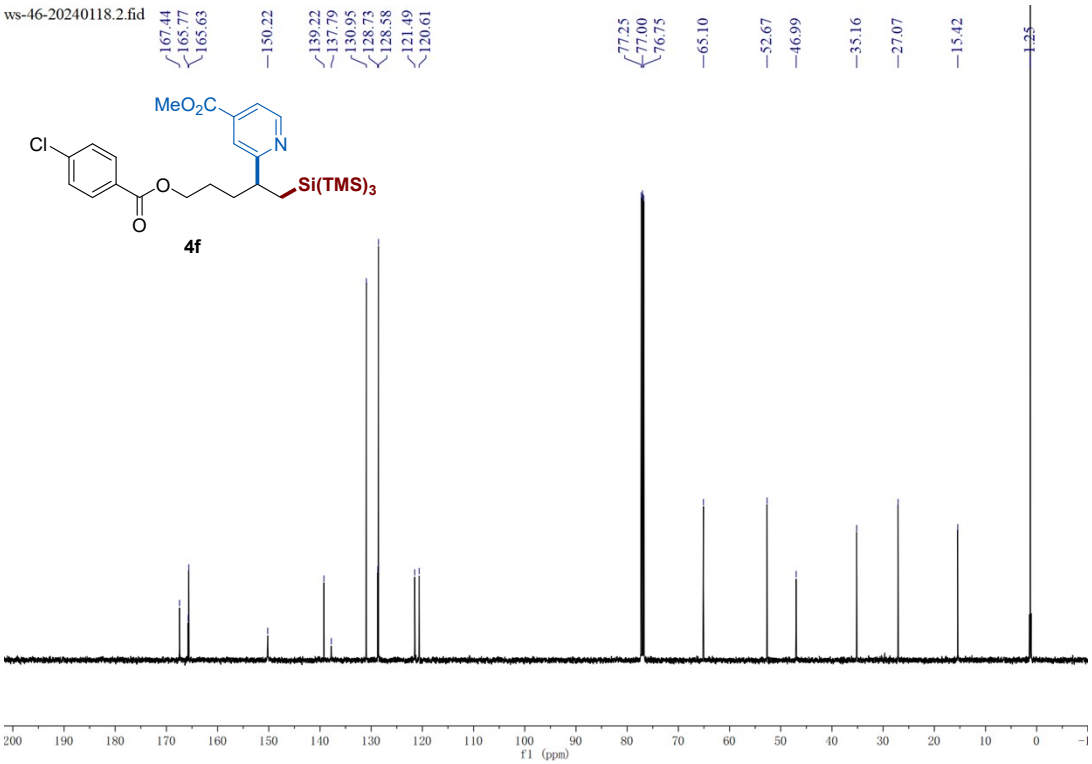


Methyl 2-(1-azido-5-((4-chlorobenzoyl) oxy) pentan-2-yl) isonicotinate (4f).

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

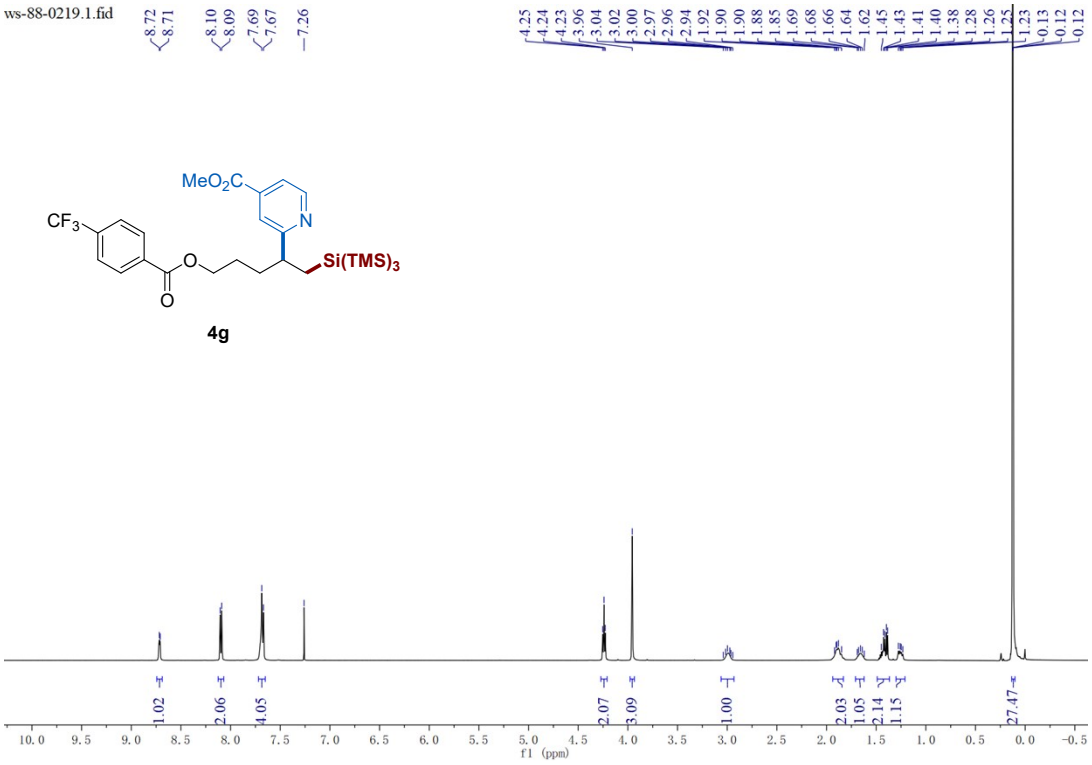


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

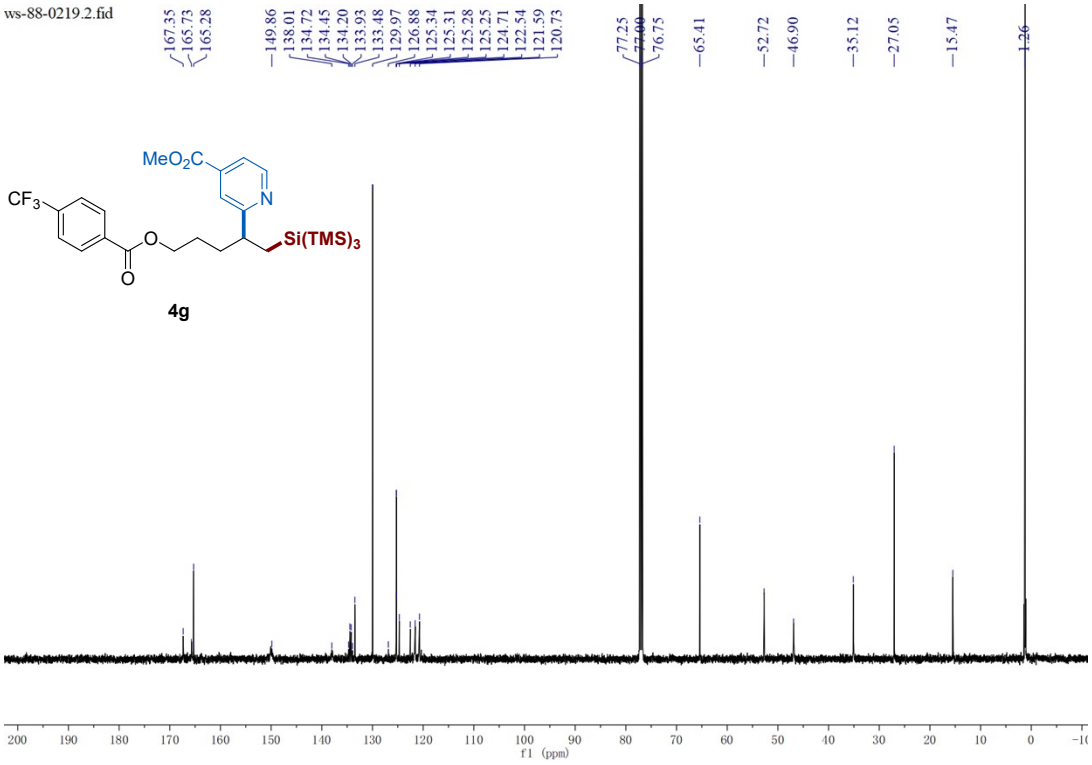


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((4-(trifluoromethyl) benzo yl) oxy) pentan-2-yl) isonicotinate (4g).

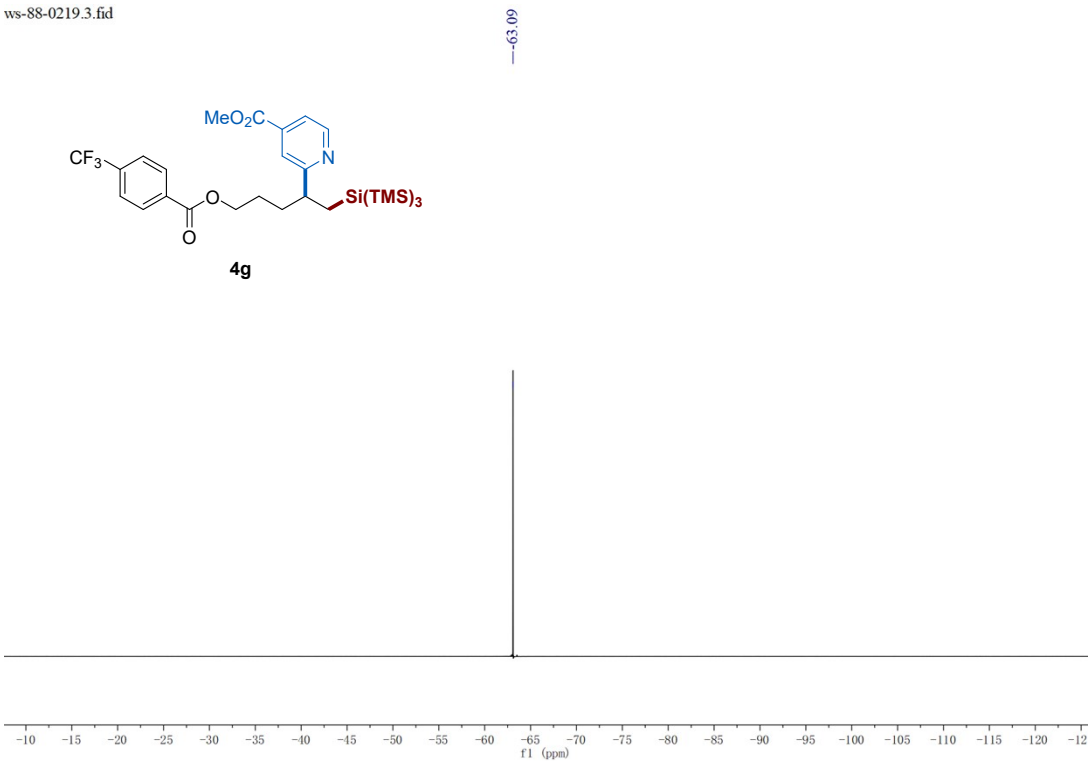
500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)



126 MHz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

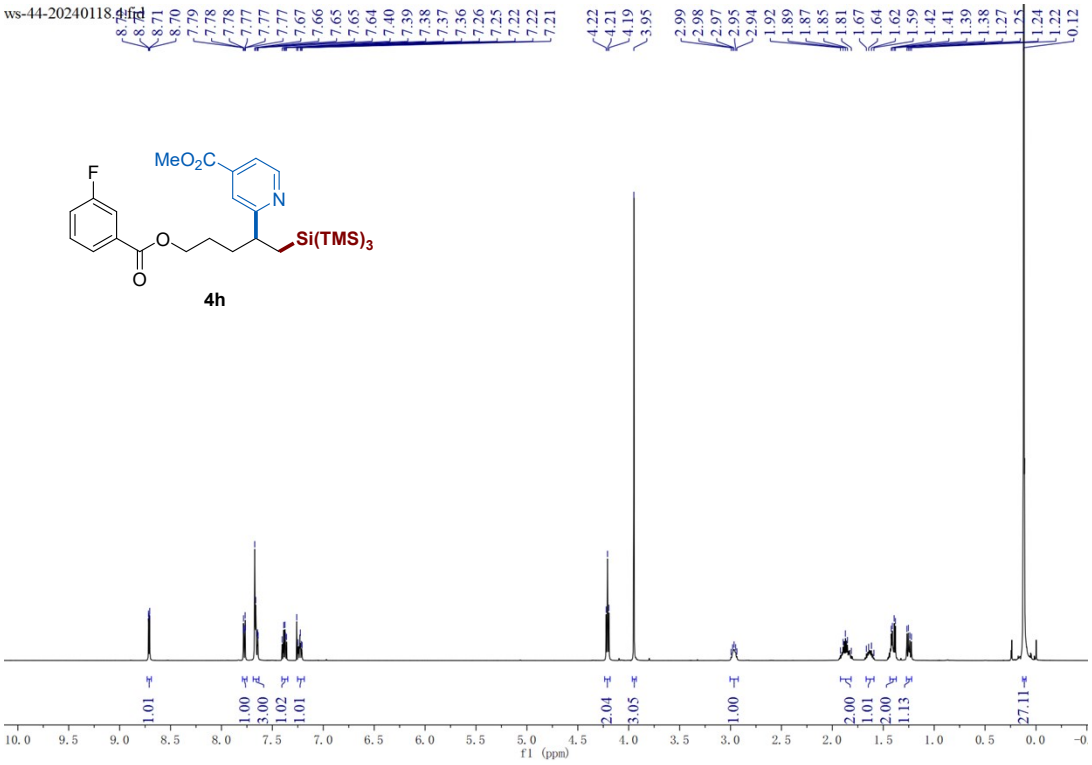


471 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$)

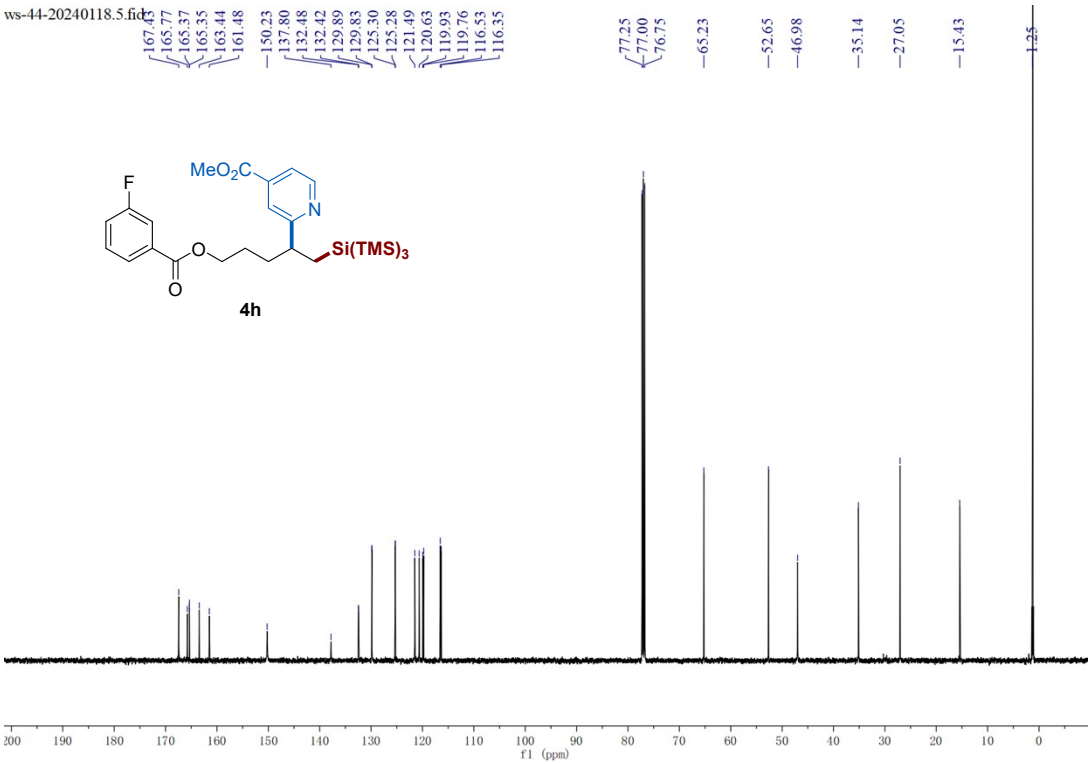


Methyl 2-(1-azido-5-((3-fluorobenzoyl) oxy) pentan-2-yl) isonicotinate (4h).

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

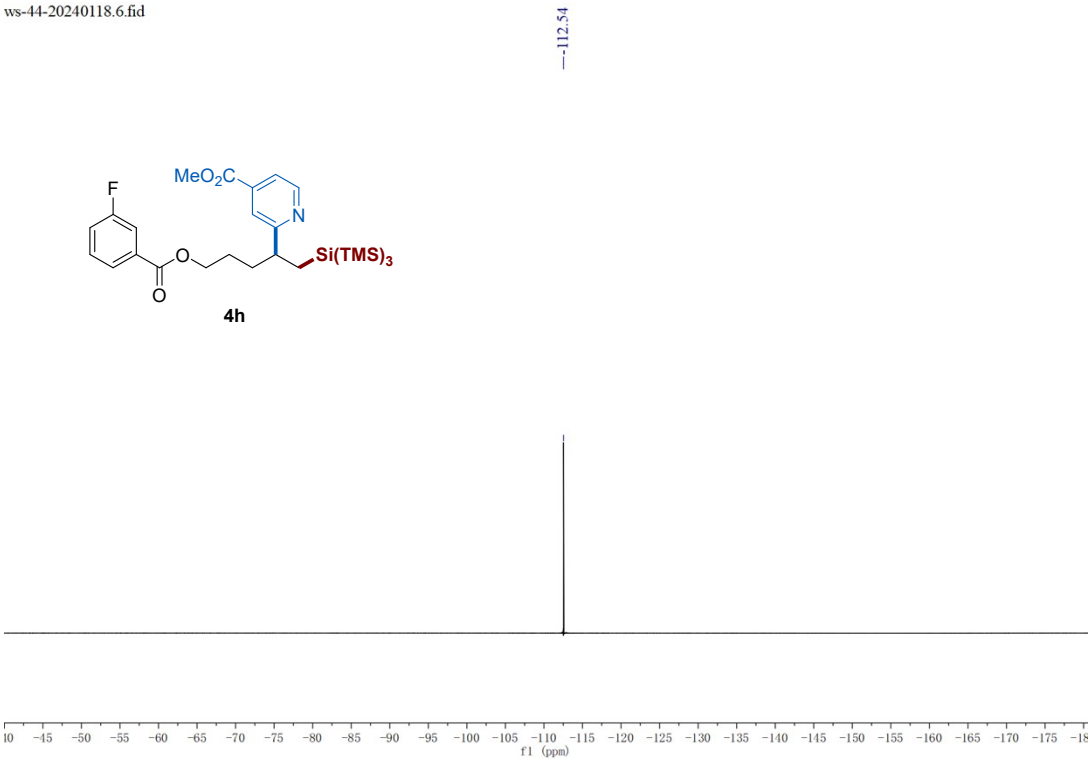


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)



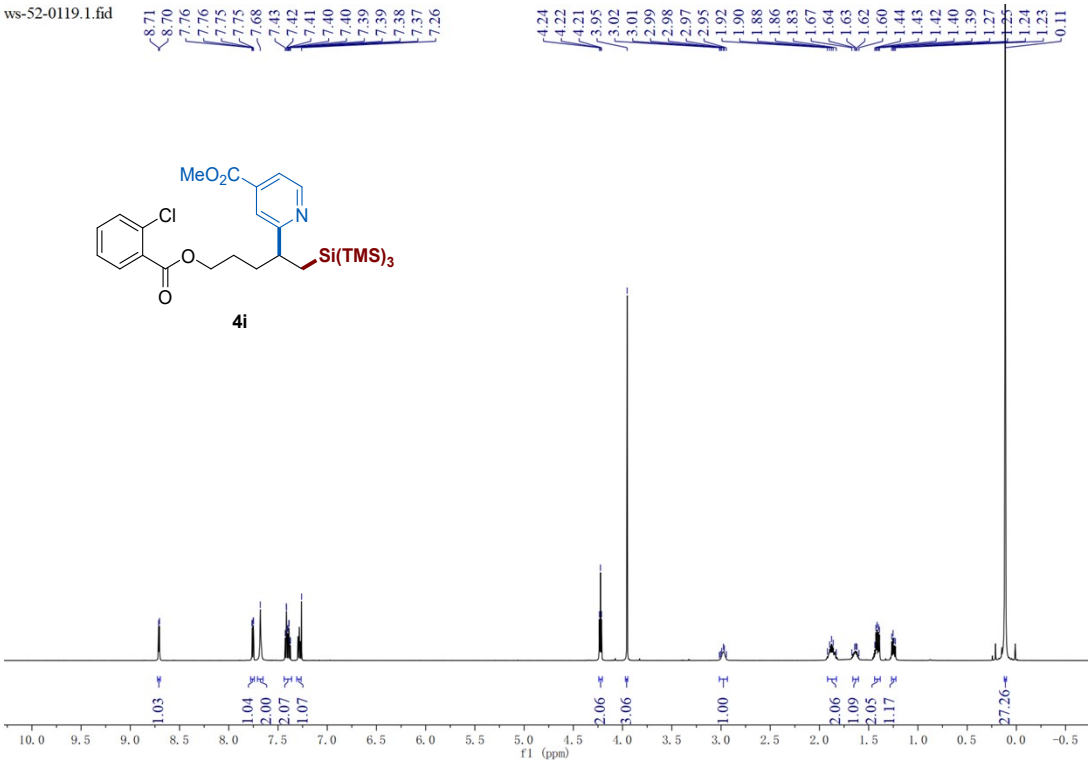
471 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$)

ws-44-20240118.6.fid

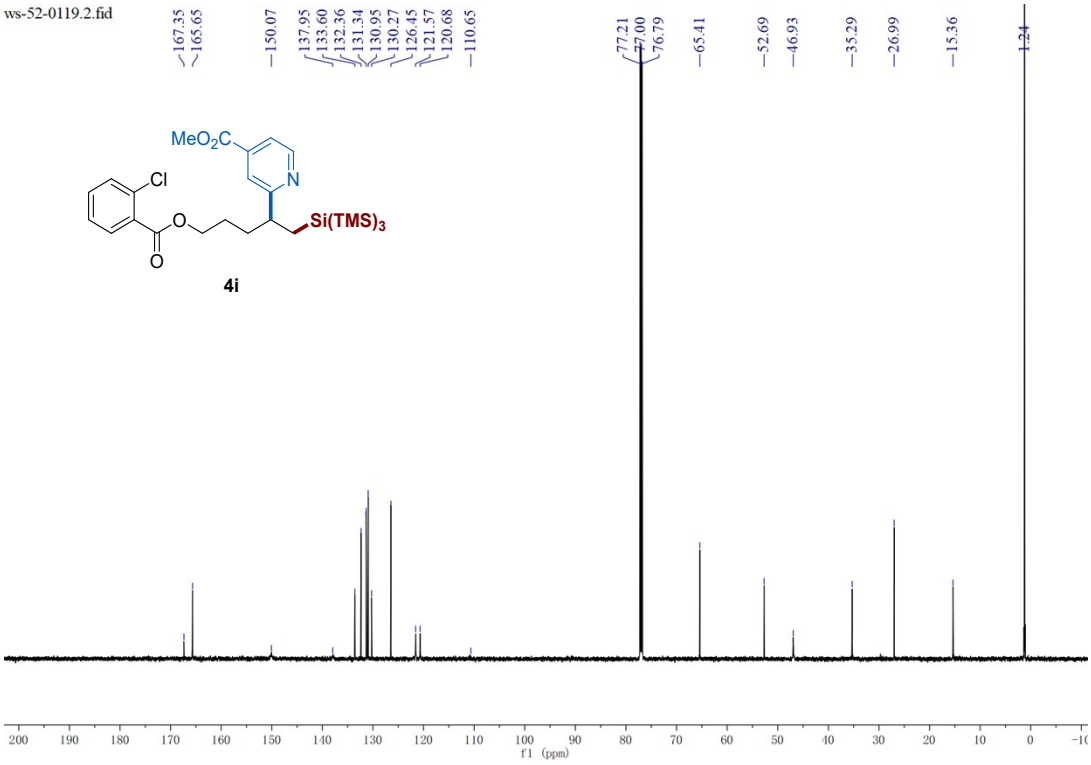


Methyl 2-(5-((2-chlorobenzoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4i).

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

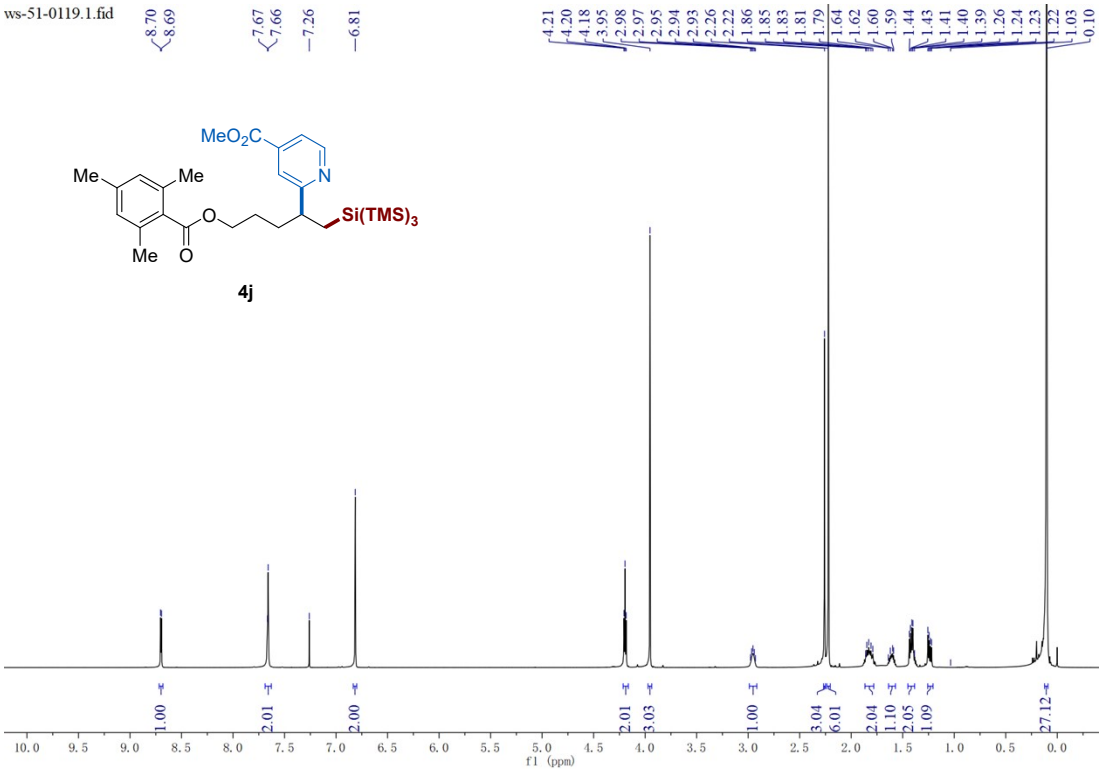


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

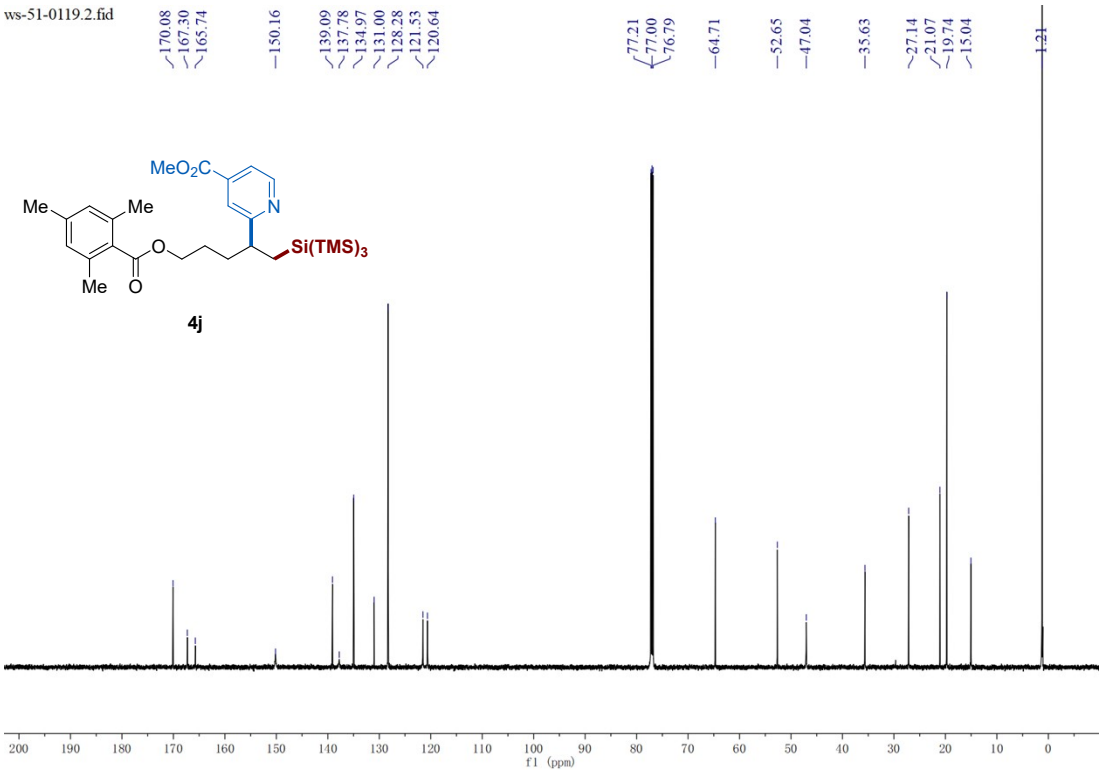


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((2,4,6-trimethylbenzoyl) o xy) pentan-2-yl) isonicotinate (4j).

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

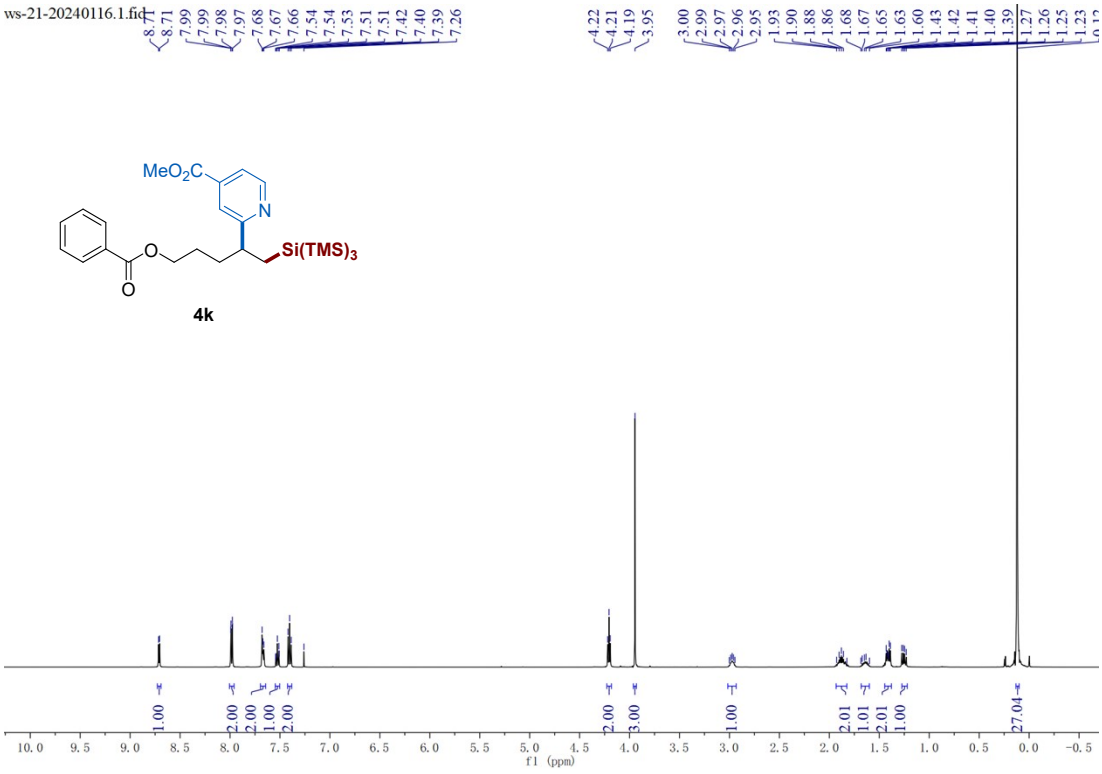


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

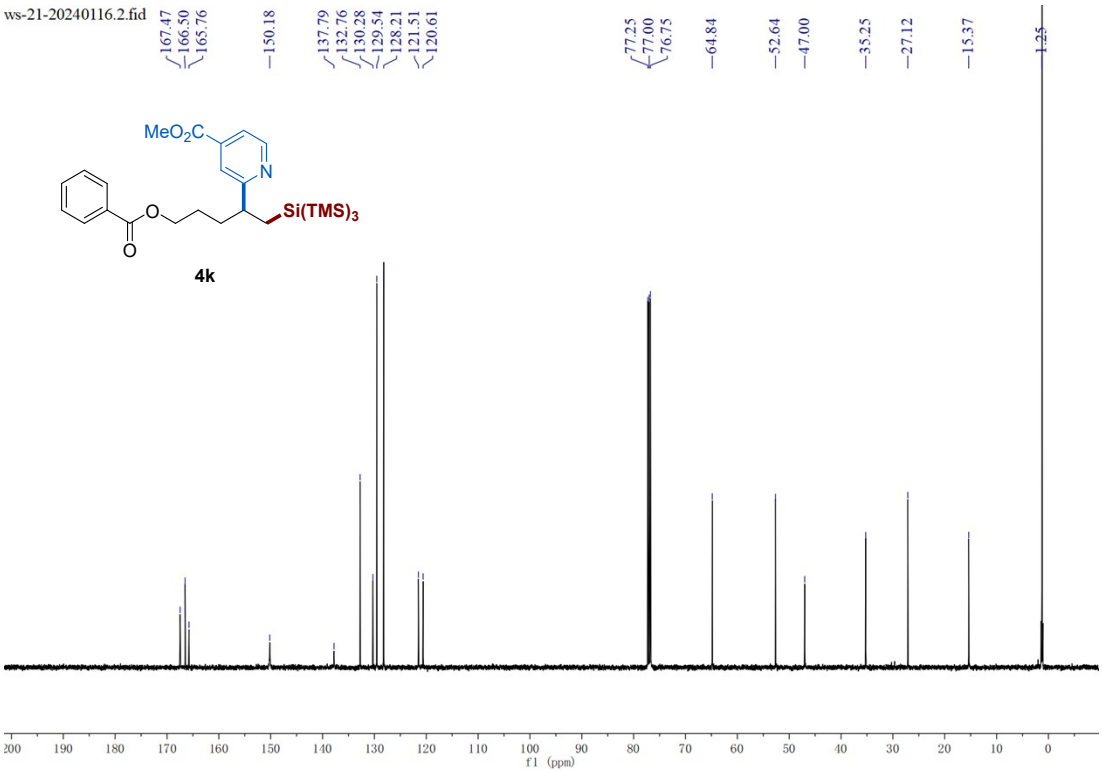


Methyl 2-(5-(benzoyloxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) i sonicotinate (4k).

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

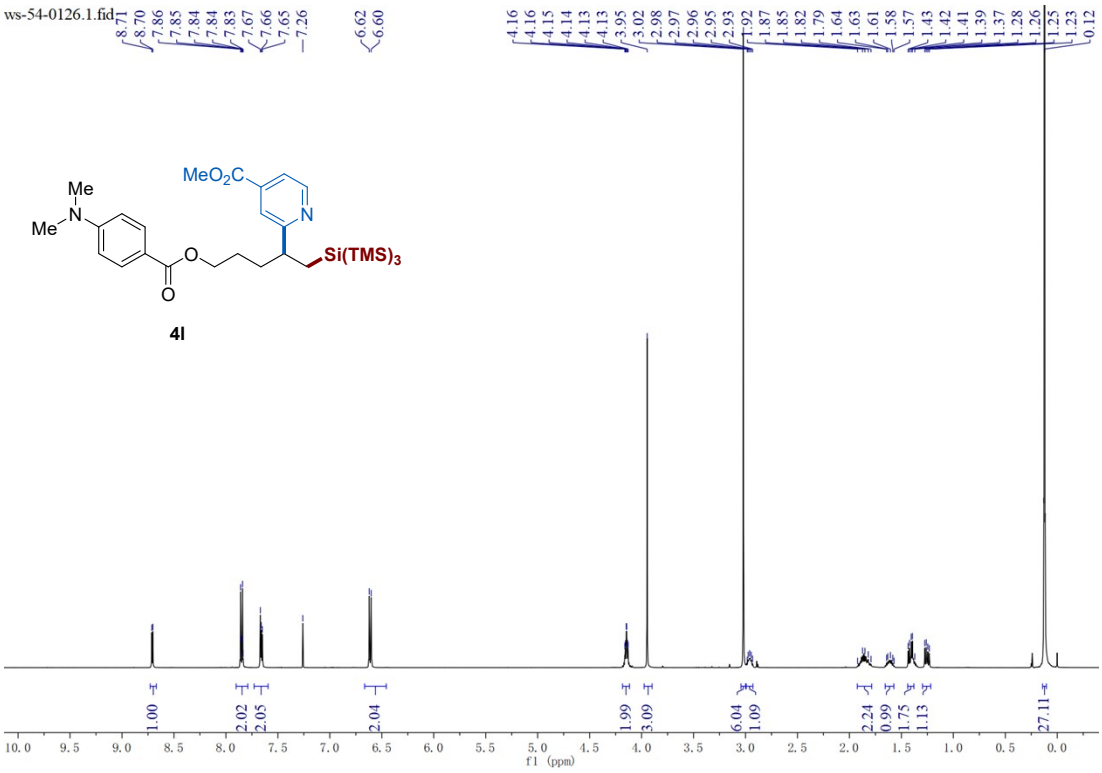


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

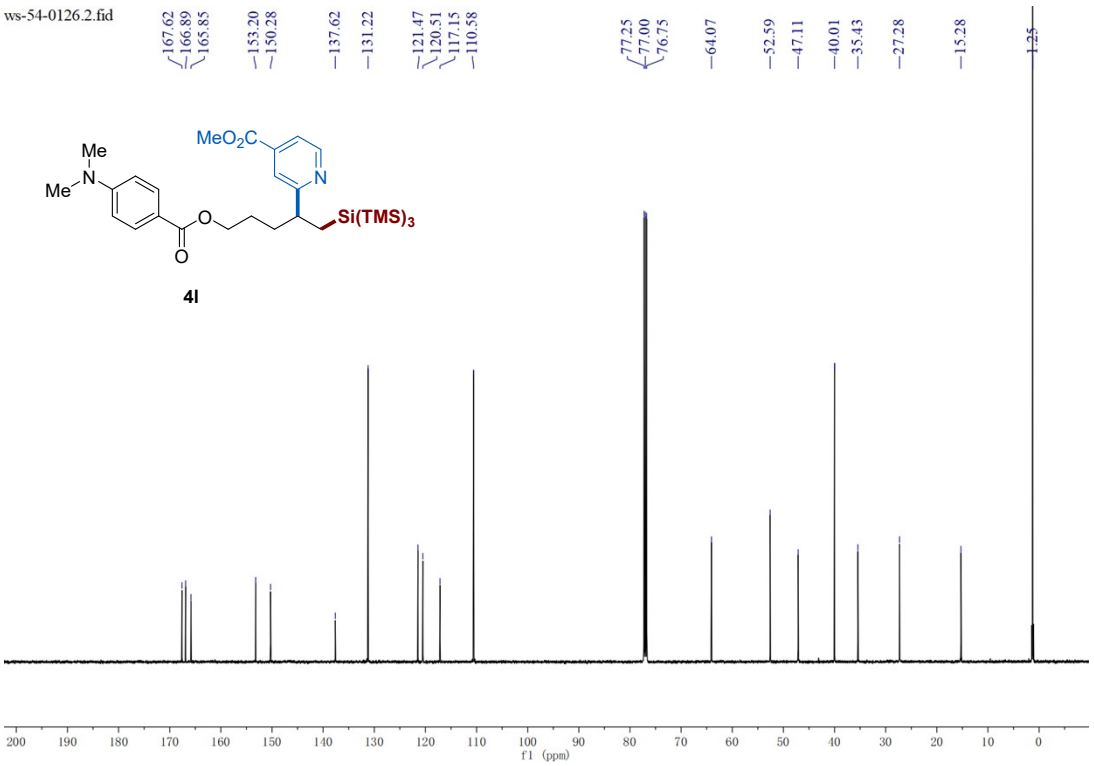


Methyl 2-(5-((4-(dimethylamino)benzoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4l)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

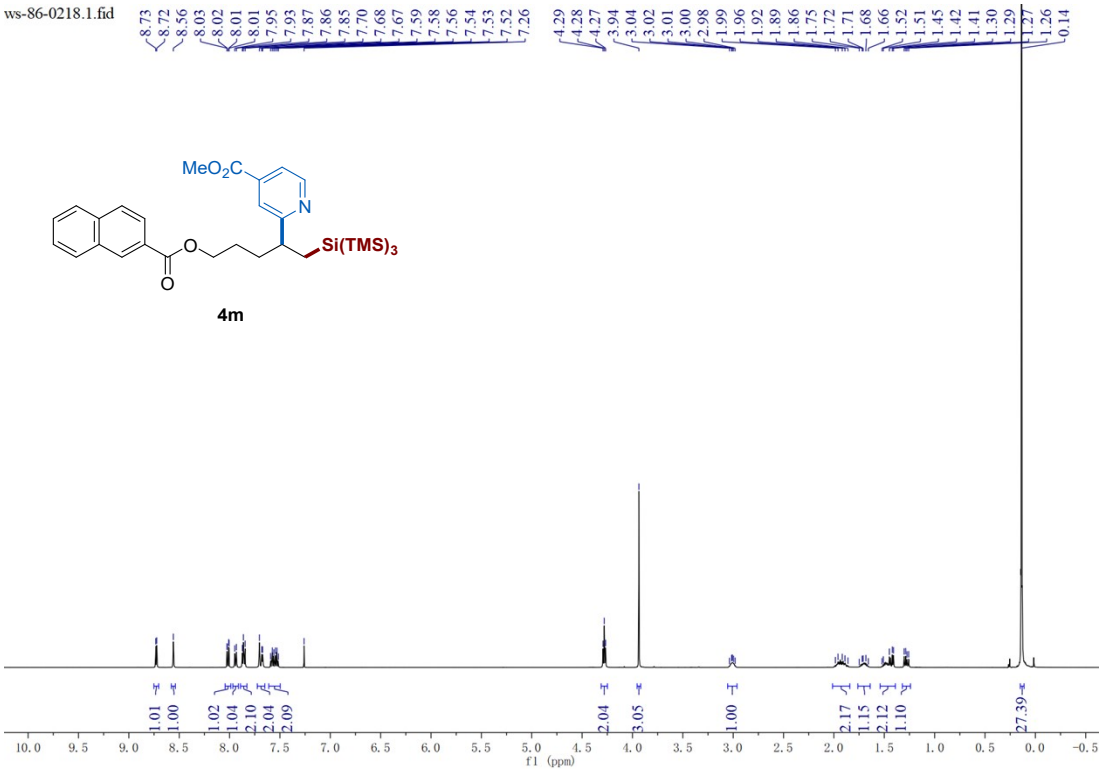


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

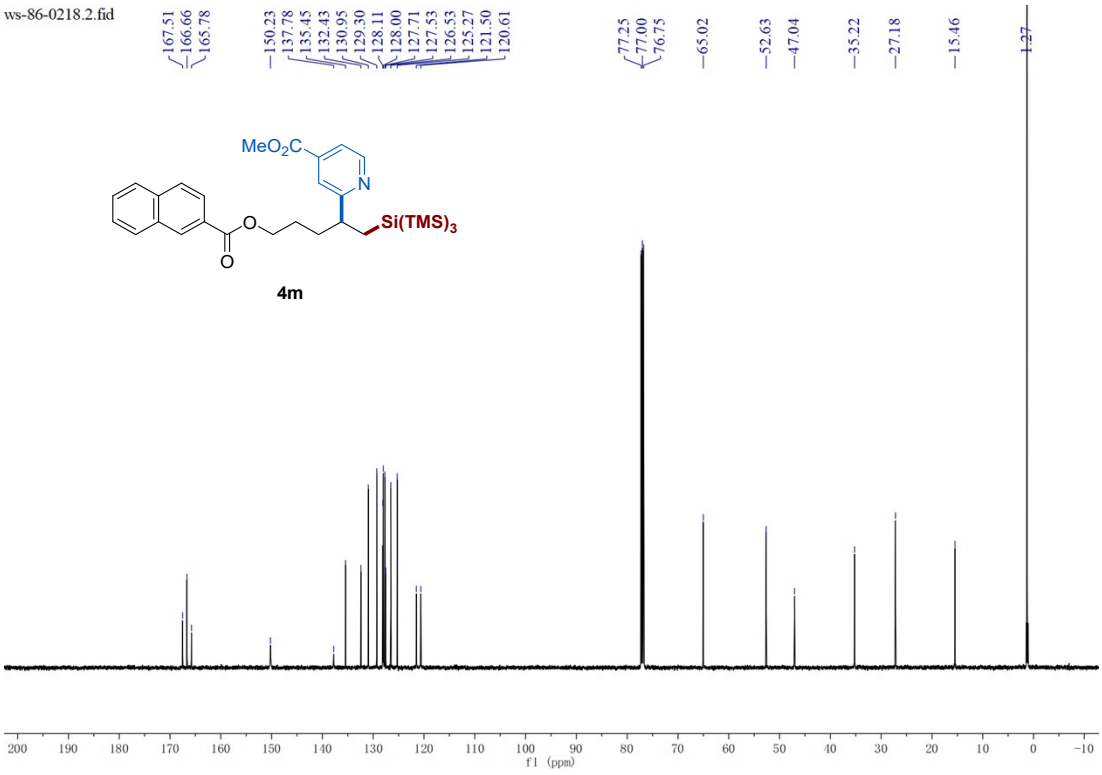


Methyl 2-(5-((2-naphthoyl) oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4m)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

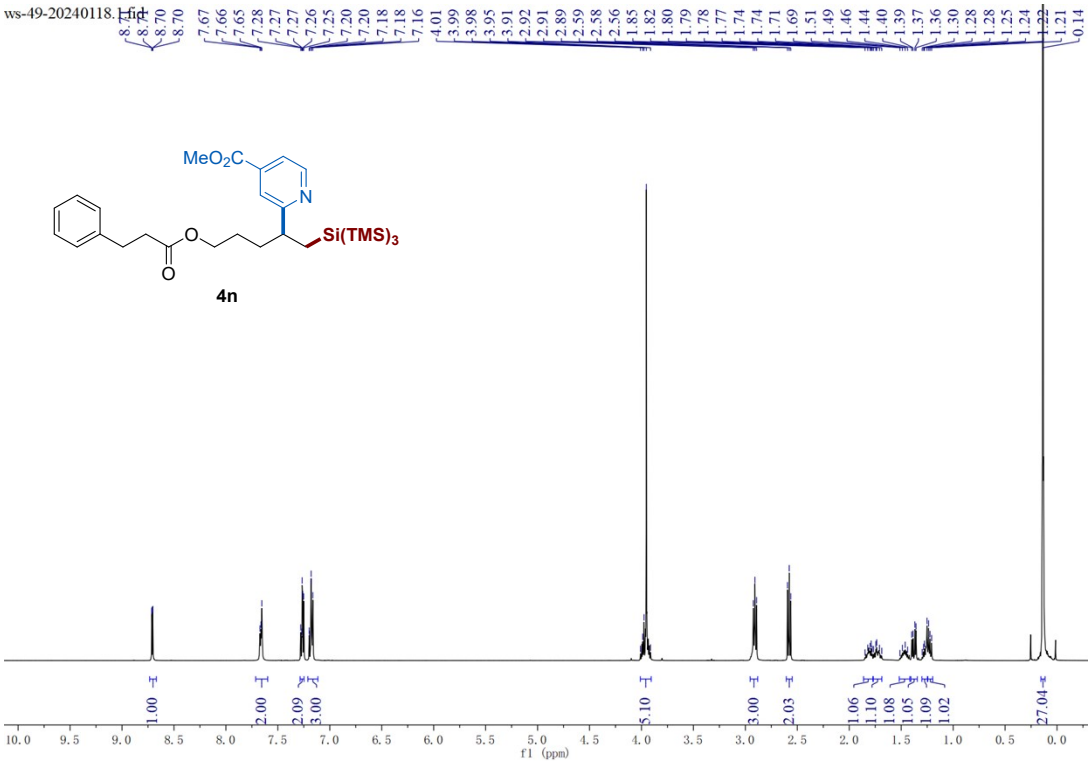


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

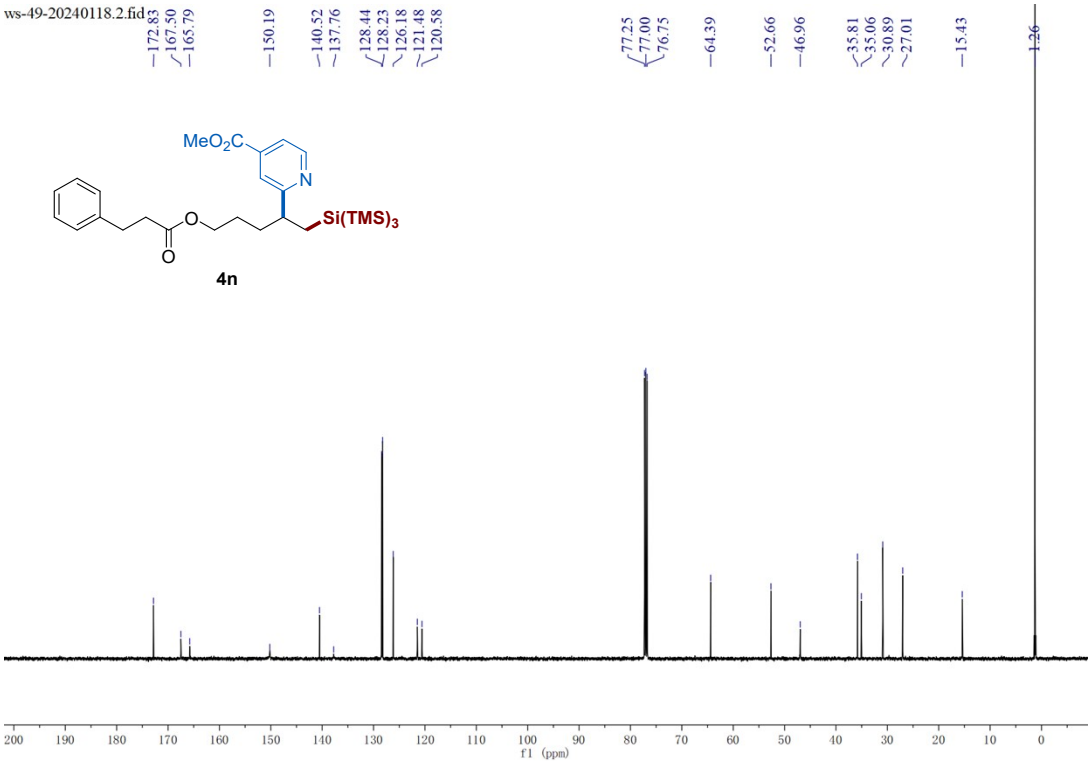


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((3-phenylpropanoyl) oxy) pentan-2-yl) isonicotinate (4n)

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

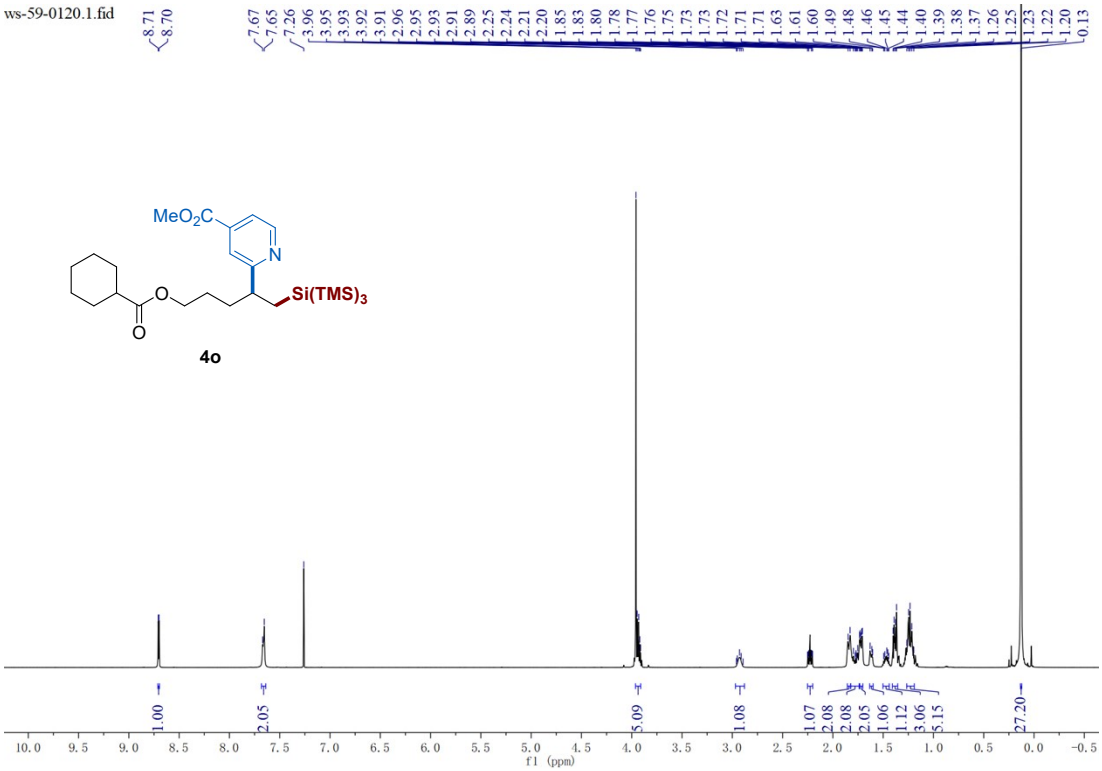


126 MHz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

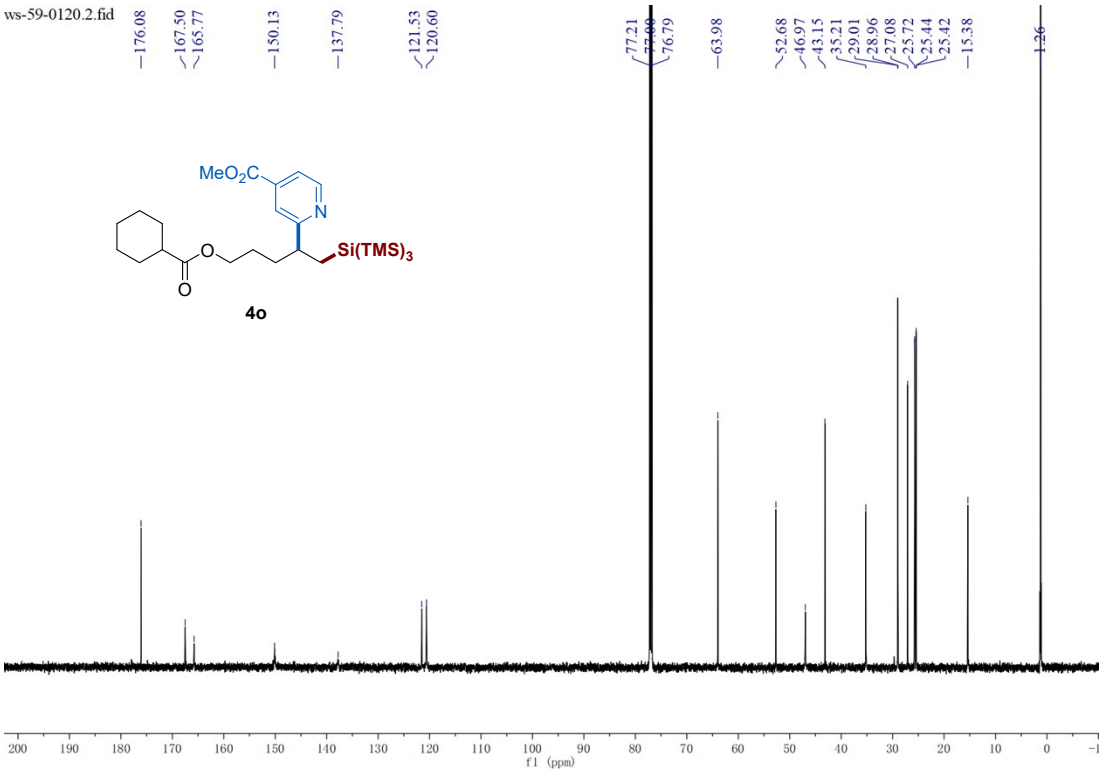


Methyl 2-(5-((cyclohexanecarbonyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4o)

600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

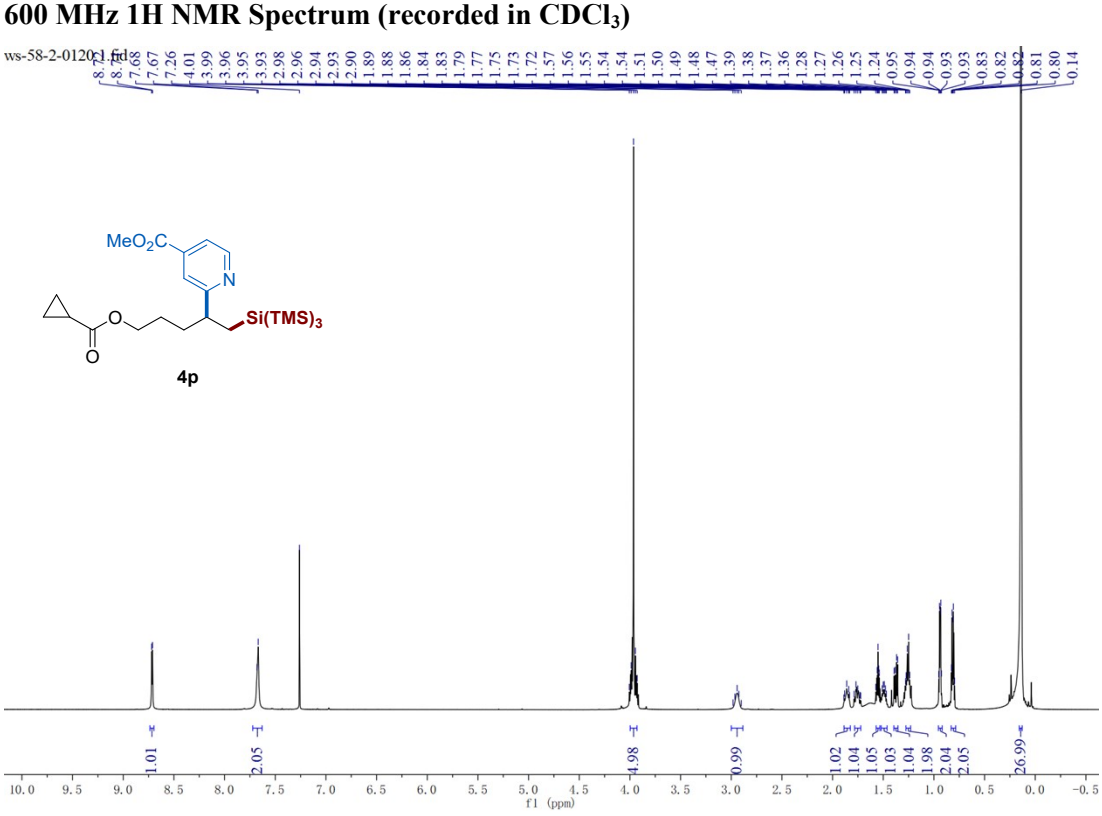


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

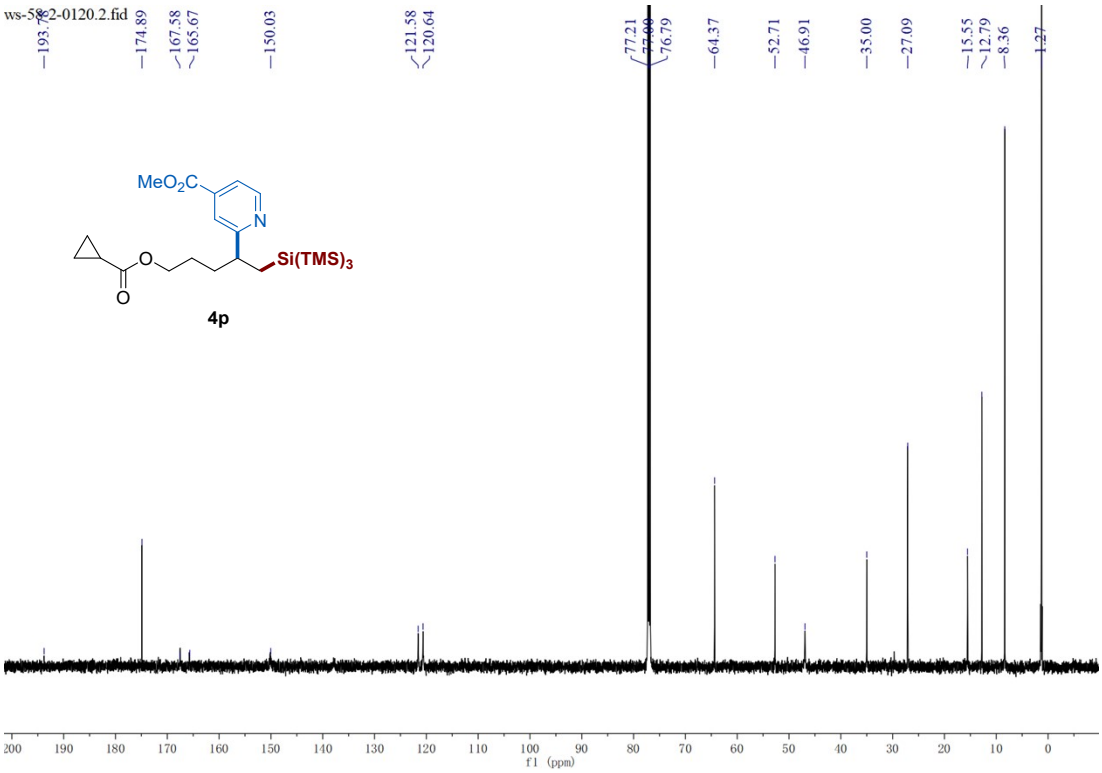


Methyl 2-(5-((cyclopropanecarbonyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) pentan-2-yl) isonicotinate (4p)

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

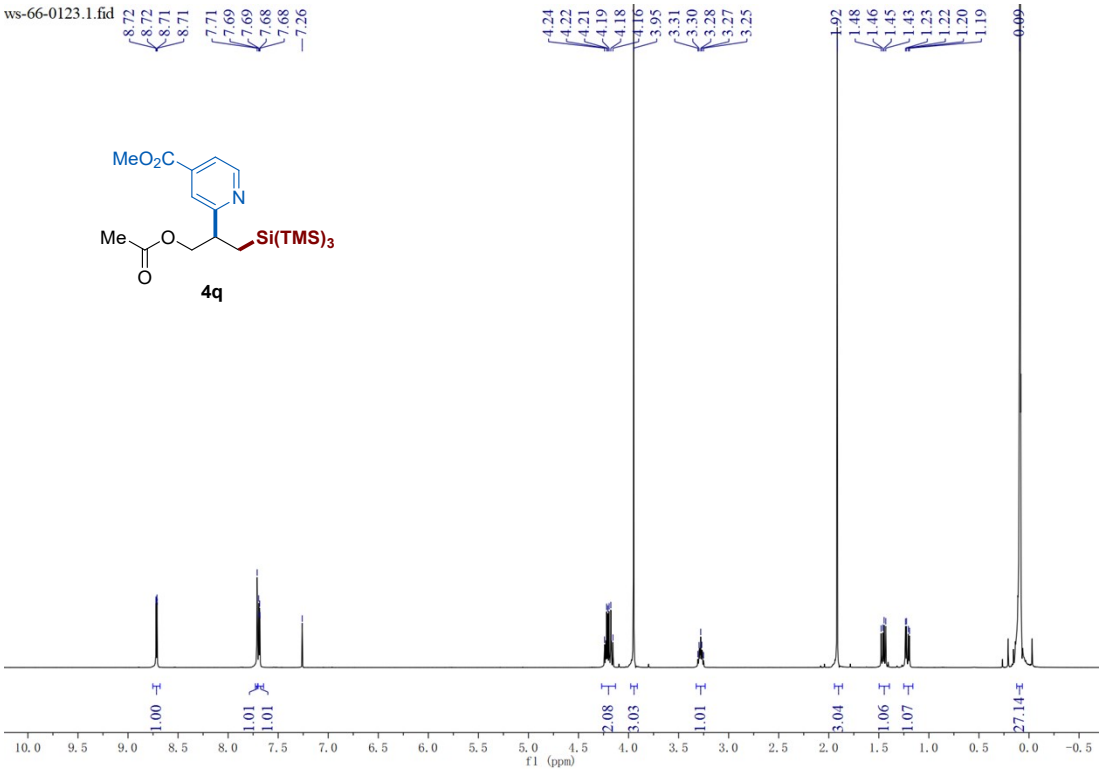


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

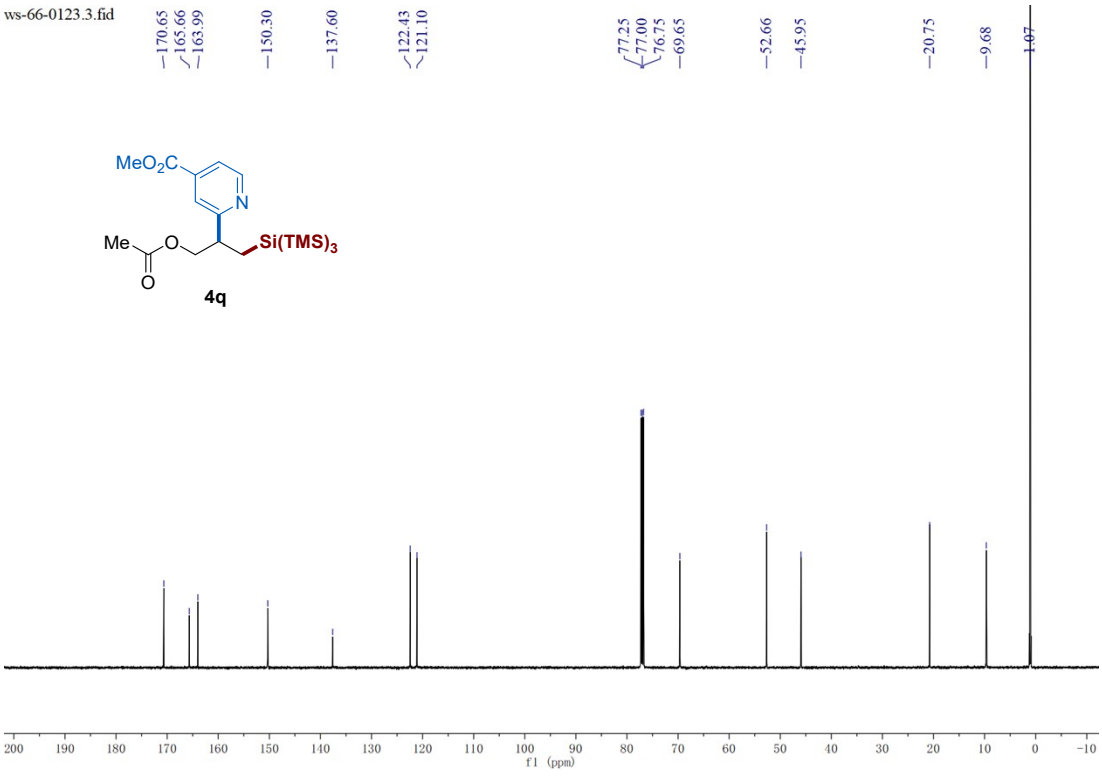


Methyl 2-(1-acetoxy-3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) propan-2-yl) isonicotinate (4q)

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

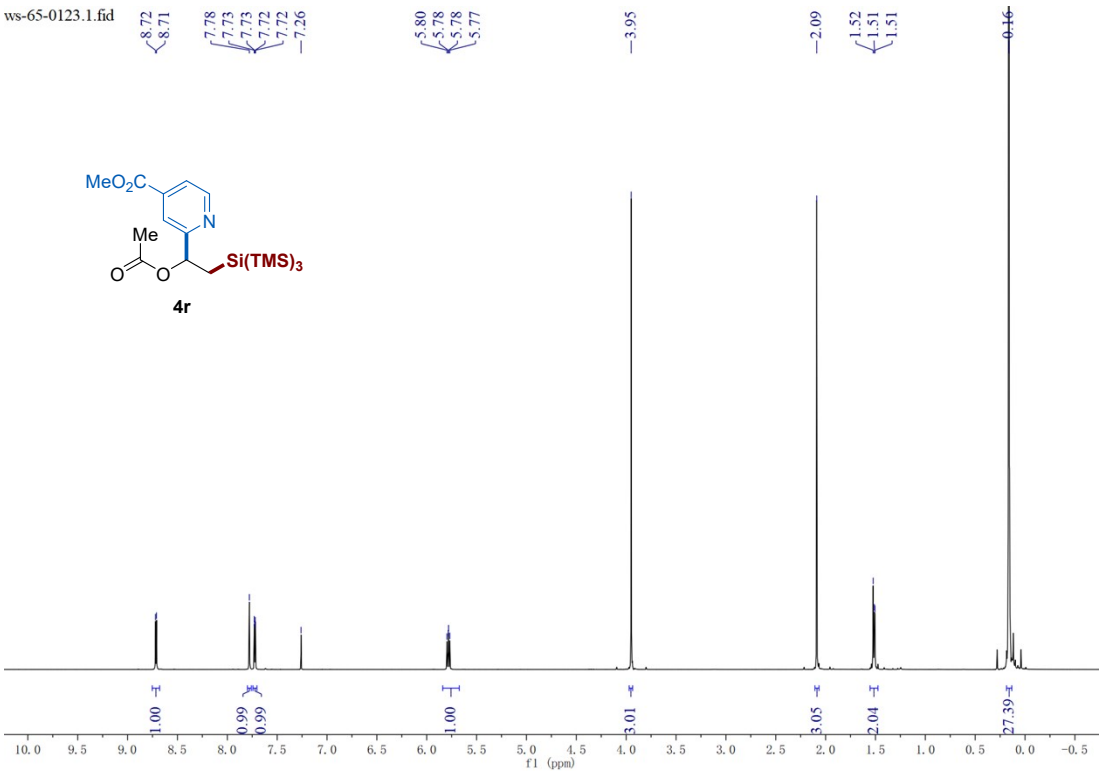


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

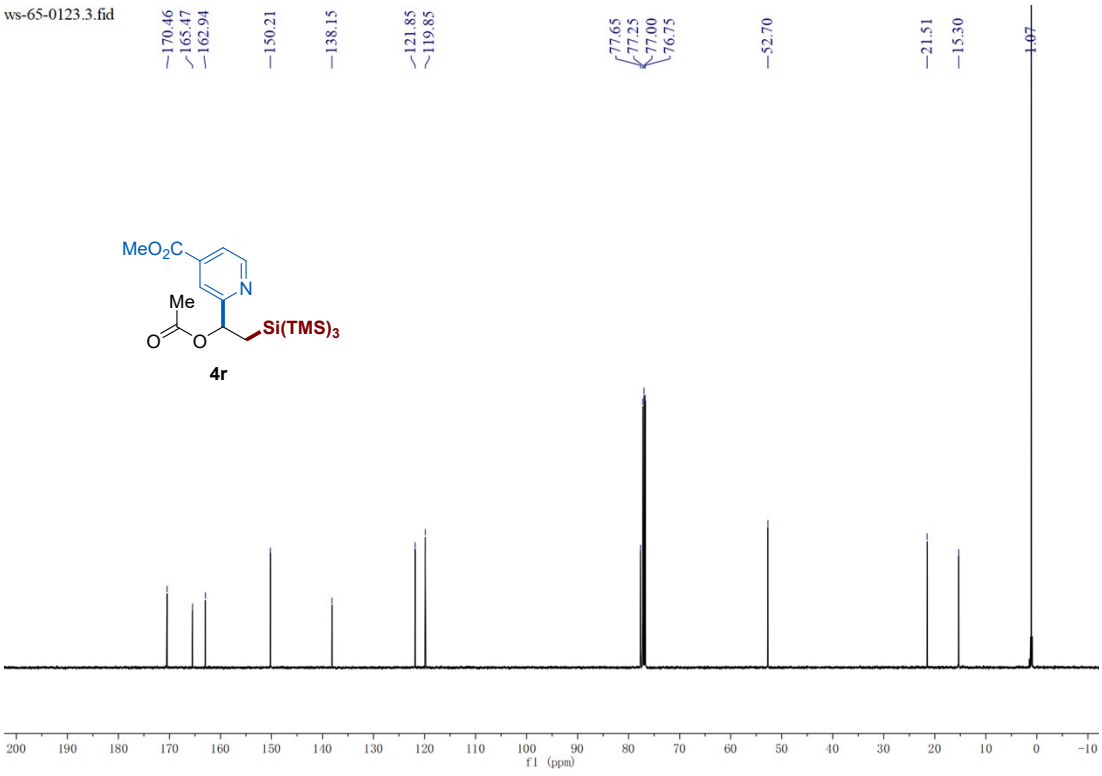


Methyl 2-(1-azido-4-phenoxybutan-2-yl) isonicotinate (4r)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

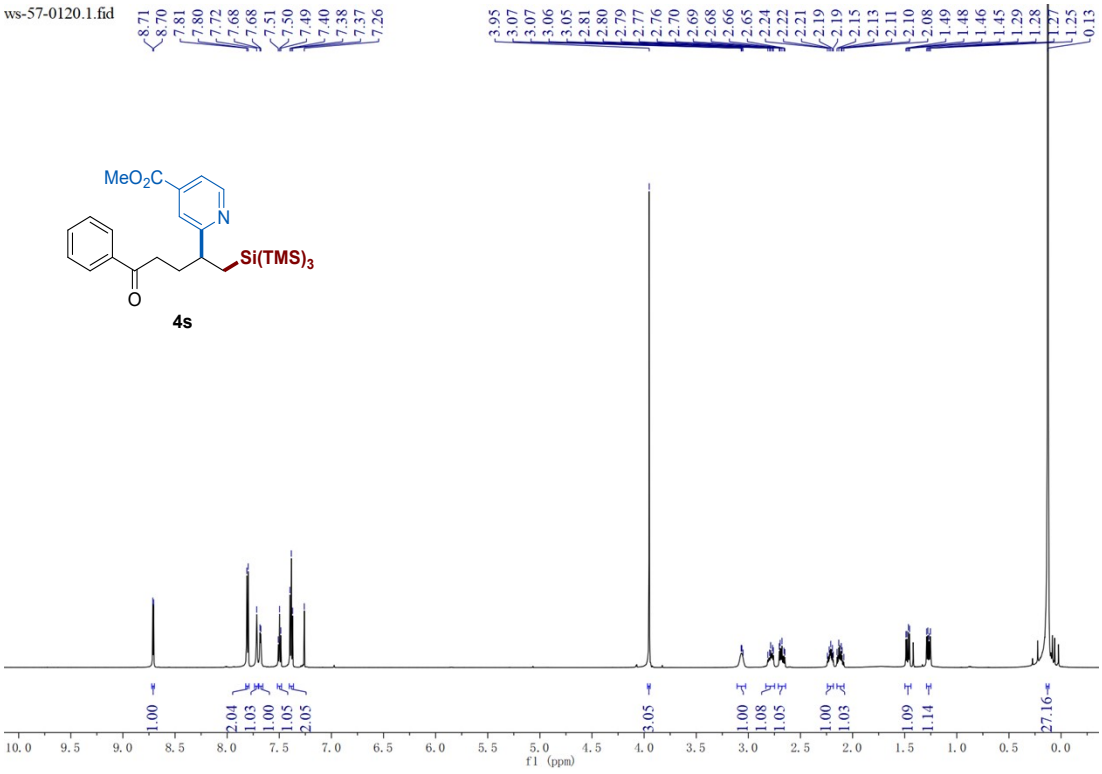


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

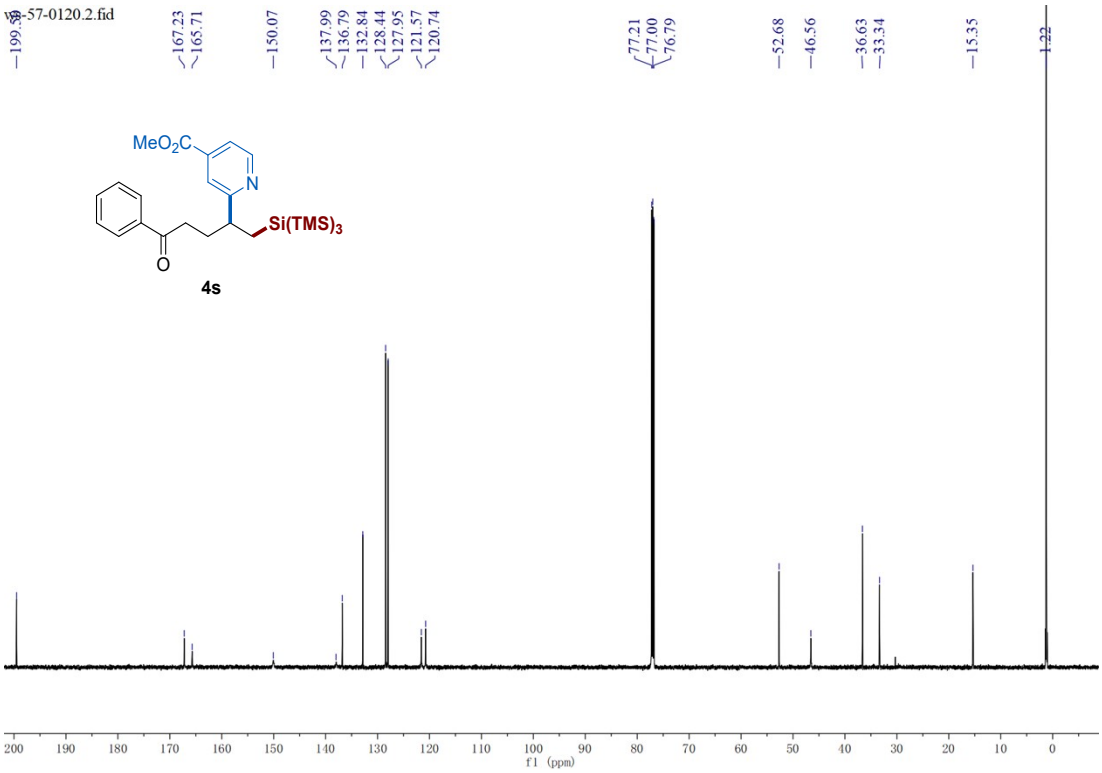


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-oxo-5-phenylpentan-2-yl) isonicotinate (4s)

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

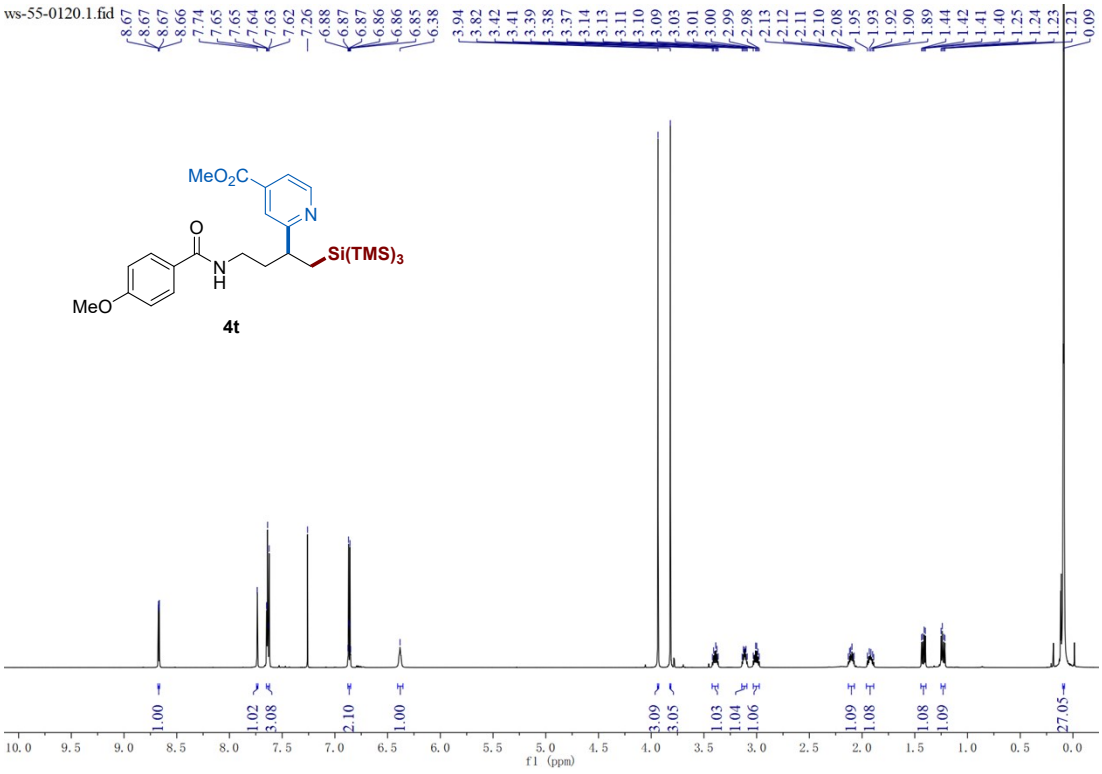


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

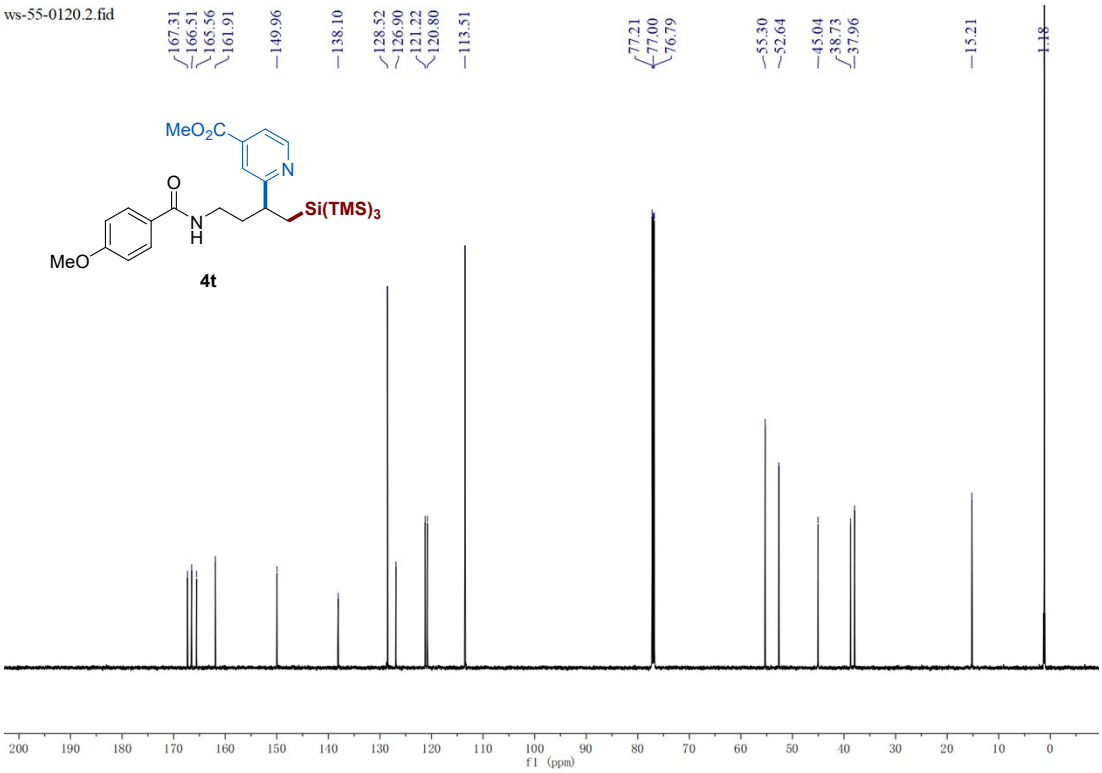


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-(4-methoxybenzamido) butan-2-yl) isonicotinate (4t)

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

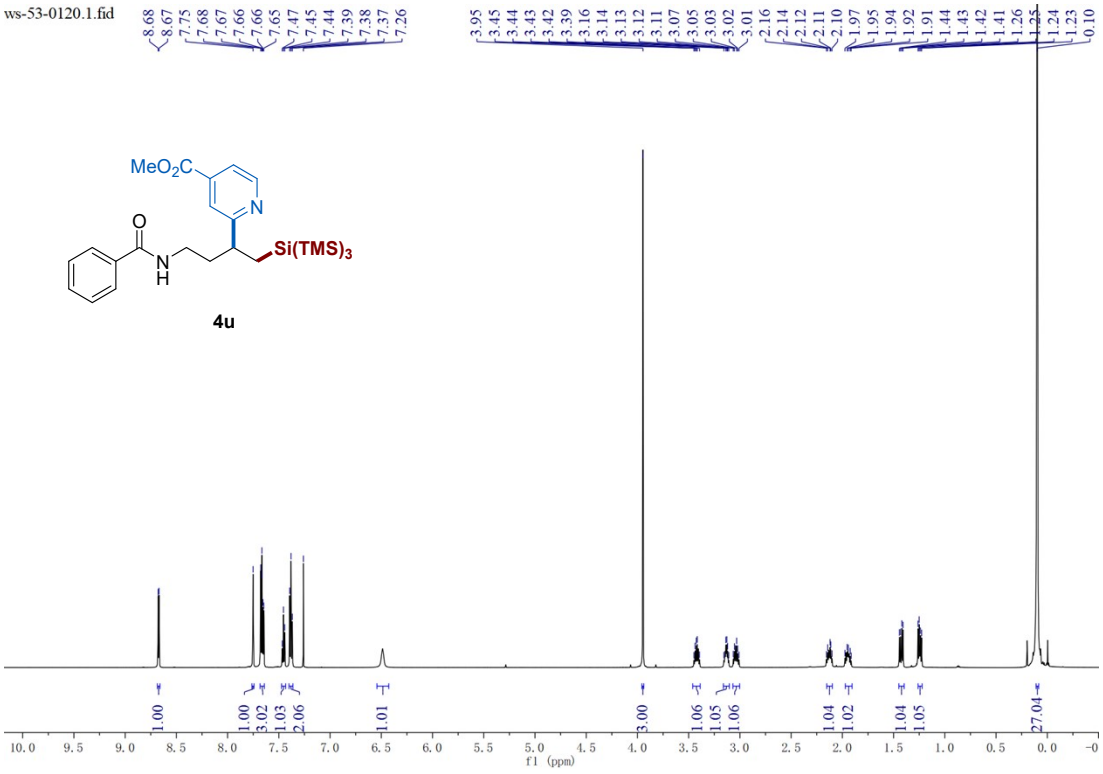


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

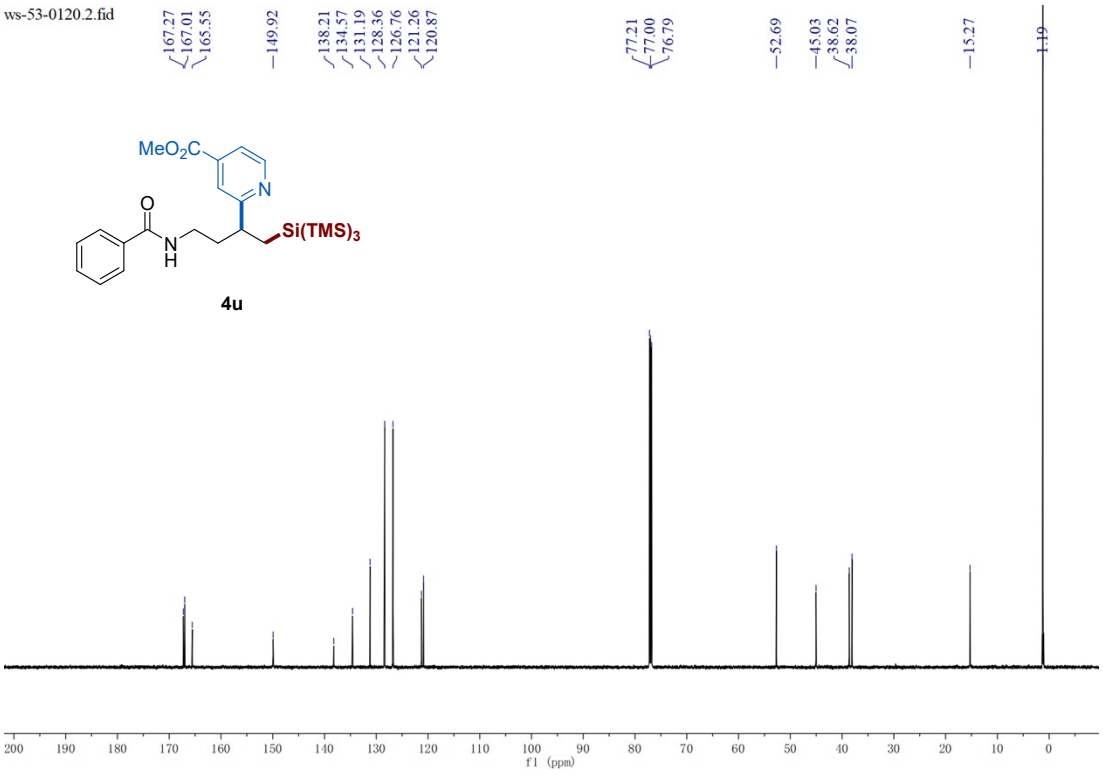


Methyl 2-(4-benzamido-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) butan-2-yl) isonicotinate (4u)

600 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

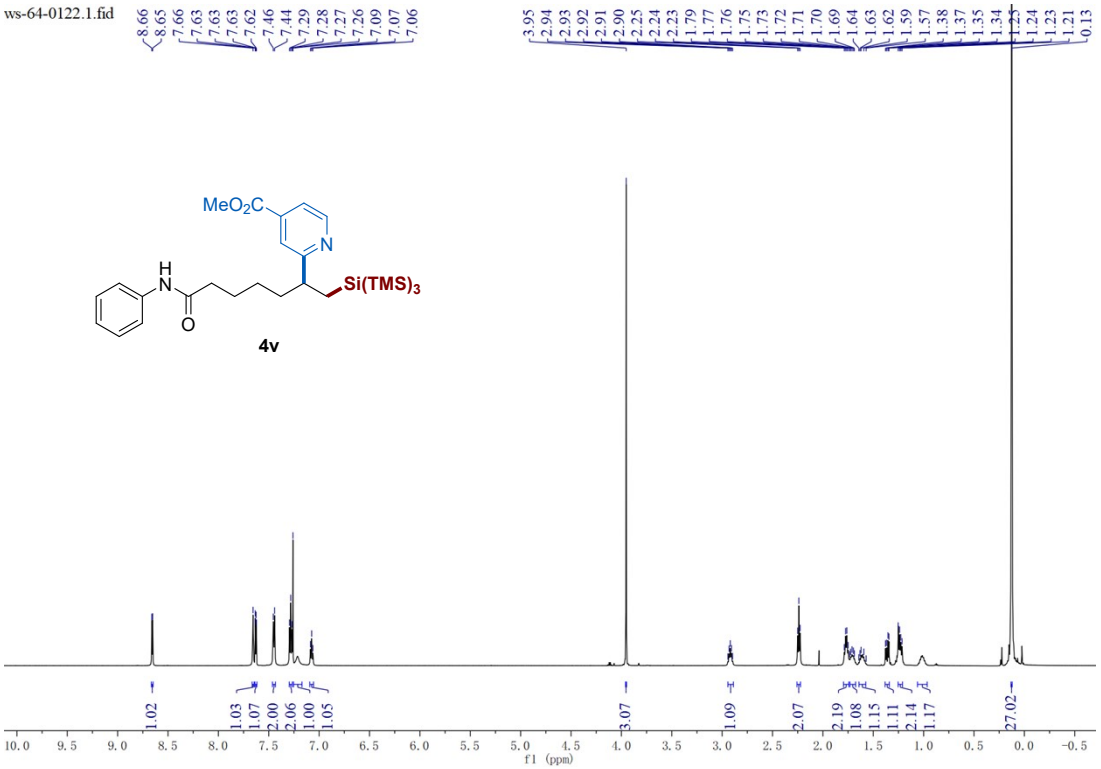


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

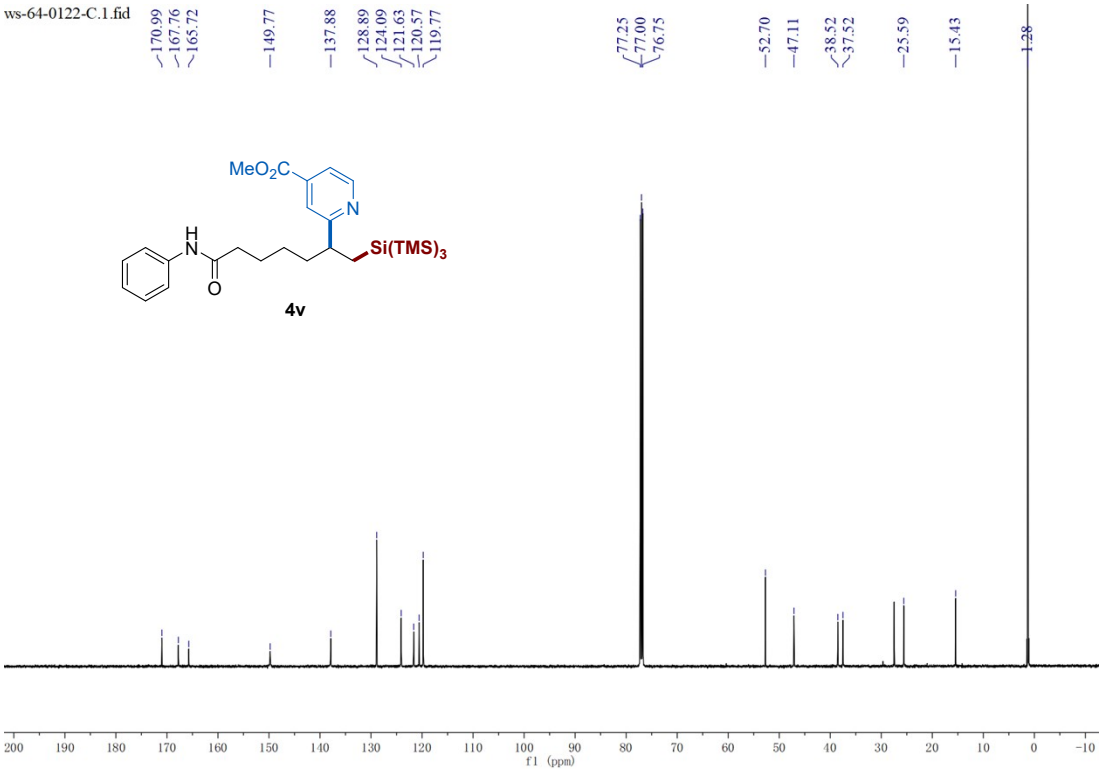


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-7-oxo-7-(phenylamino)heptan-2-yl)isonicotinate (4v)

600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

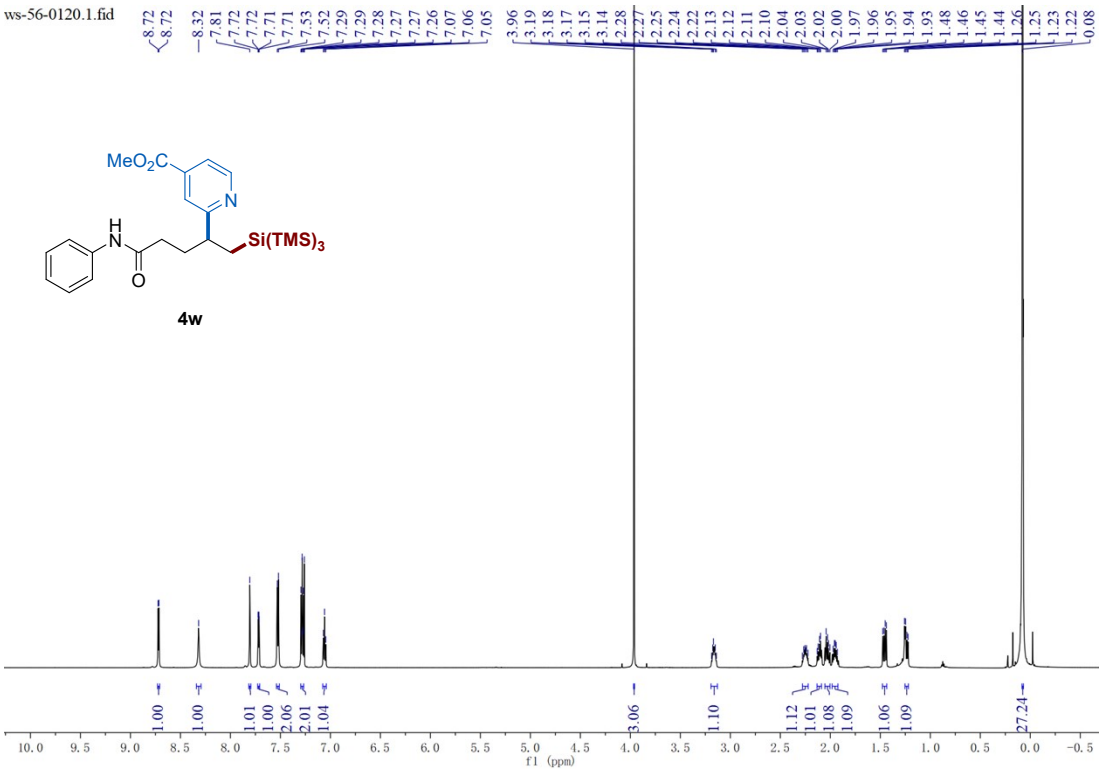


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

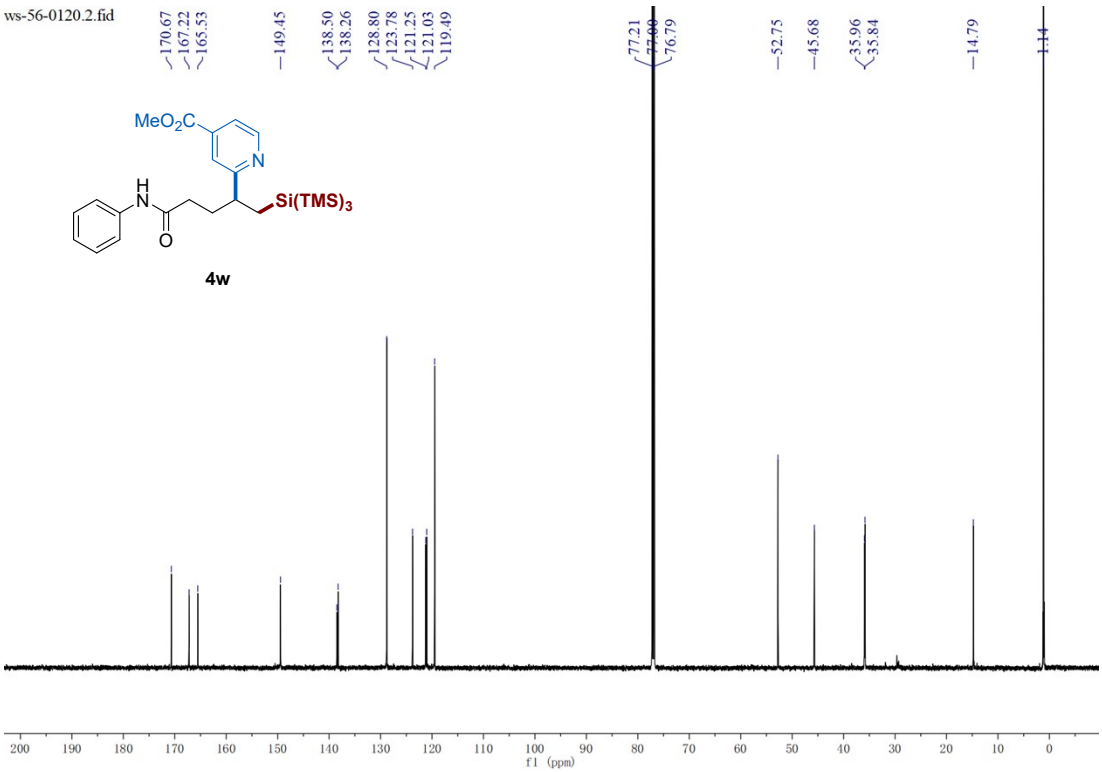


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-oxo-5-(phenylamino) pentan-2-yl) isonicotinate (4w)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

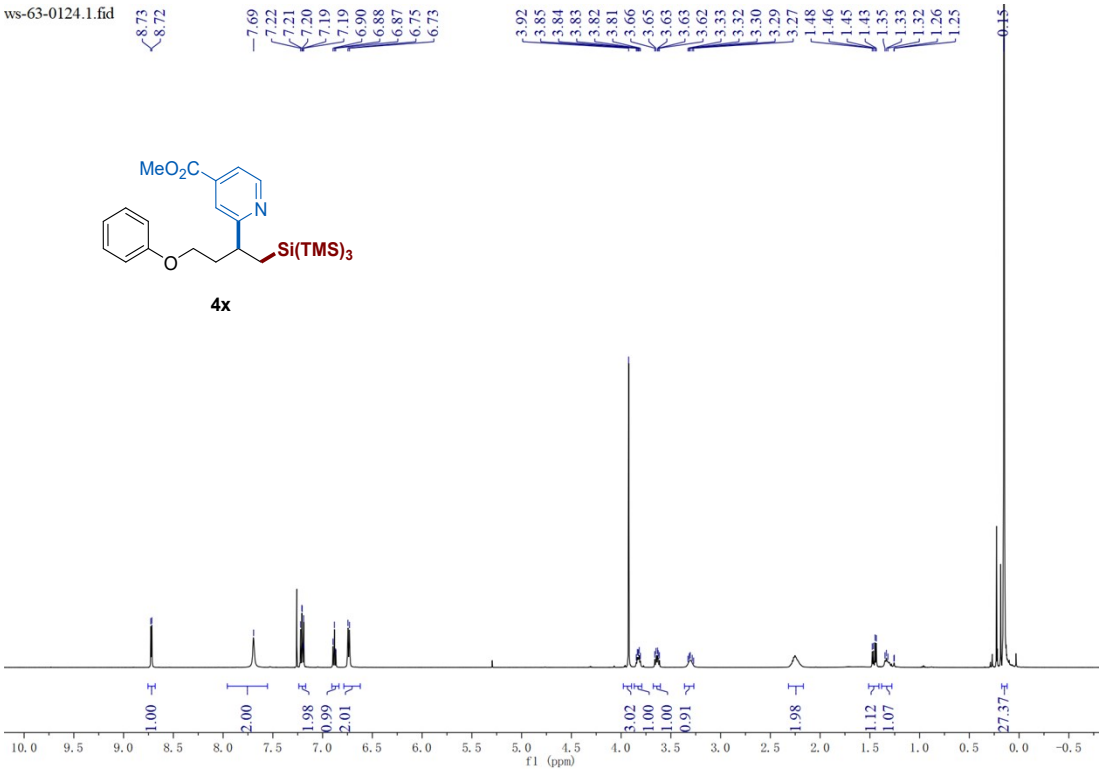


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

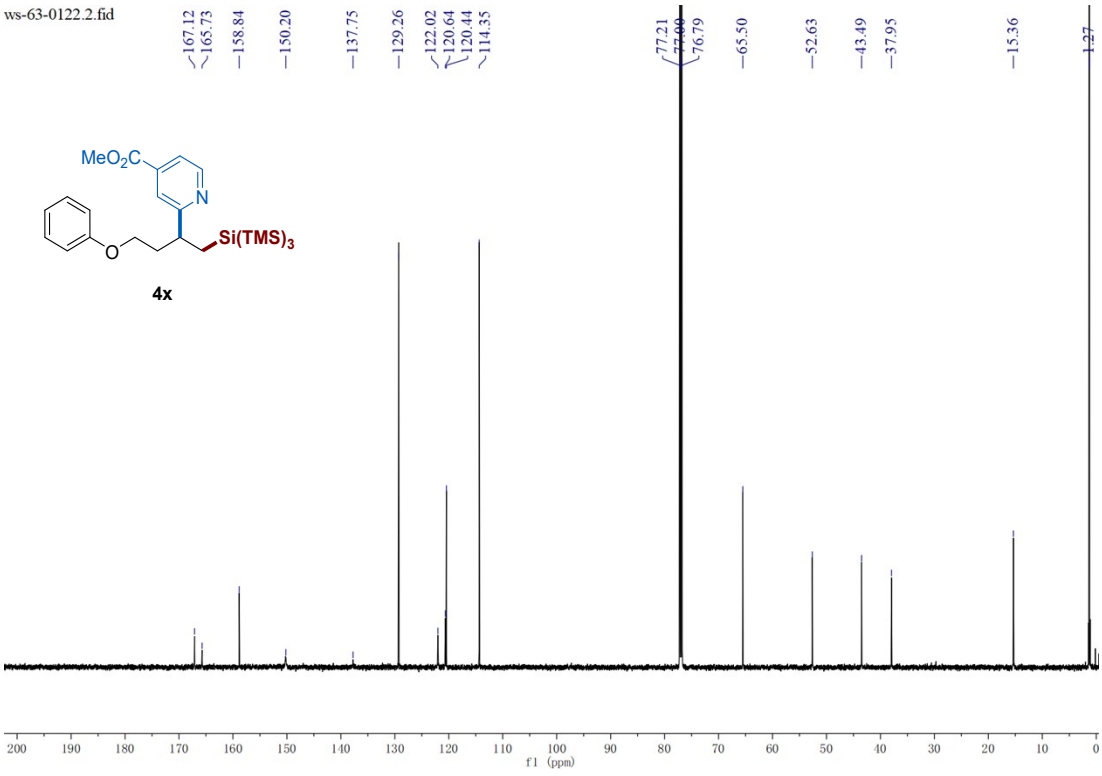


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-phenoxybutan-2-yl) isonicotinate (4x)

600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

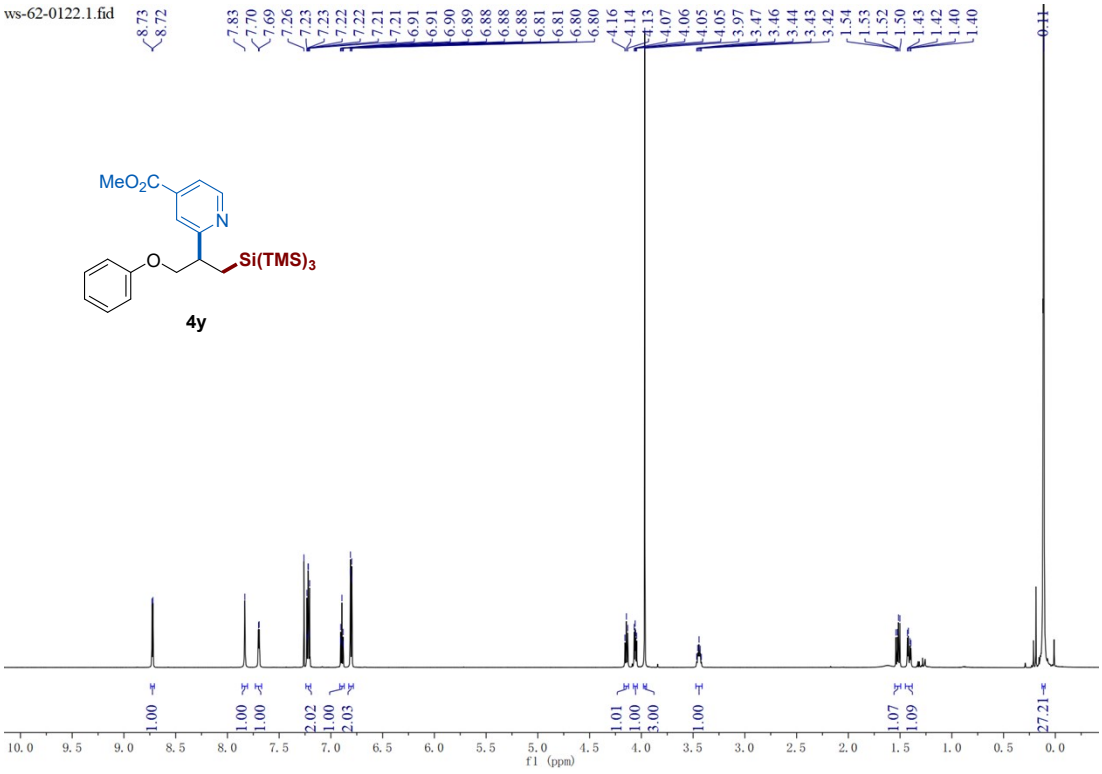


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

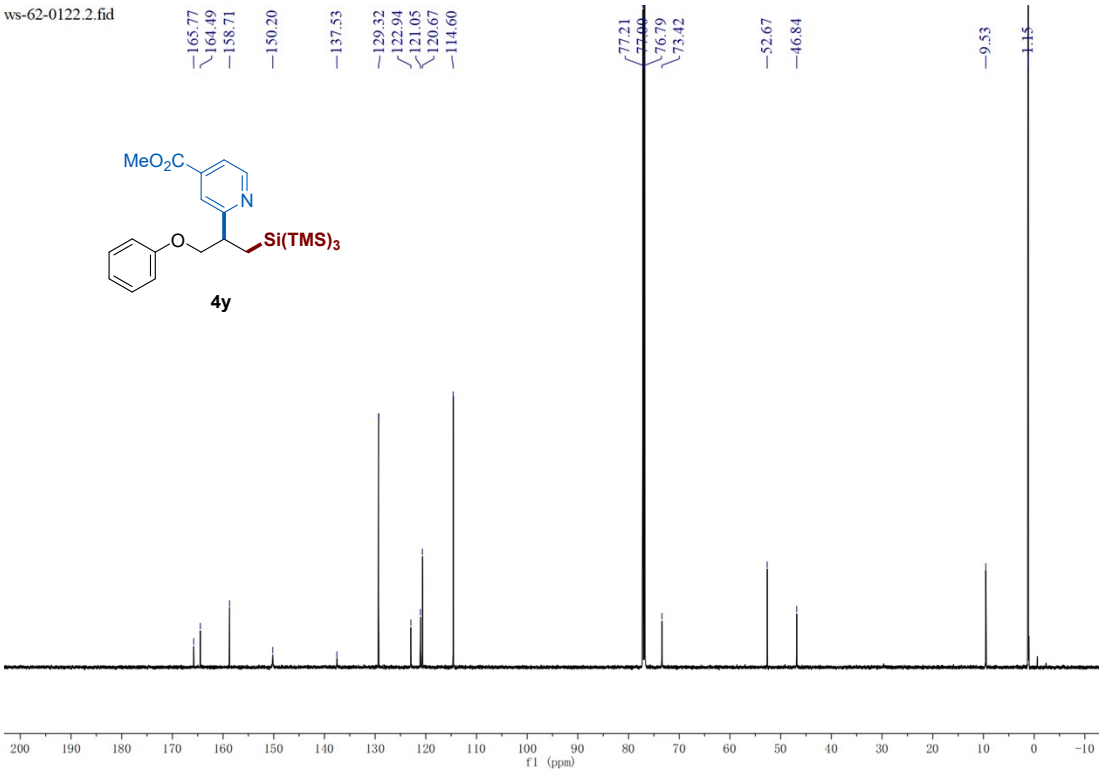


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-3-phenoxypropan-2-yl) isoni cotinate (4y)

600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

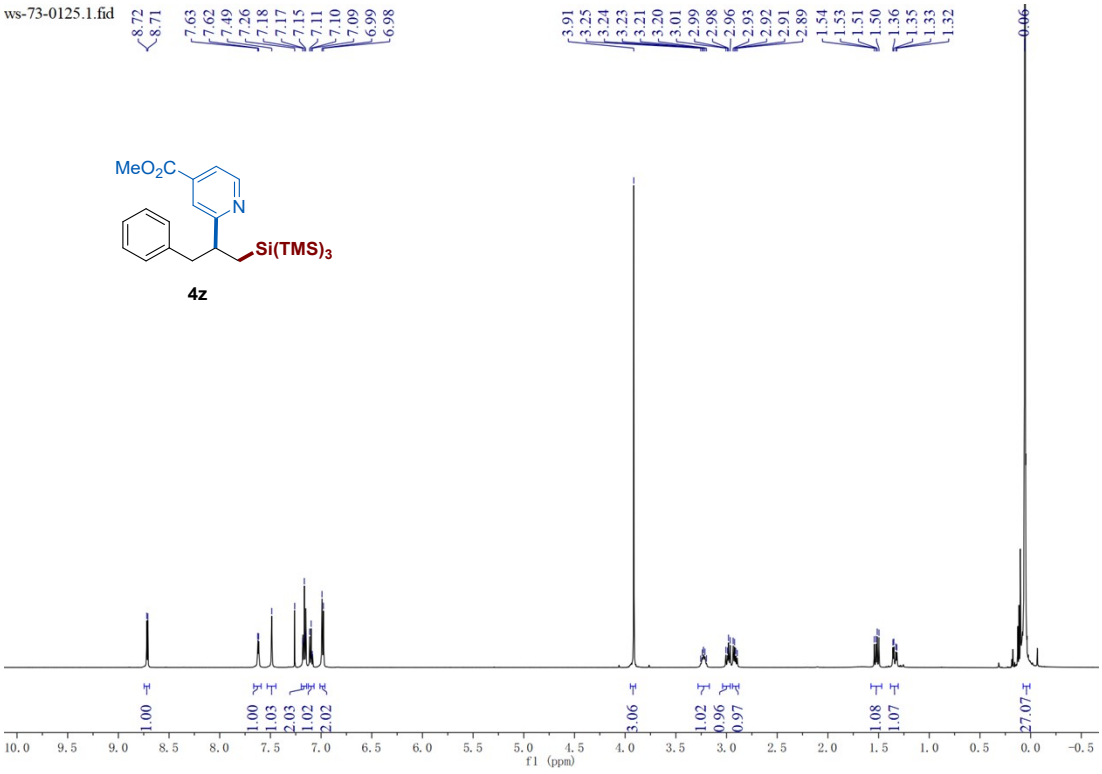


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

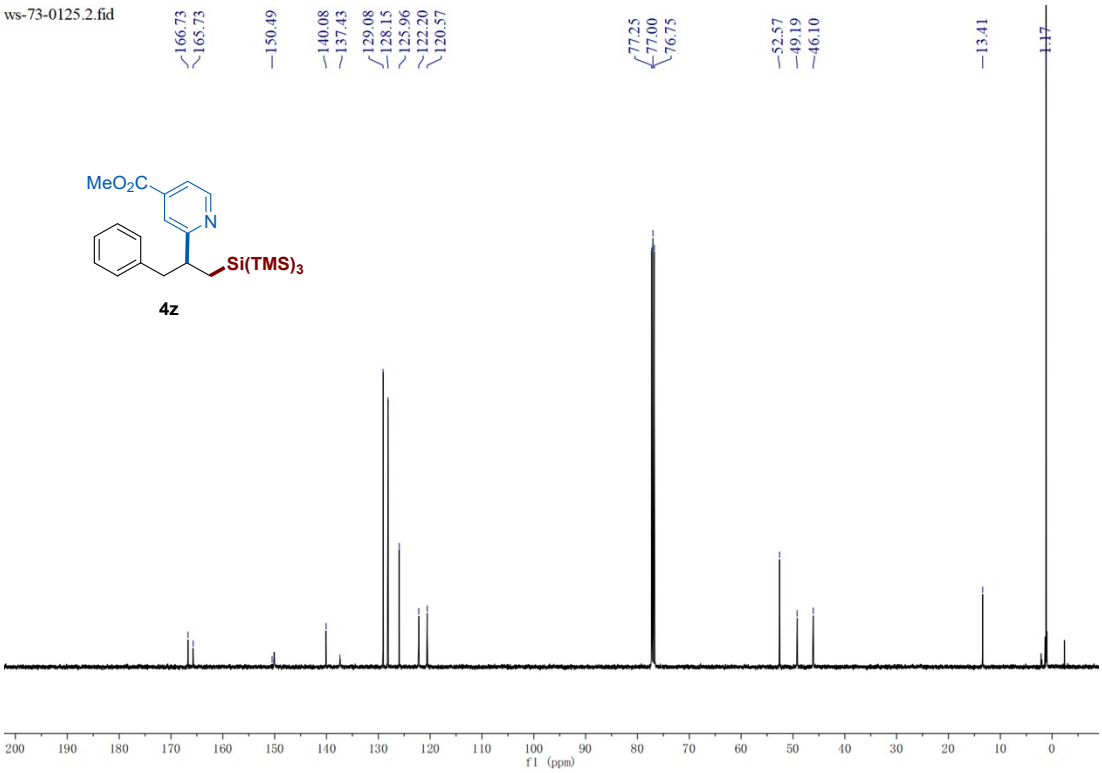


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-3-phenylpropan-2-yl)isonicotinate (4z)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

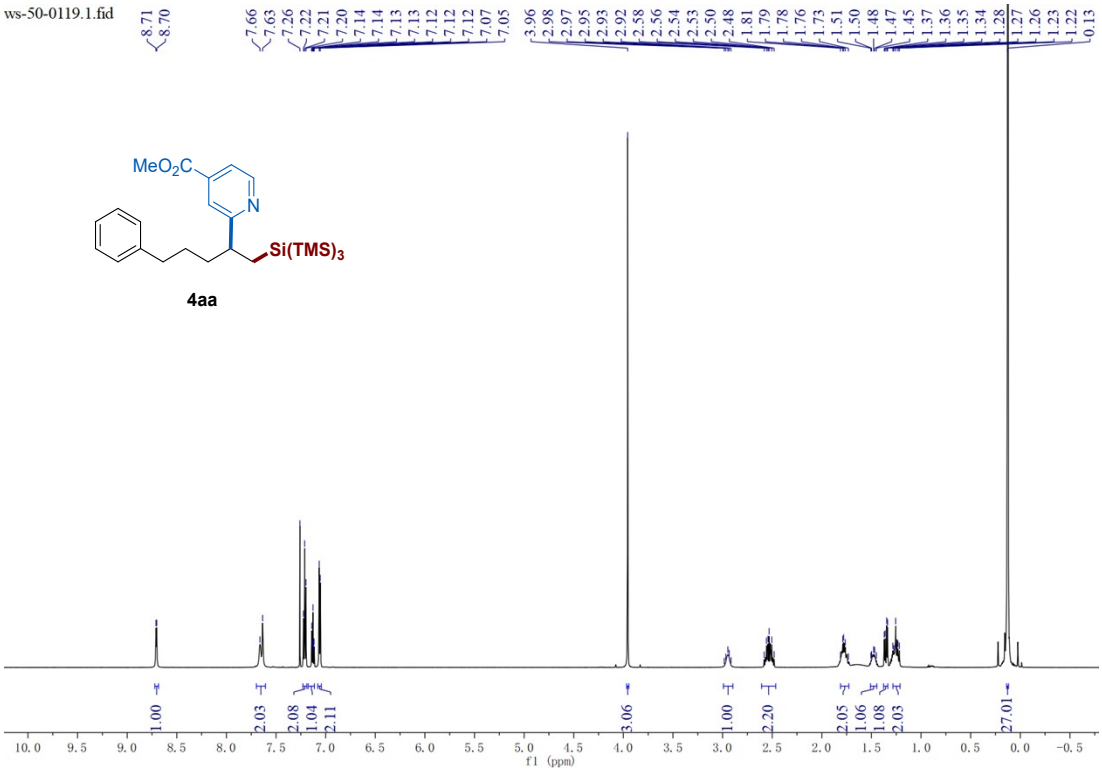


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

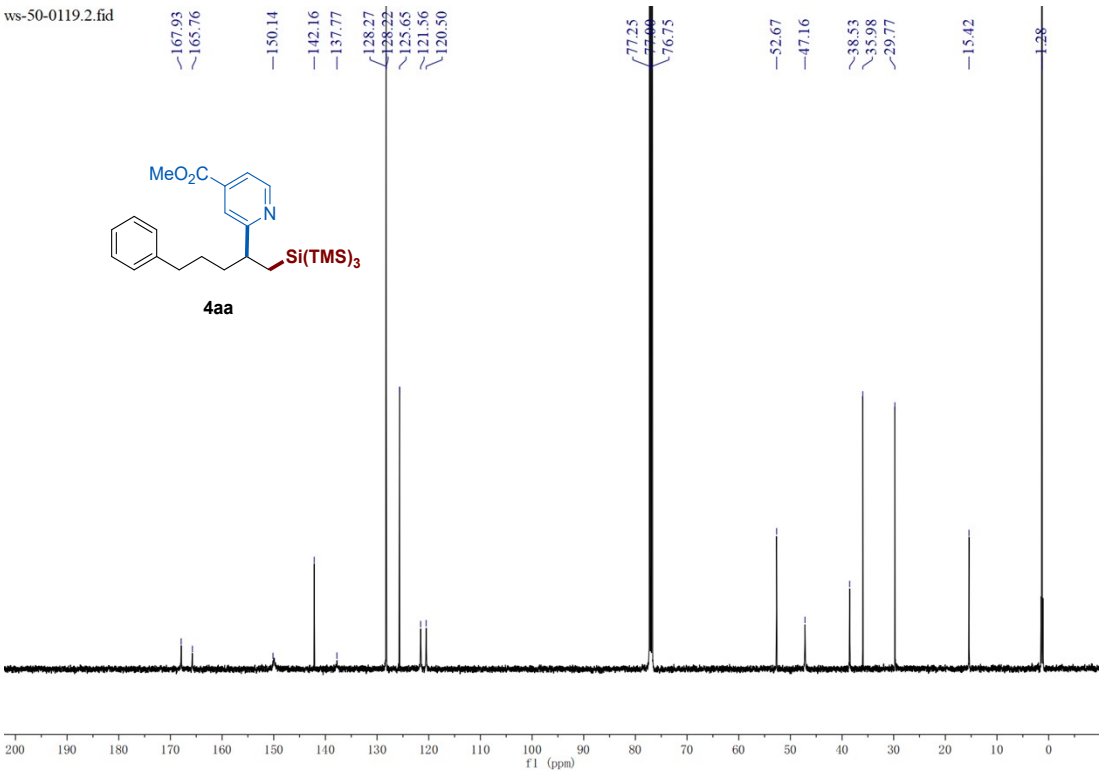


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) octan-2-yl) isonicotinate (4aa)

600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

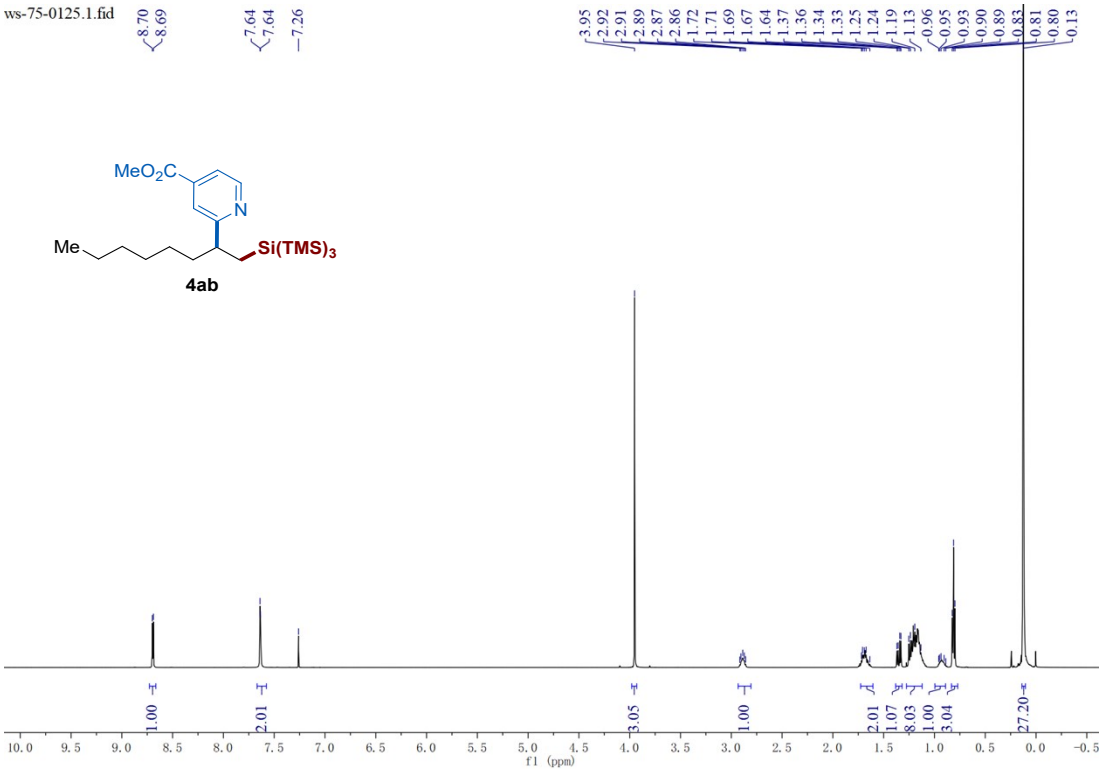


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

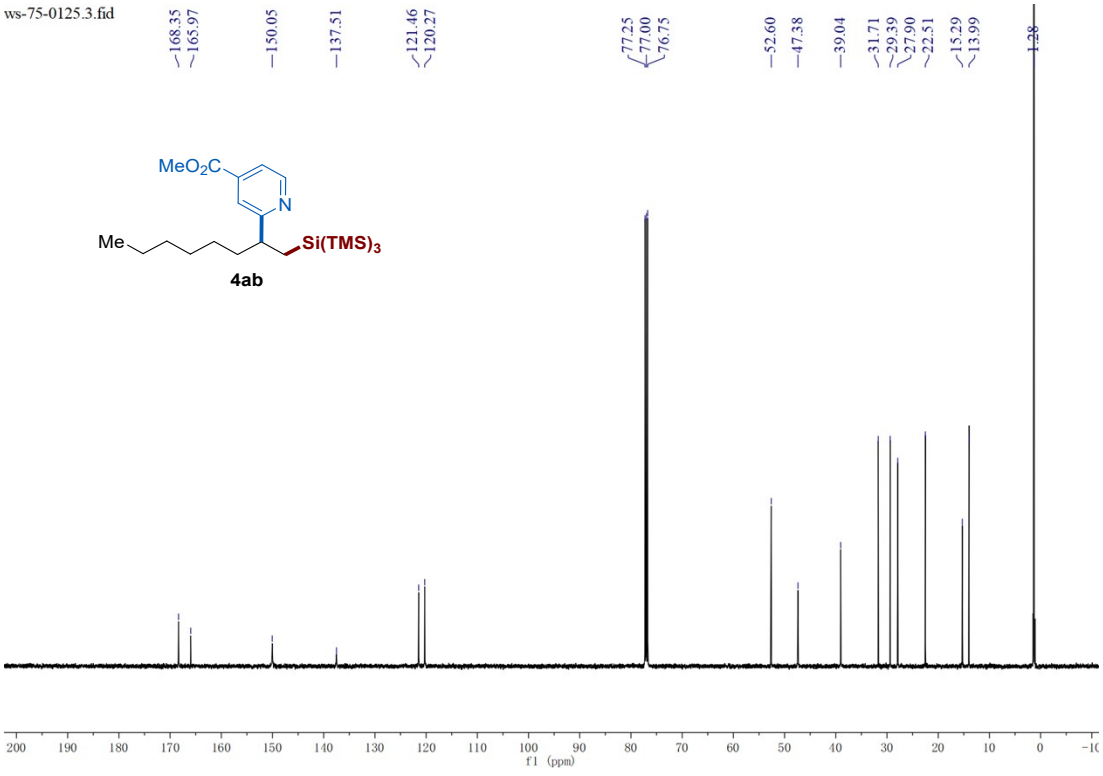


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) octan-2-yl) isonicotinate (4ab)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

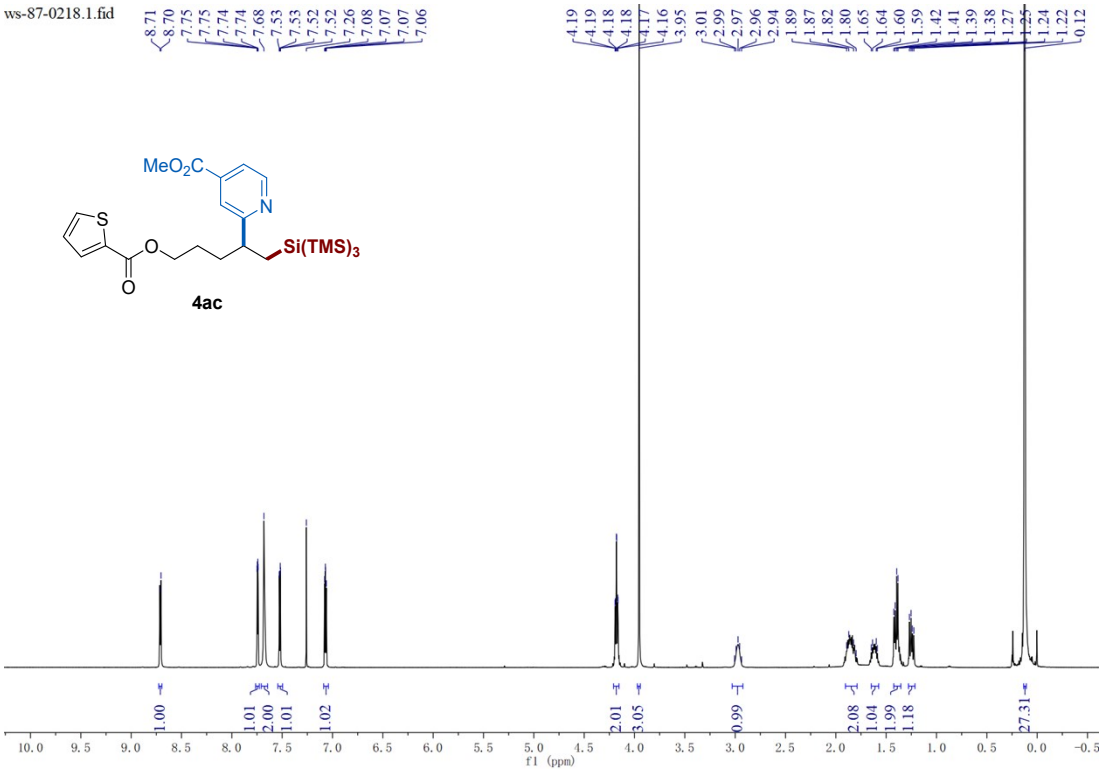


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

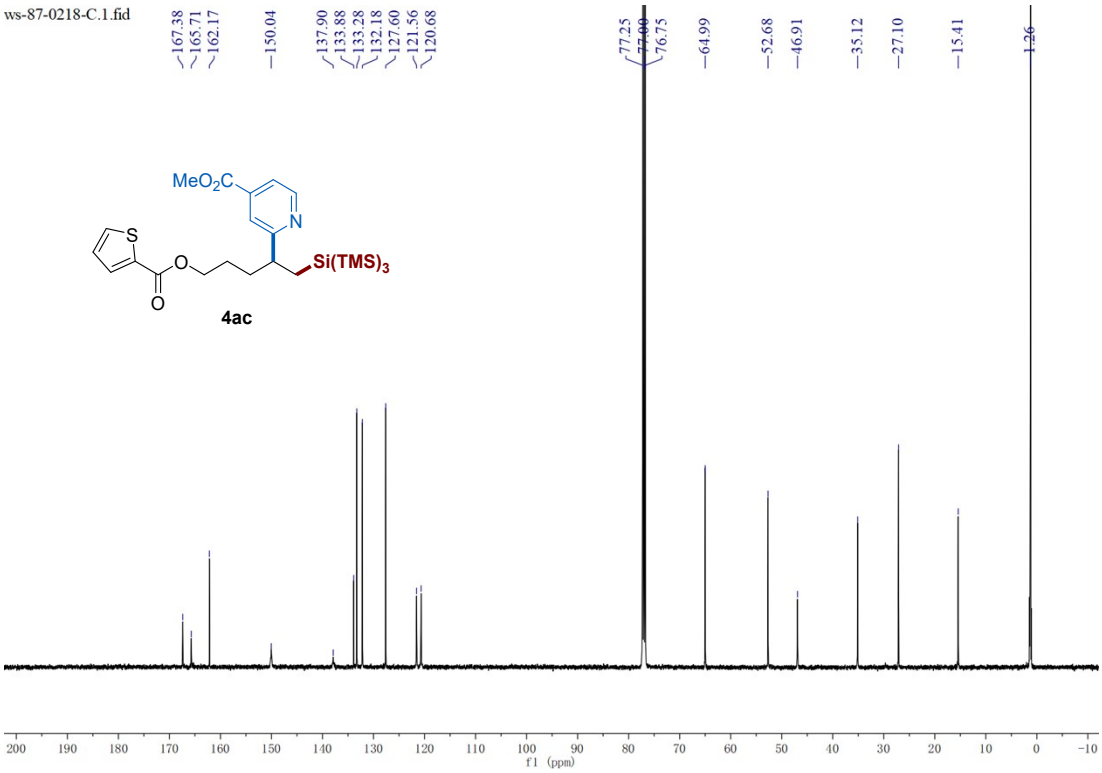


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-5-((thiophene-2-carbonyl) oxy) pentan-2-yl) isonicotinate (4ac).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

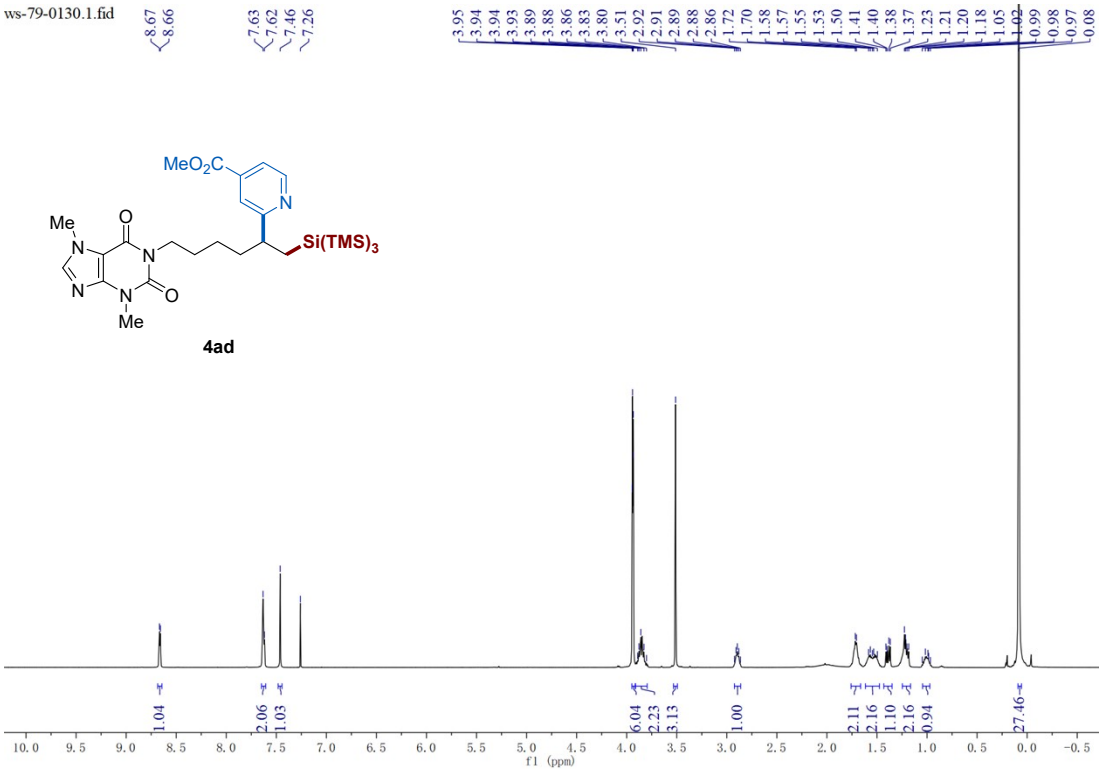


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

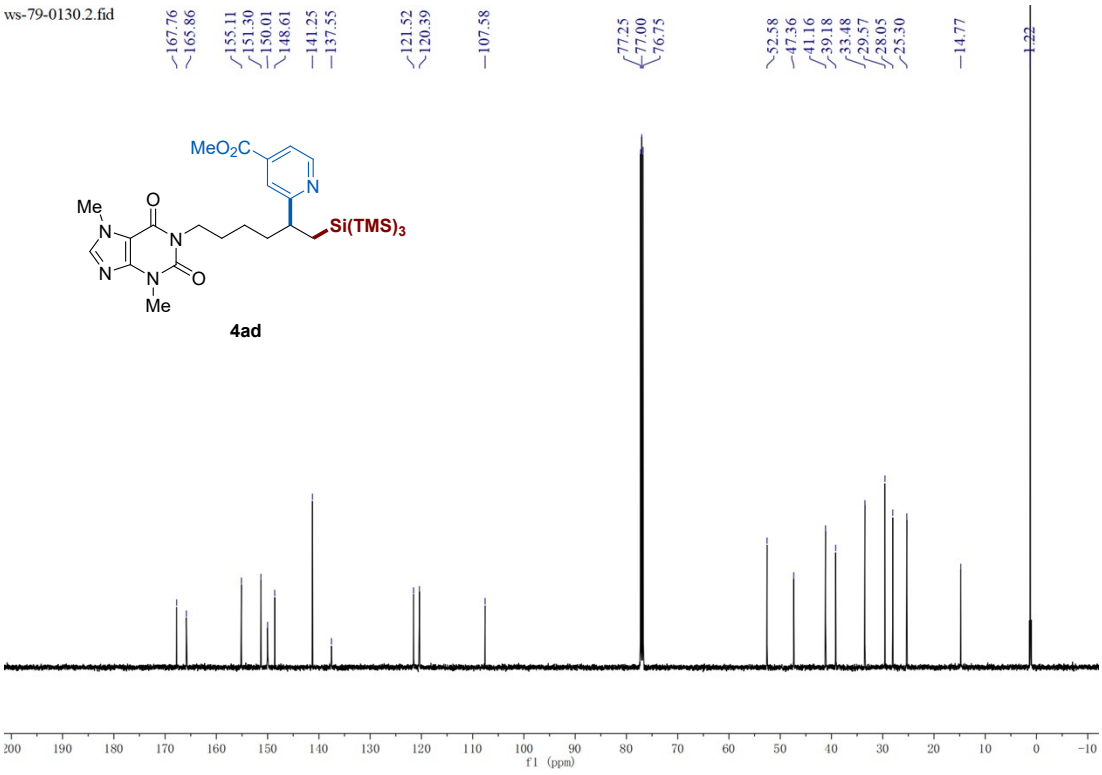


Methyl 2-(6-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl) hexan-2-yl) isonicotinate (4ad).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

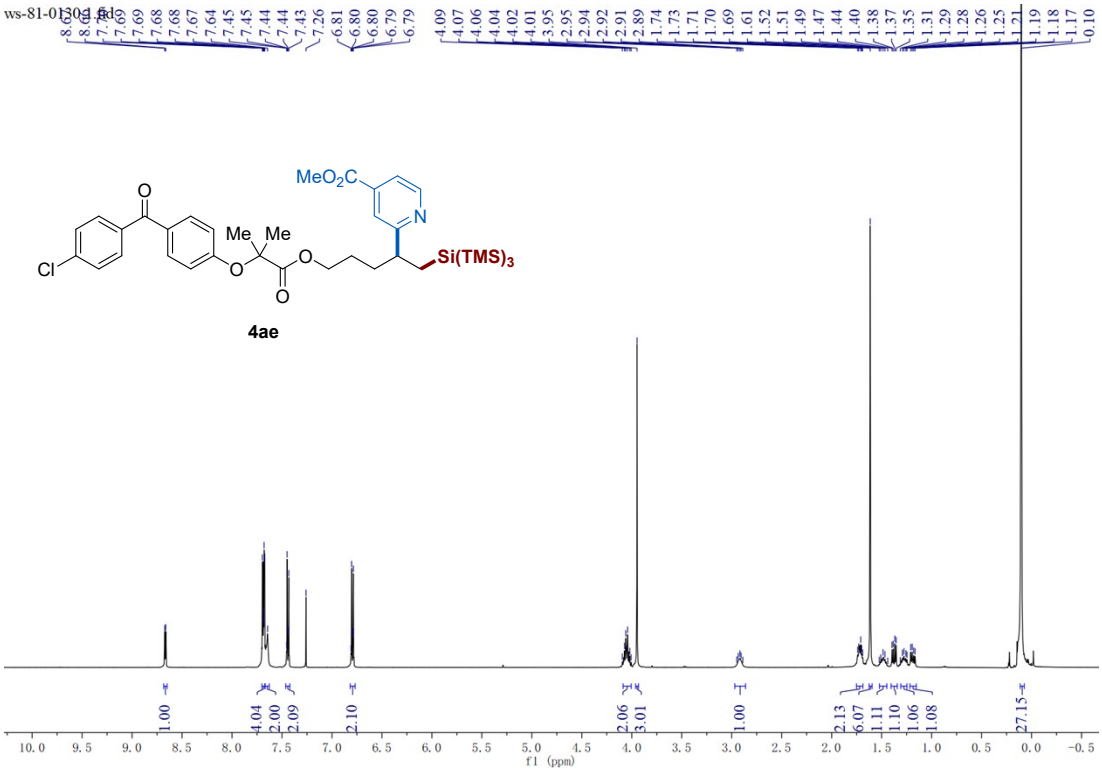


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

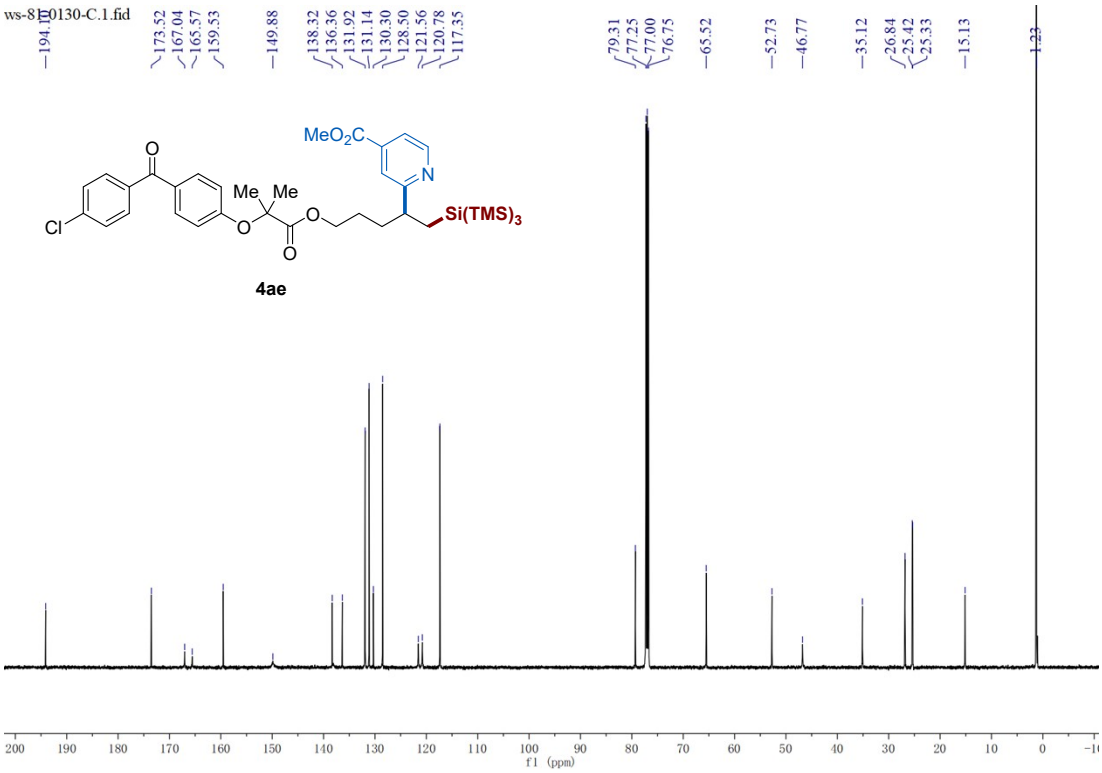


Methyl 2-(5-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4ae).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

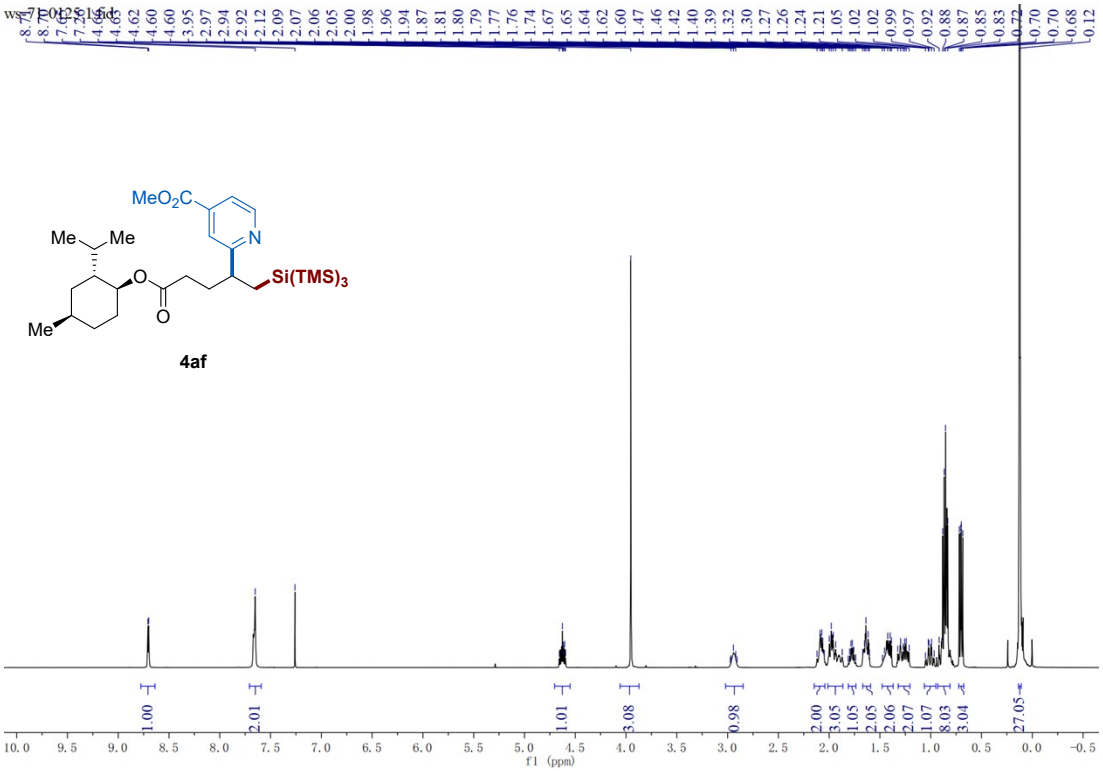


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

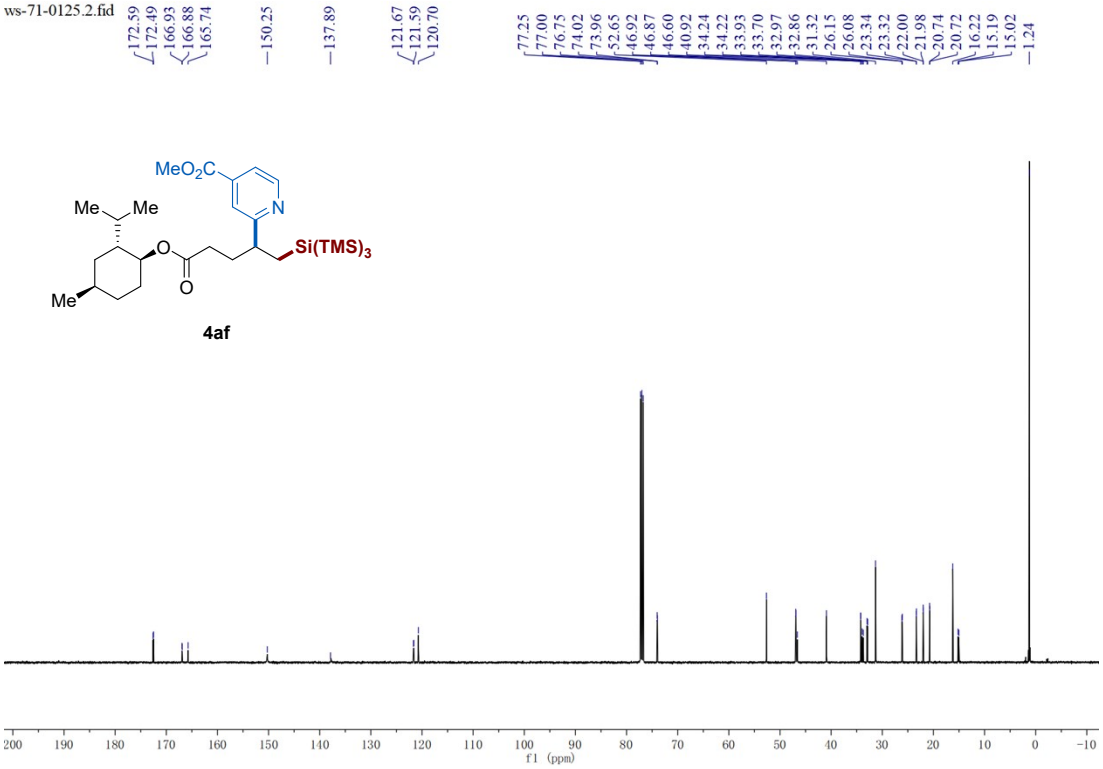


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-(((1R,2S,4S)-2-isopropyl-4-methylcyclohexyl)oxy)-5-oxopentan-2-yl)isonicotinate (4af).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

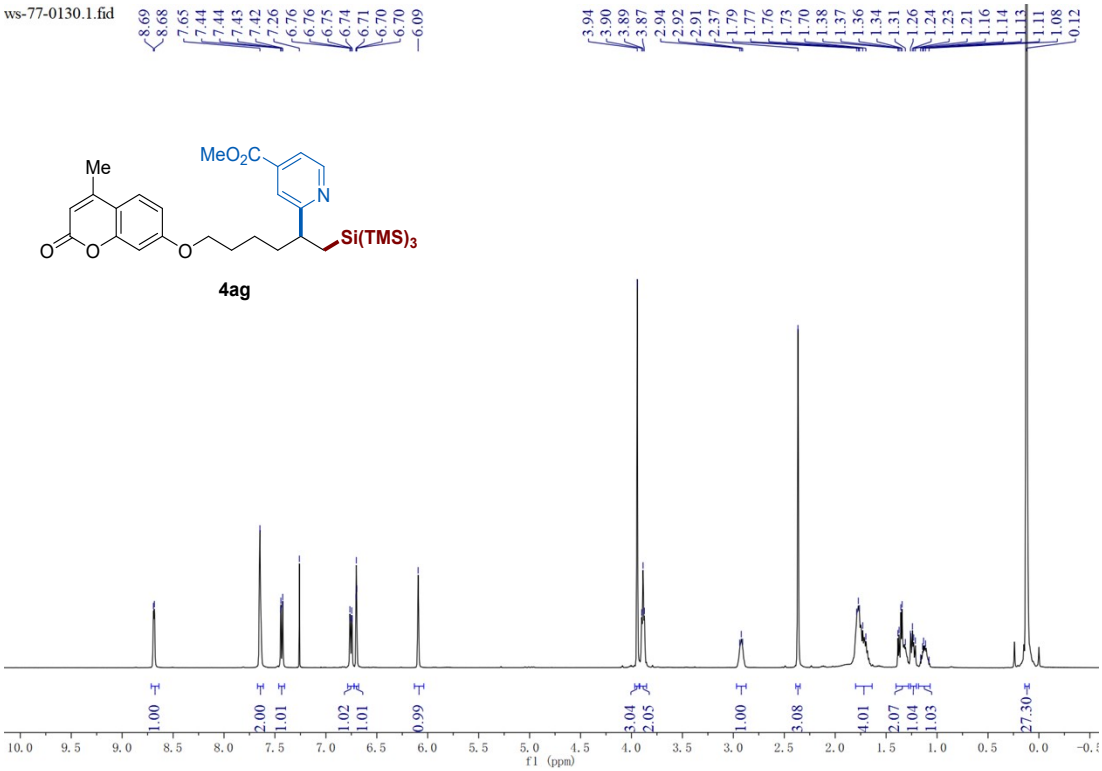


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

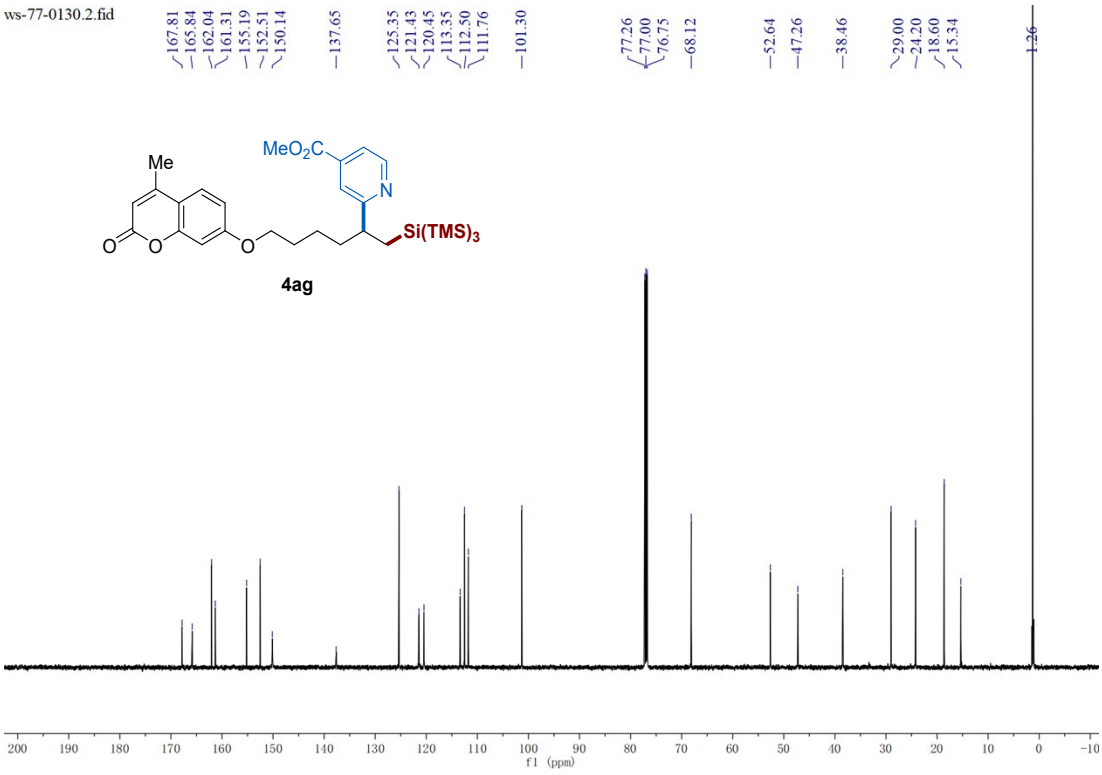


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-6-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)hexan-2-yl)isonicotinate (4ag).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

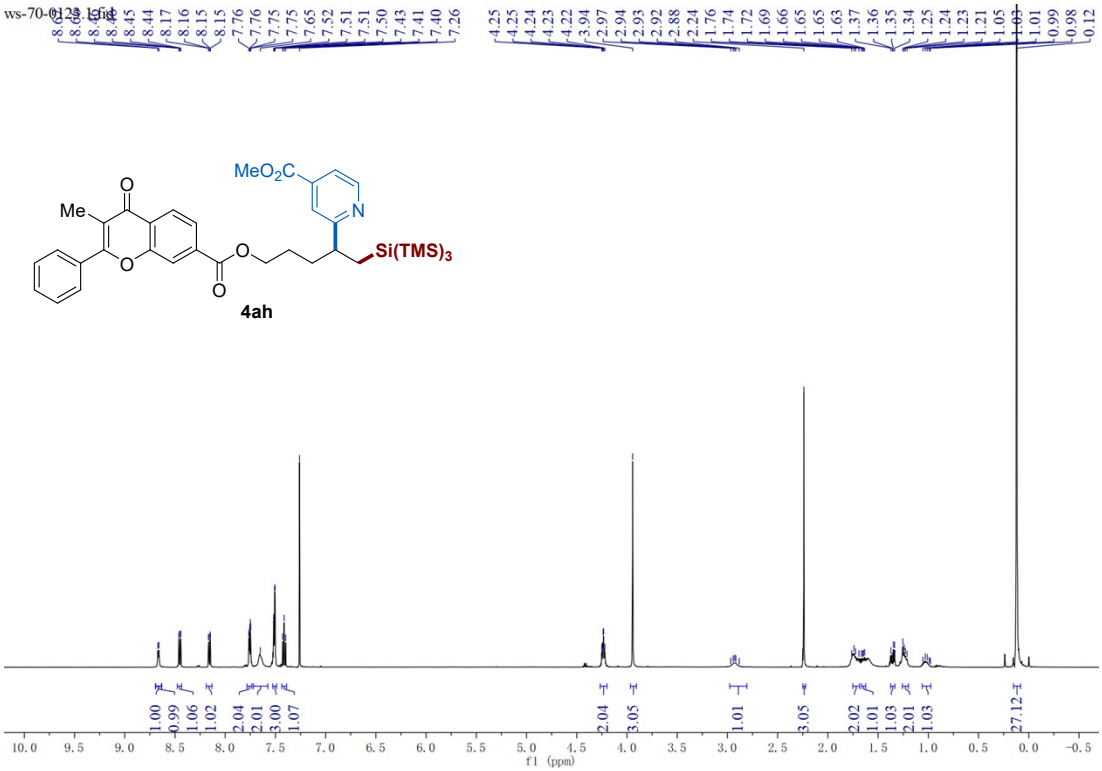


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

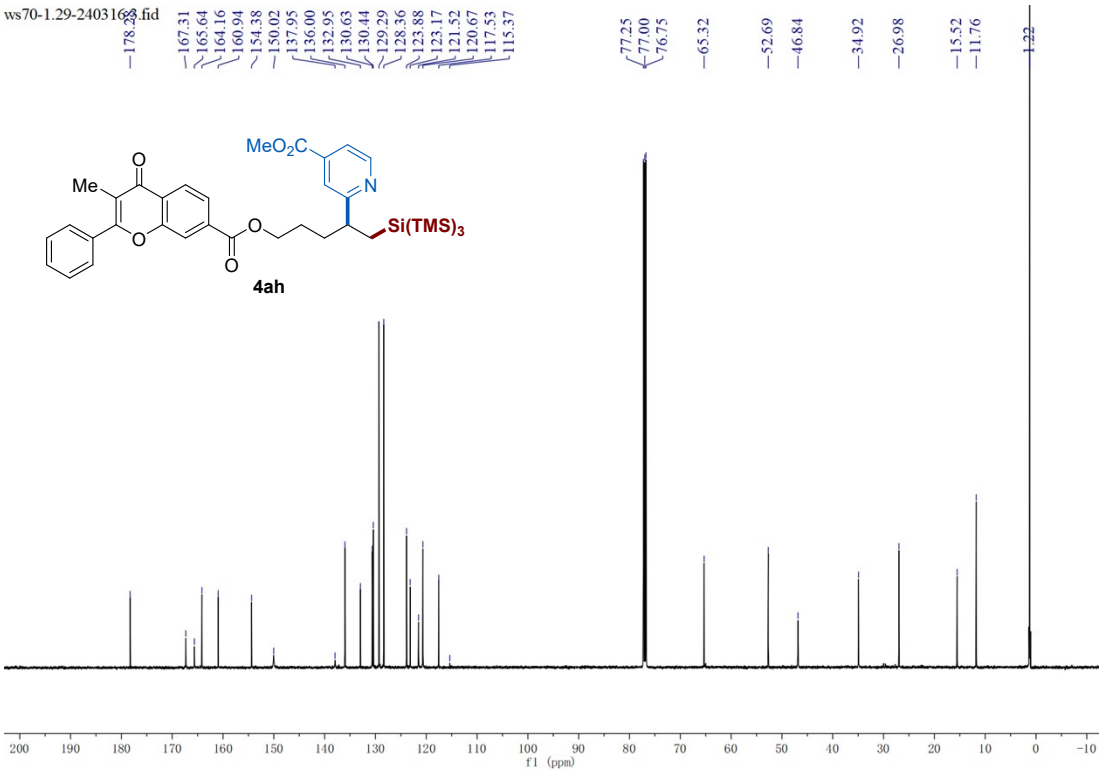


Methyl 2-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-((3-methyl-4-oxo-2-phenyl-4H-chromene-7-carbonyl)oxy)pentan-2-yl)isonicotinate (4ah).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

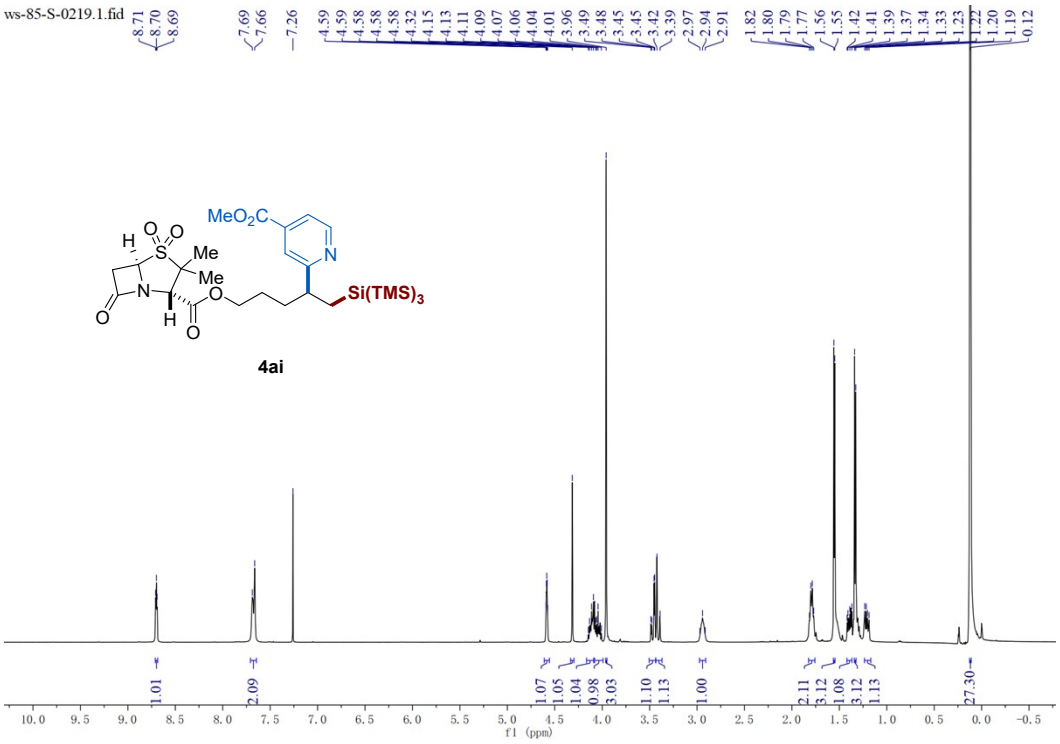


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

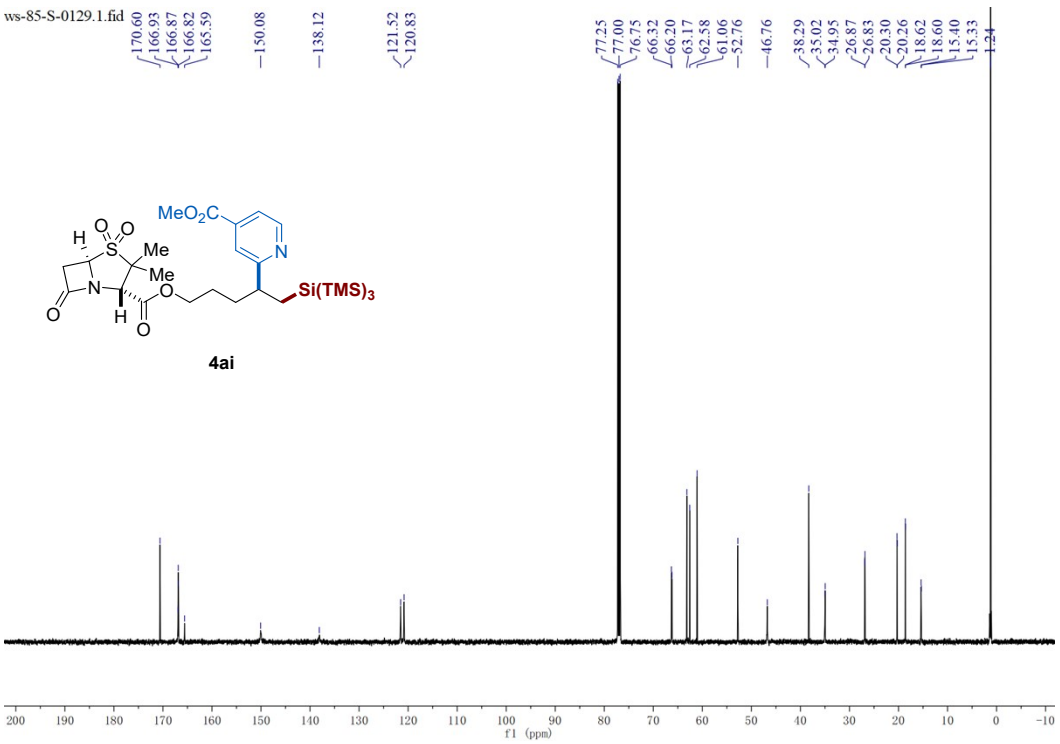


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-(4-(methoxycarbonyl) pyridin-2-yl) pentyl (2R,5S)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo [3.2.0] heptane-2-carboxylate 4,4-dioxide (4ai).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

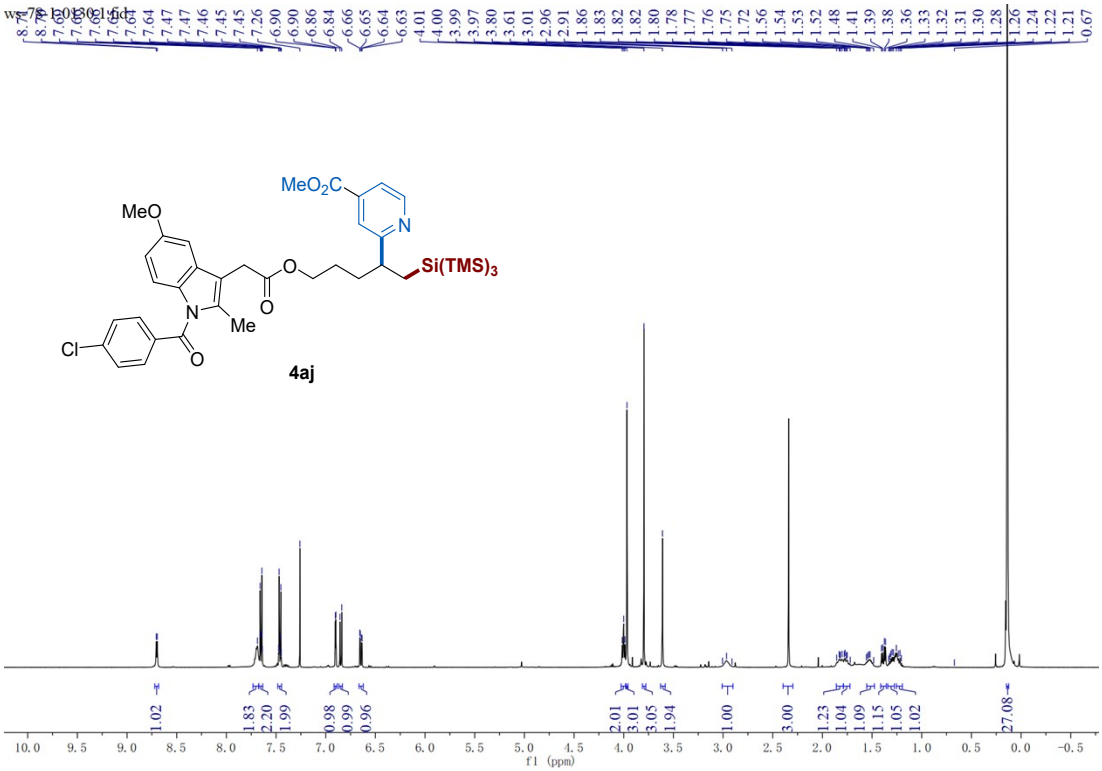


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

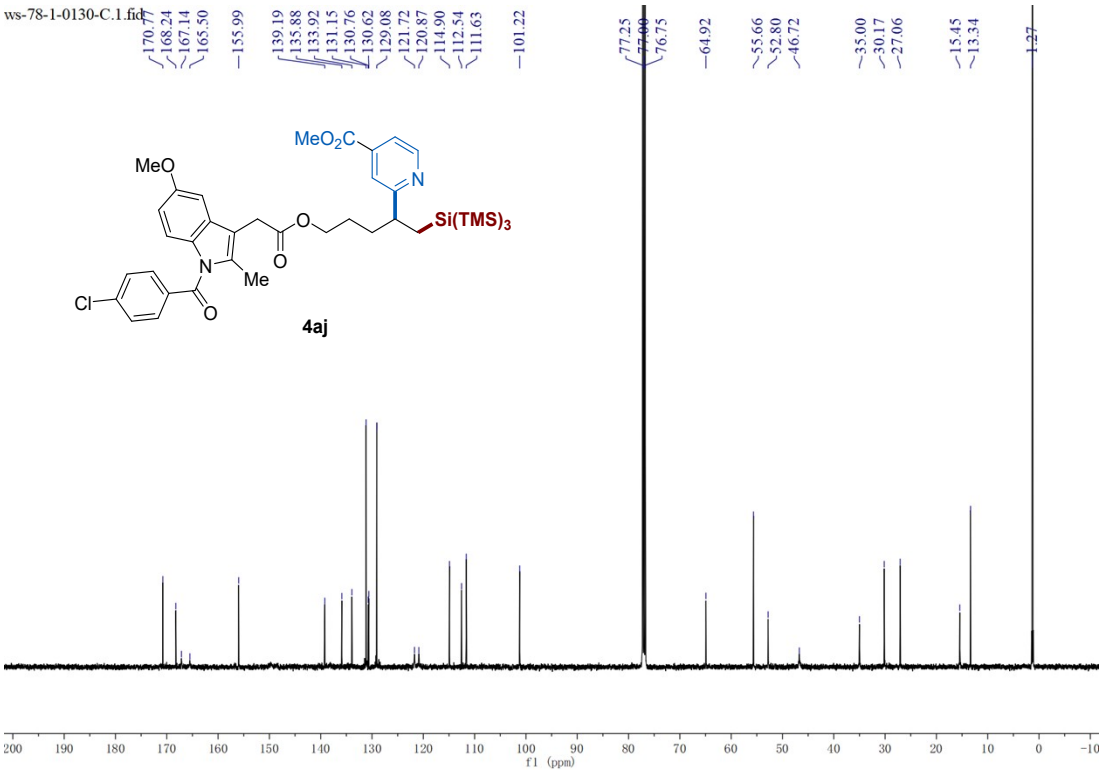


Methyl 2-(5-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentan-2-yl)isonicotinate (4aj).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

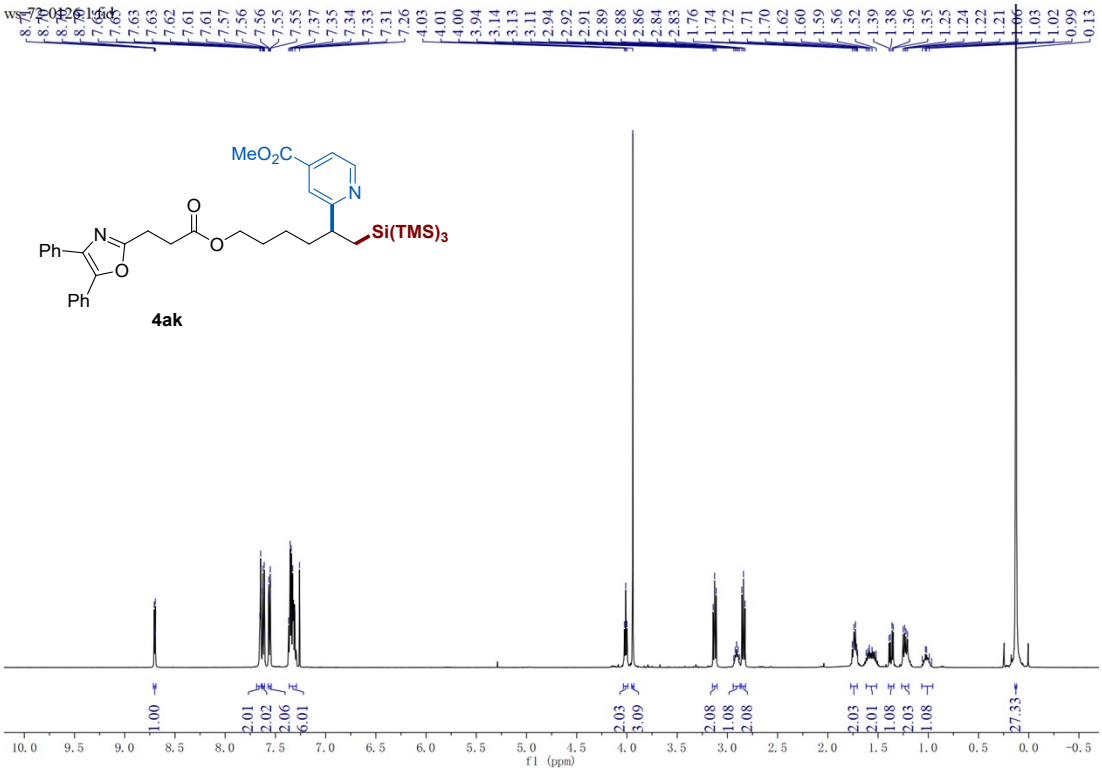


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

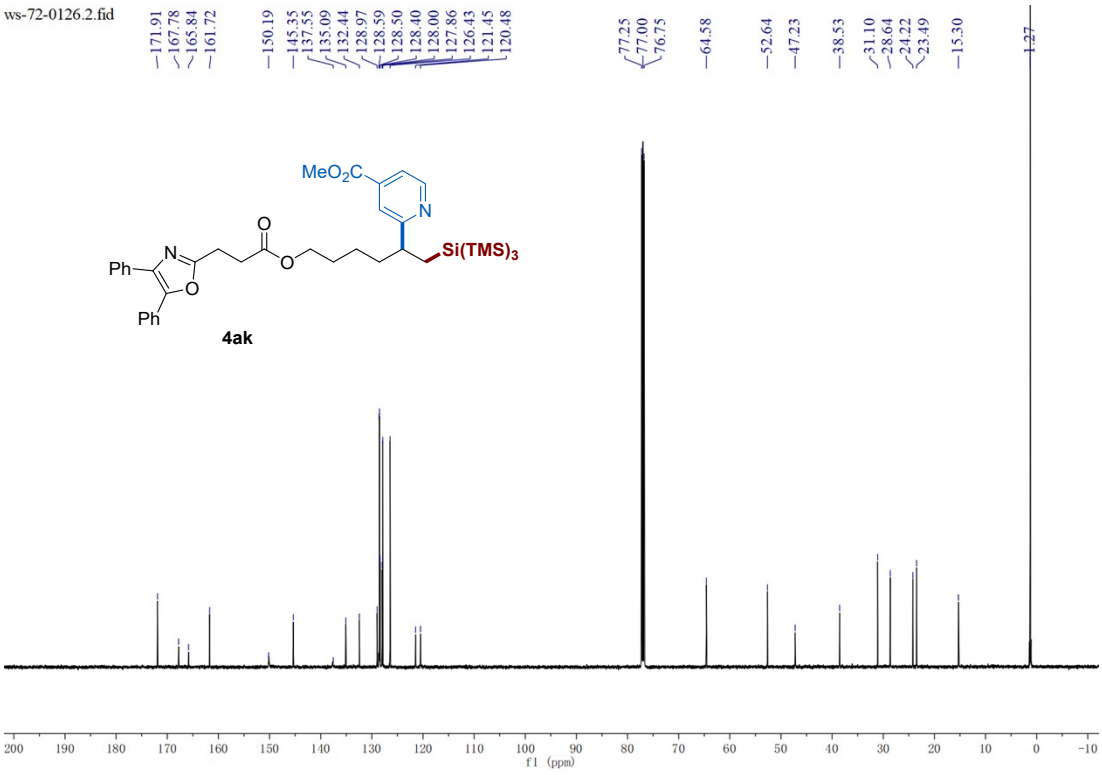


Methyl 2-(6-((3-(4,5-diphenyloxazol-2-yl)propanoyl)oxy)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)hexan-2-yl)isonicotinate (4ak).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

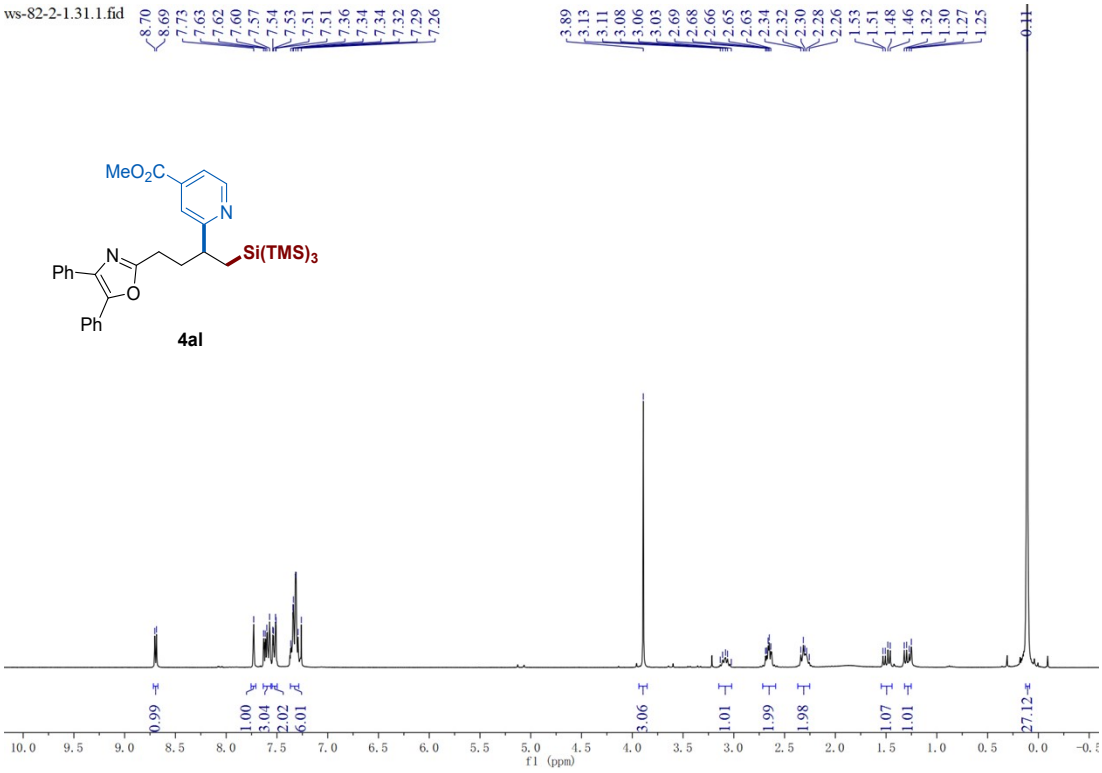


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

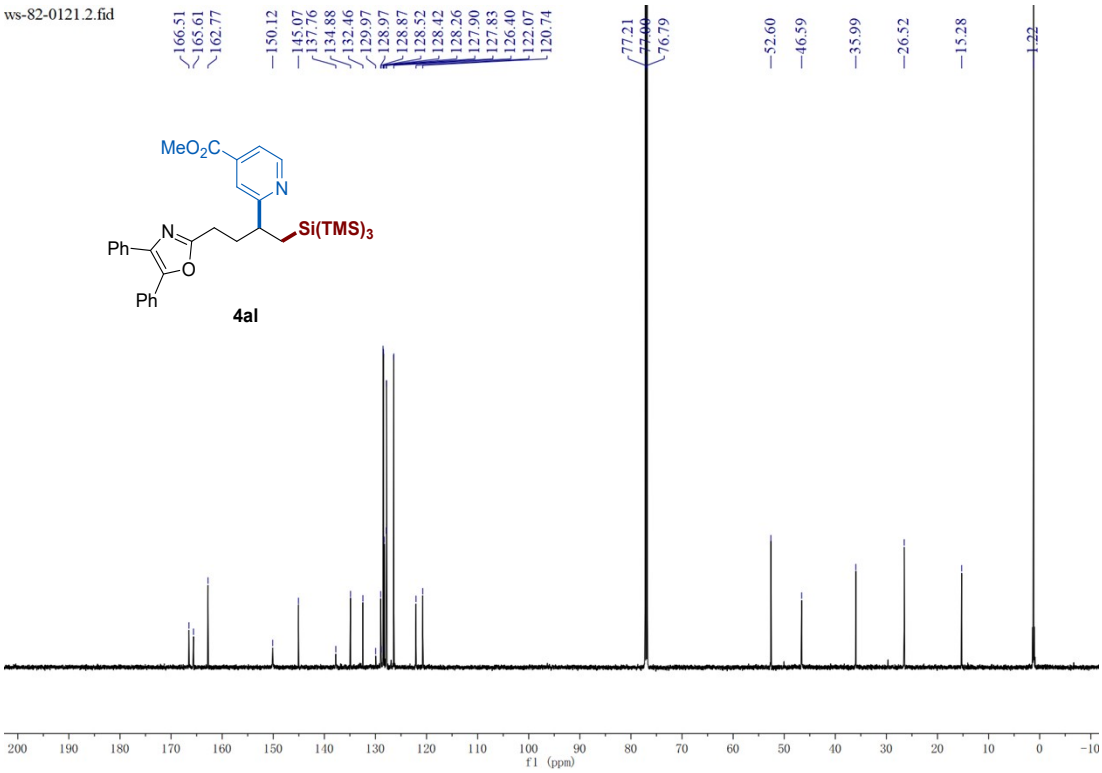


Methyl 2-(4-(4,5-diphenyloxazol-2-yl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)butan-2-yl)isonicotinate (4al).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

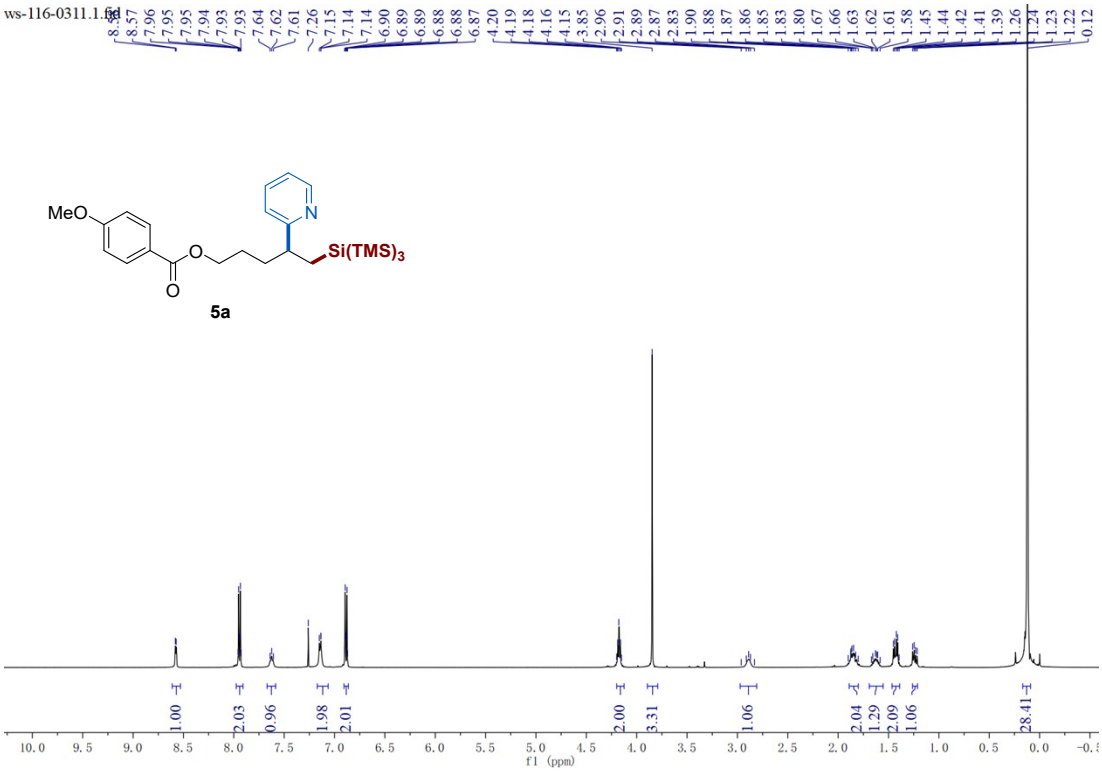


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

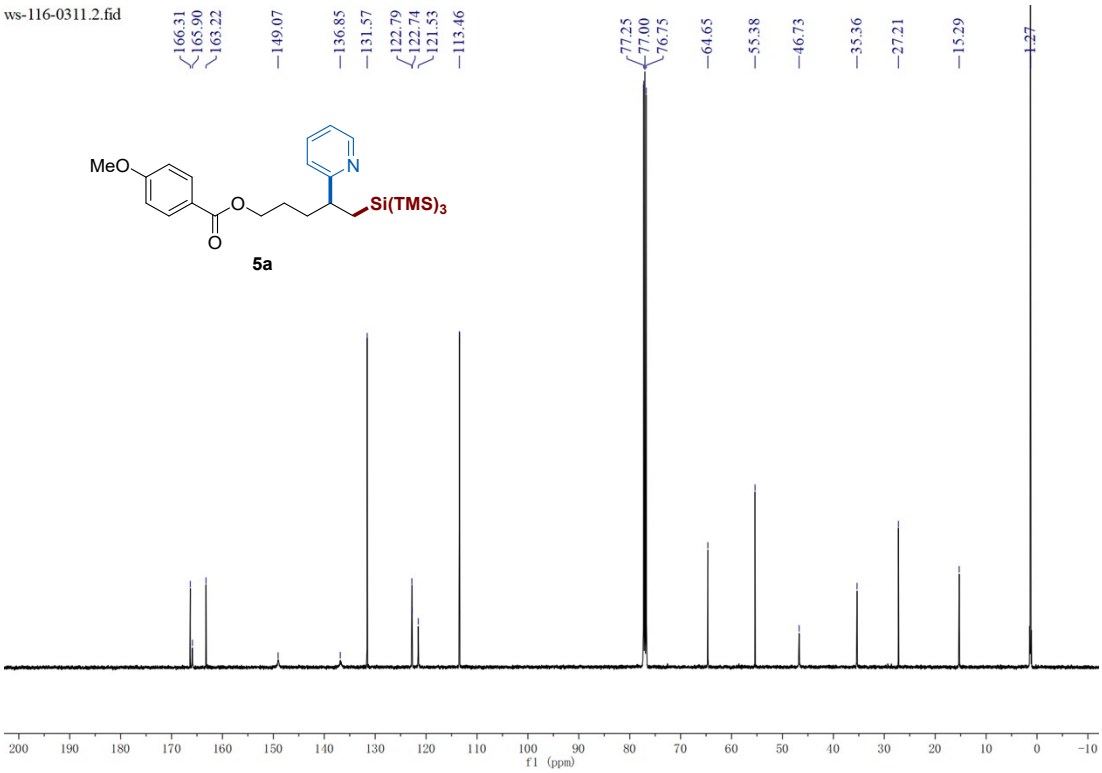


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-(pyridin-2-yl) pentyl 4-methoxybenzoate (5a).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

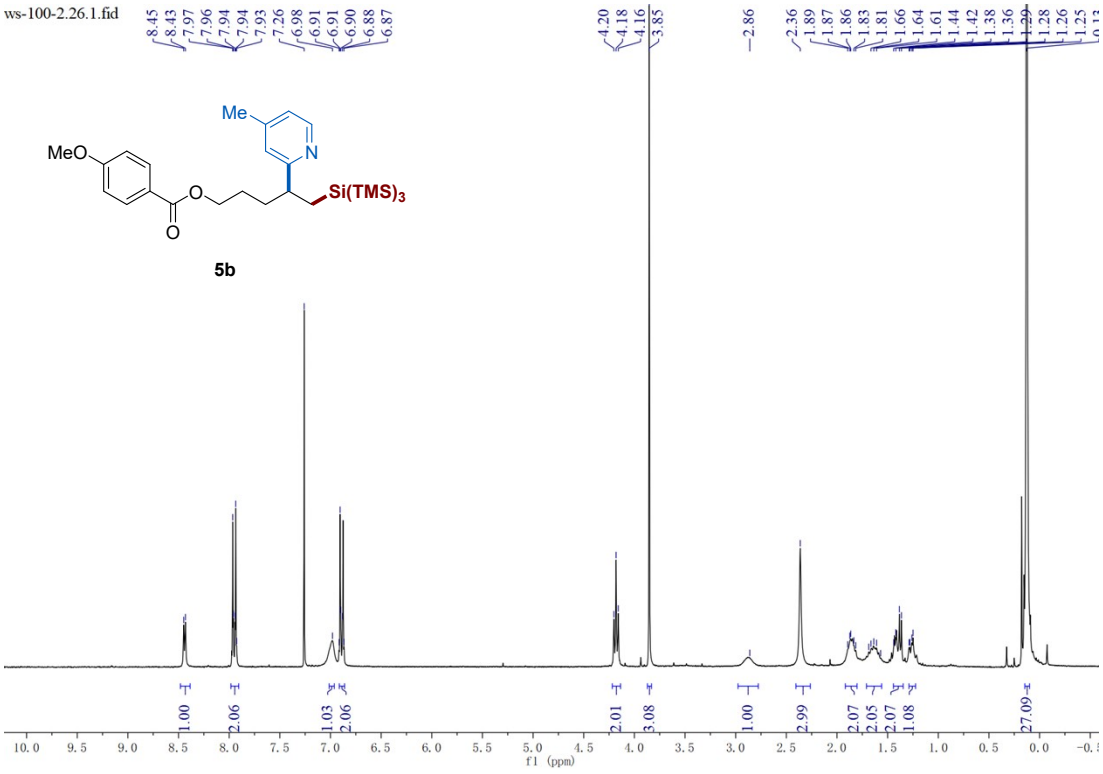


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

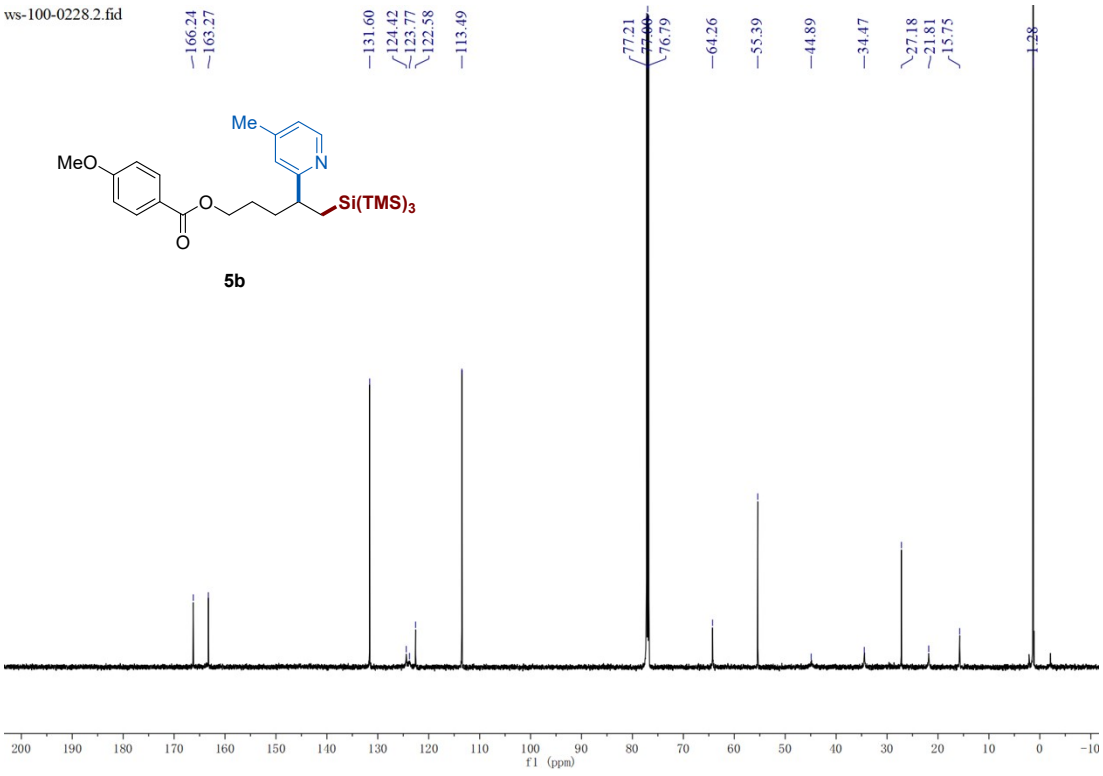


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-methylpyridin-2-yl)pentyl 4-methoxybenzoate (5b).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

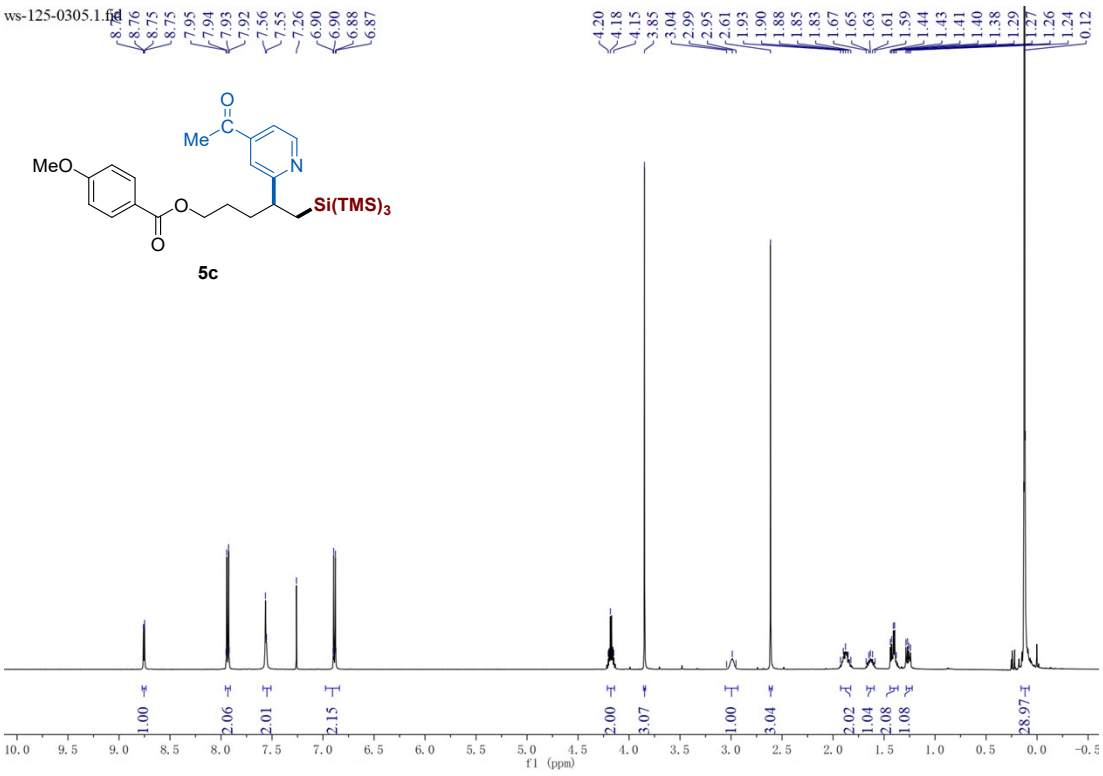


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

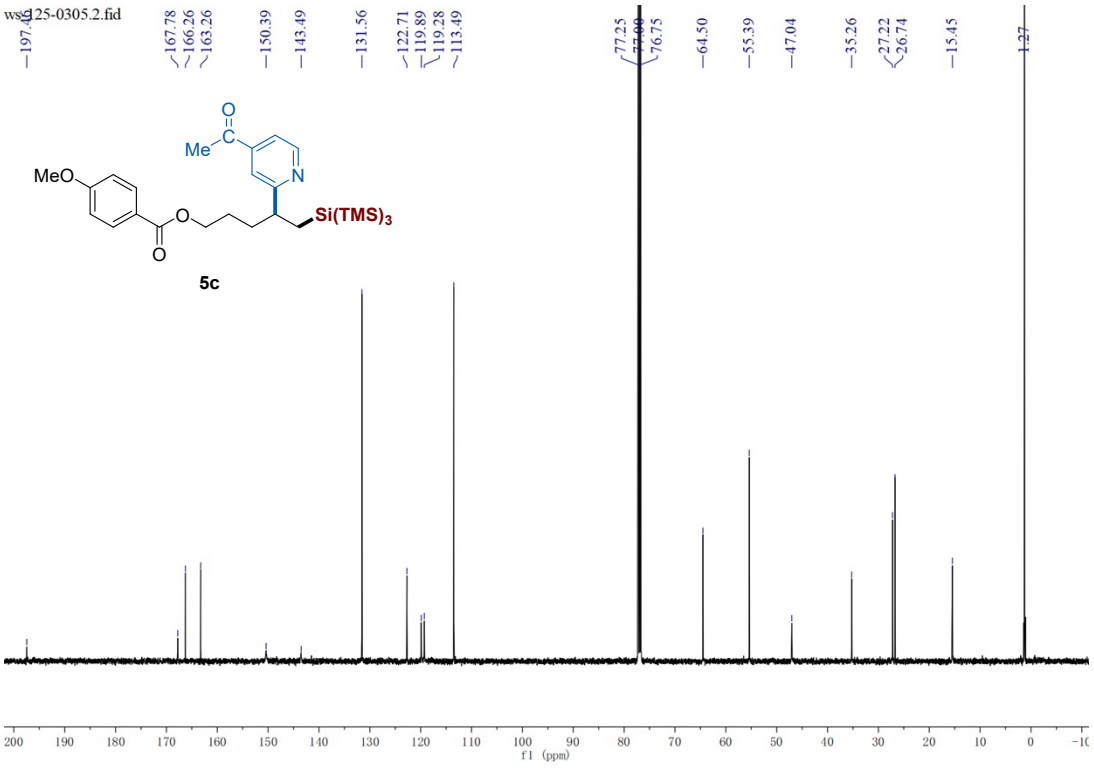


4-(4-Acetylpyridin-2-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5c).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

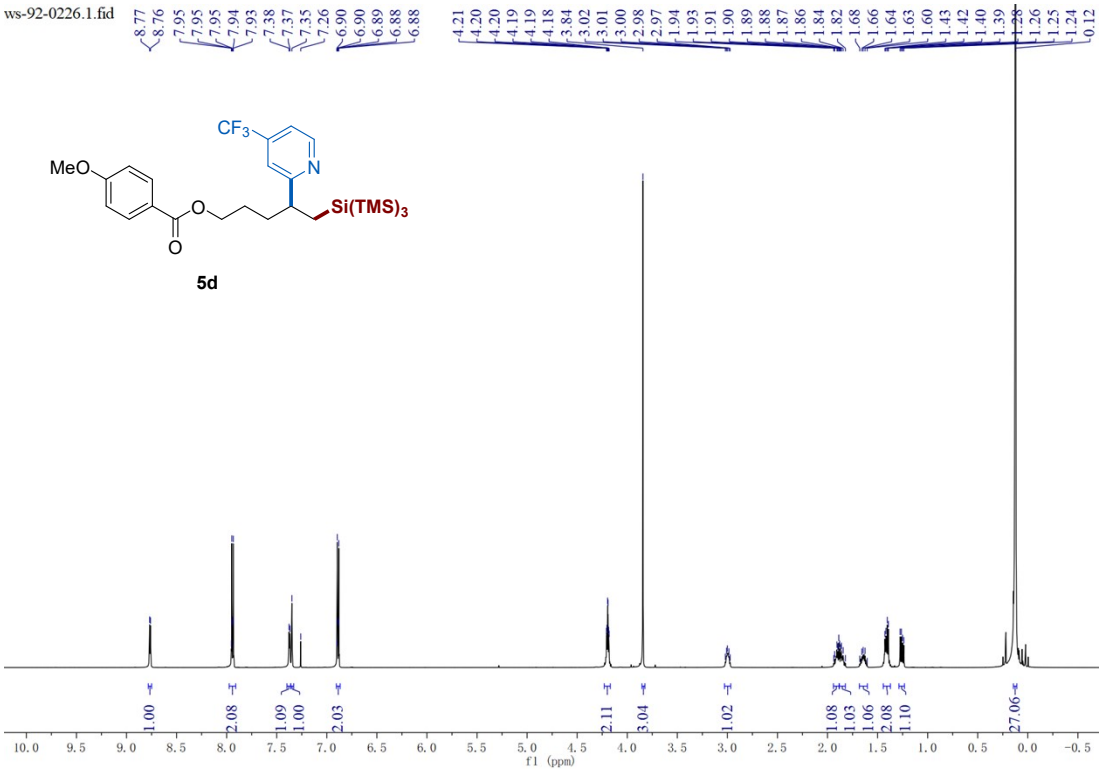


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

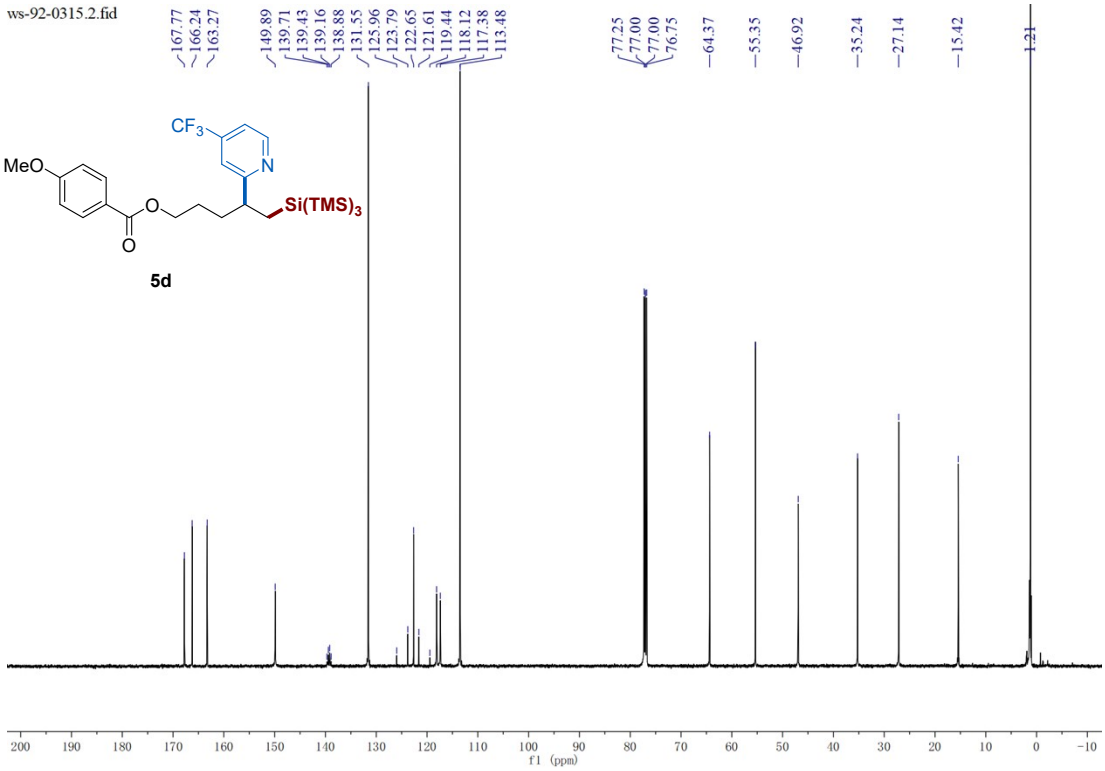


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-(trifluoromethyl)pyridin-2-yl)pentyl 4-methoxybenzoate (5d).

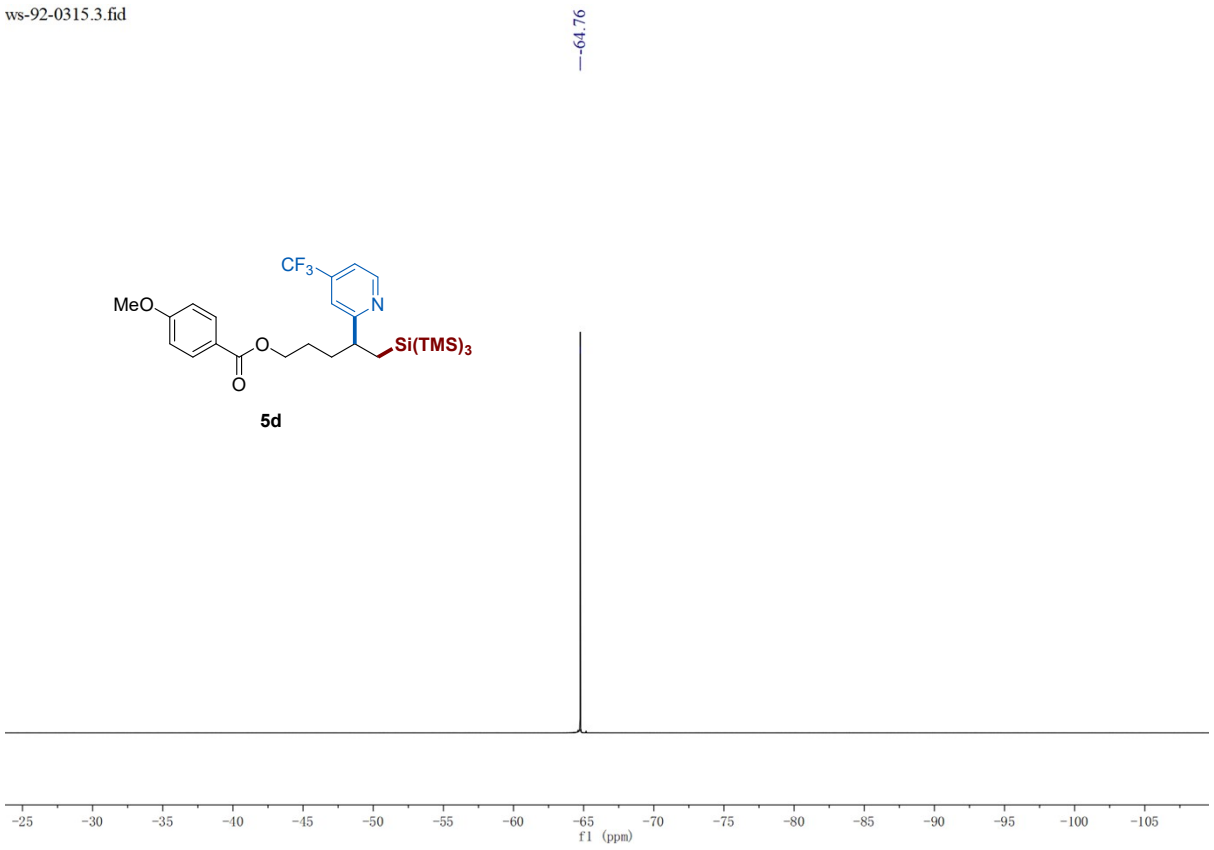
600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

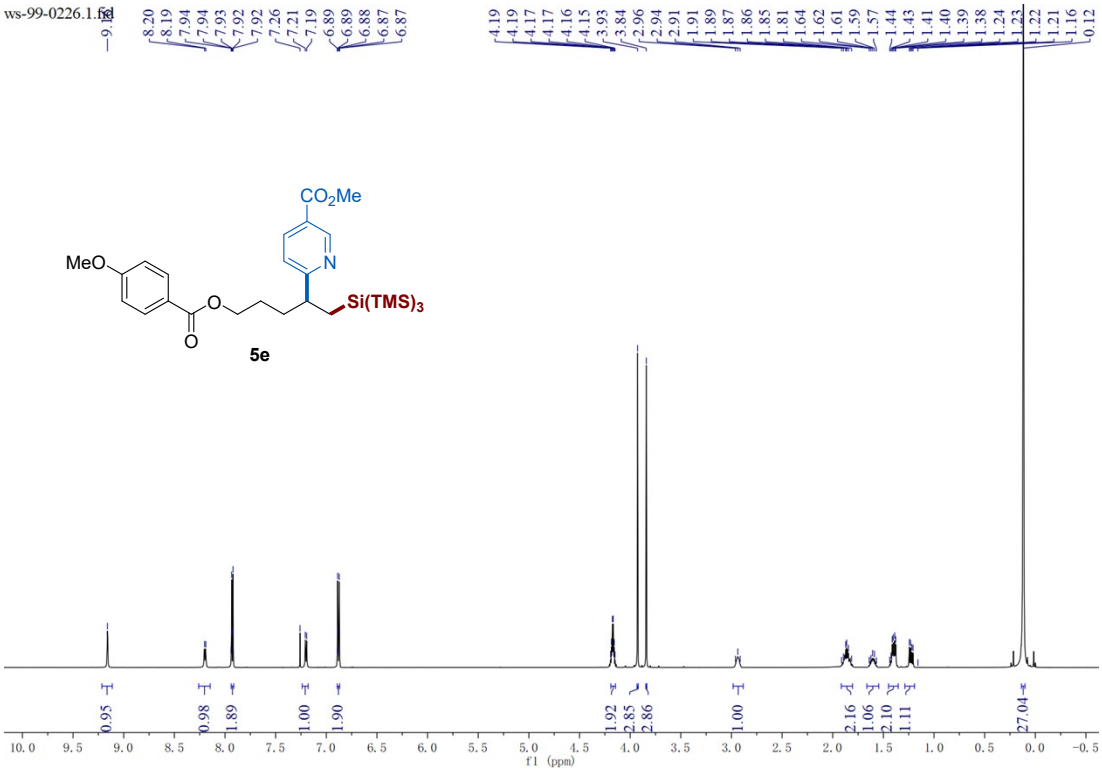


471 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$)

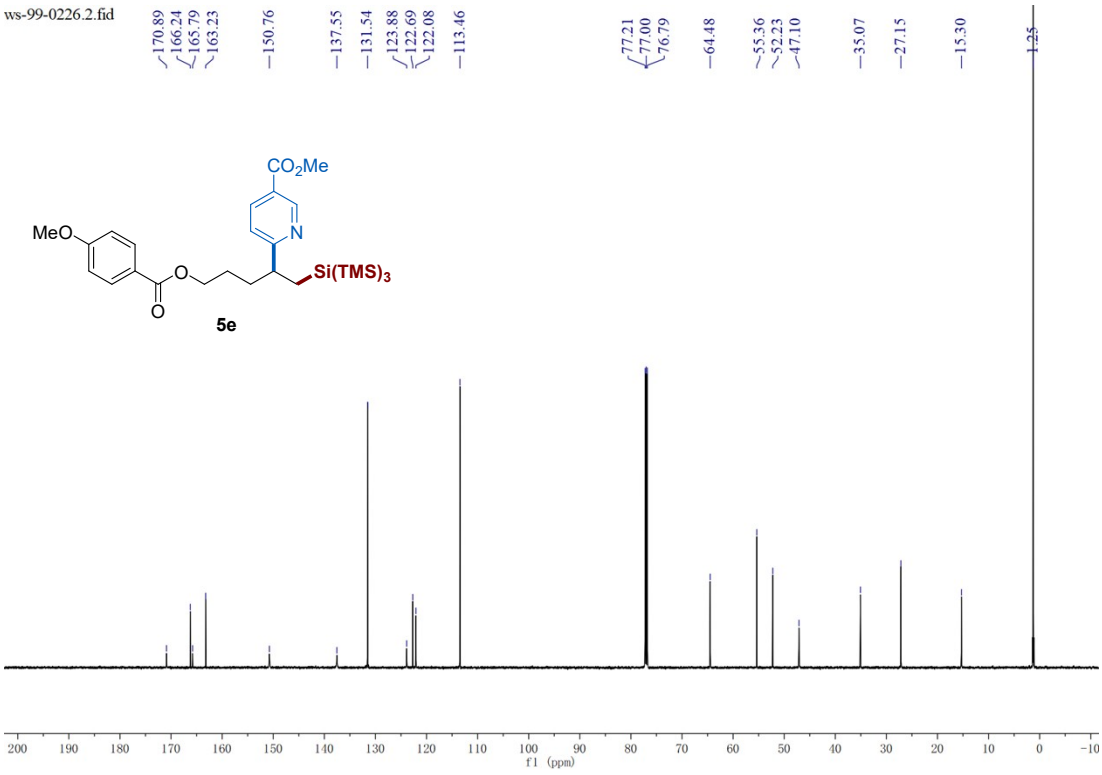


Methyl 6-(1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-5-((4-methoxybenzoyl)oxy)pentan-2-yl)nicotinate (5e).

600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

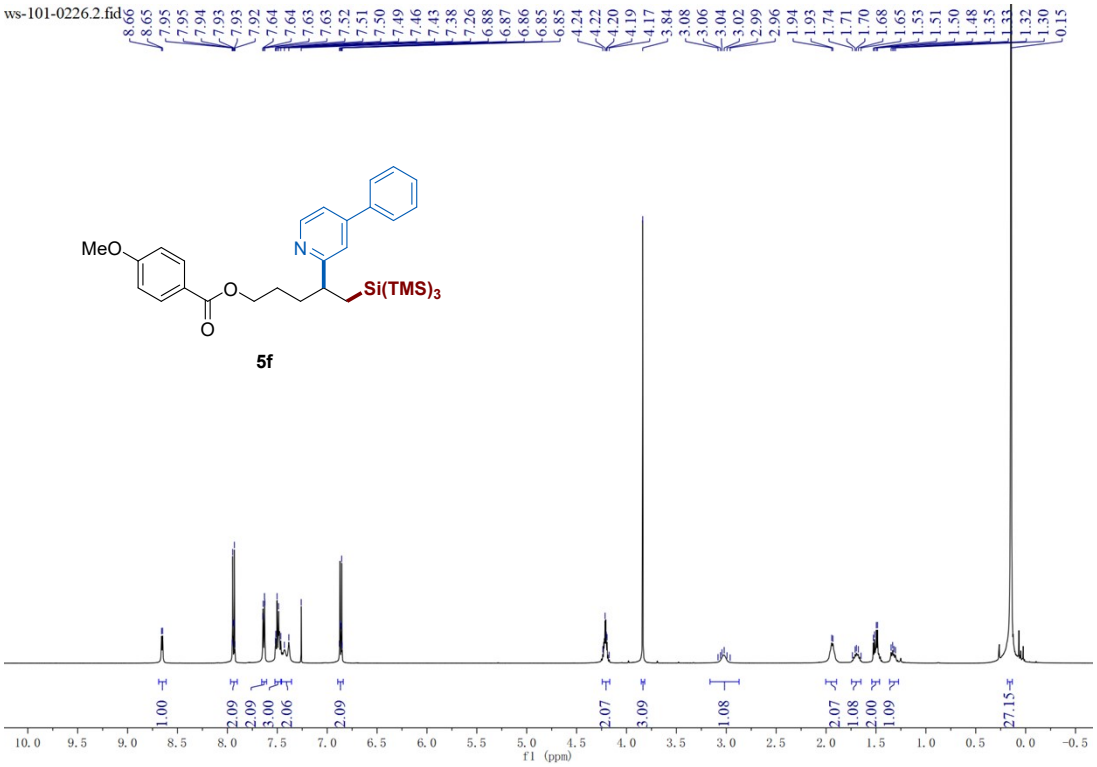


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

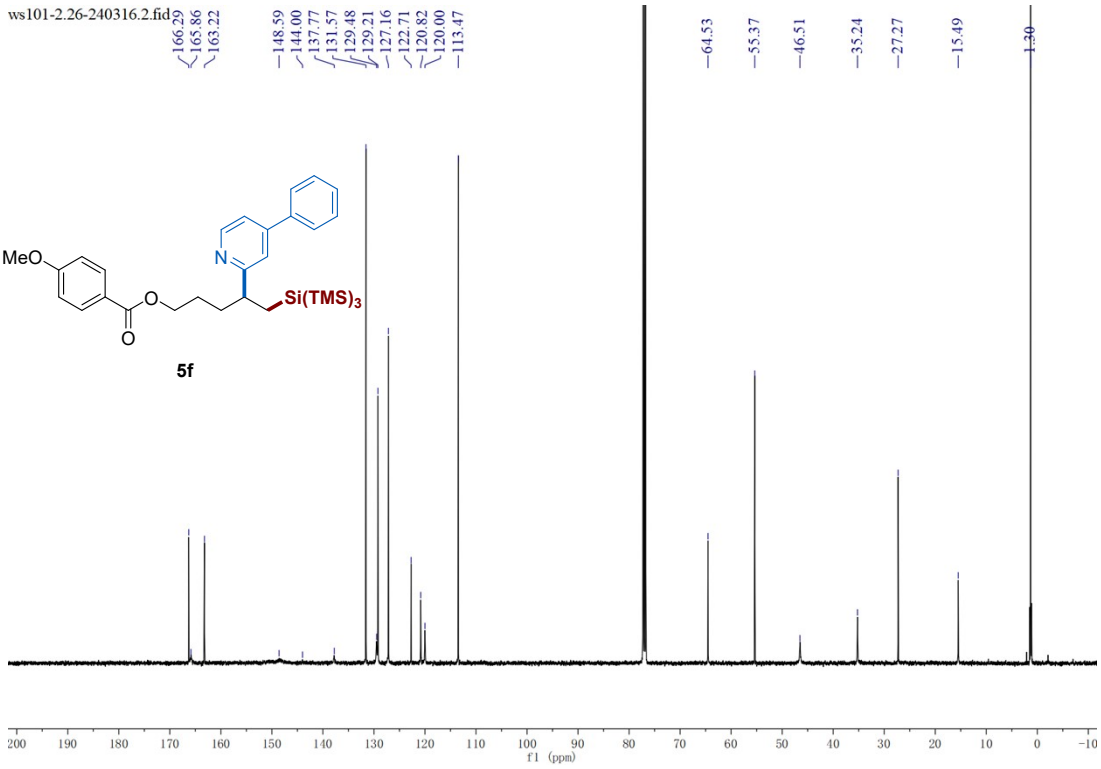


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-phenylpyridin-2-yl)pentyl 4-methoxybenzoate (5f)

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

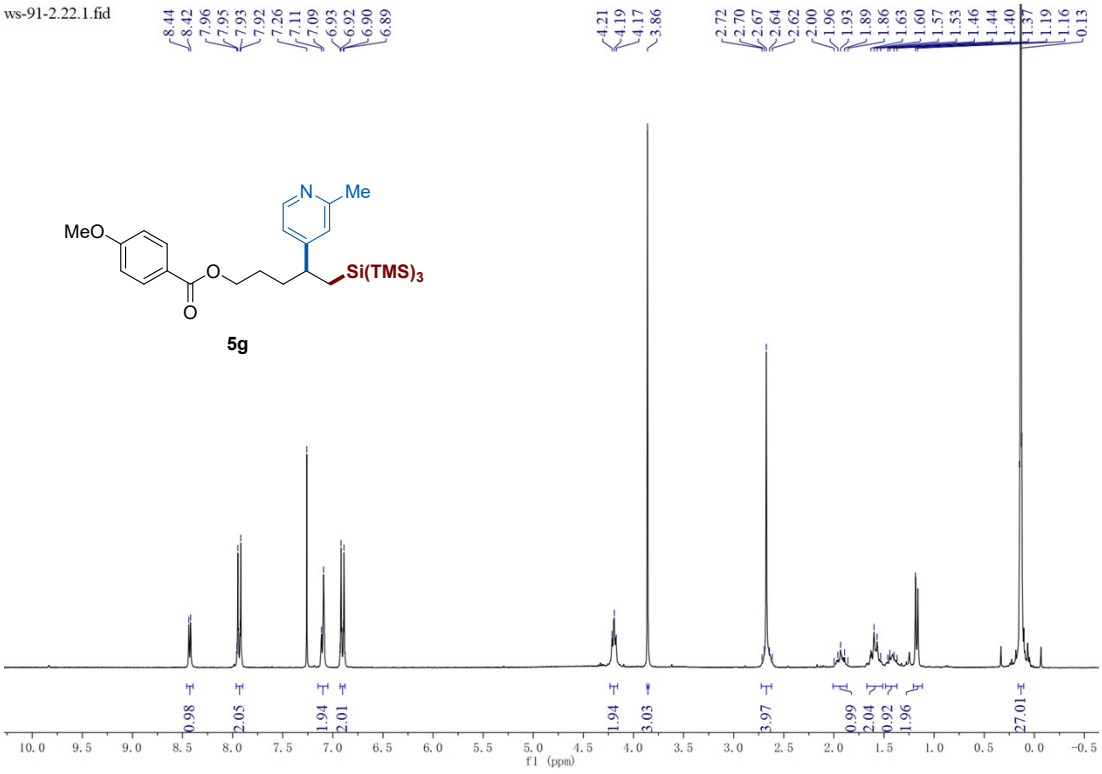


126 Hz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

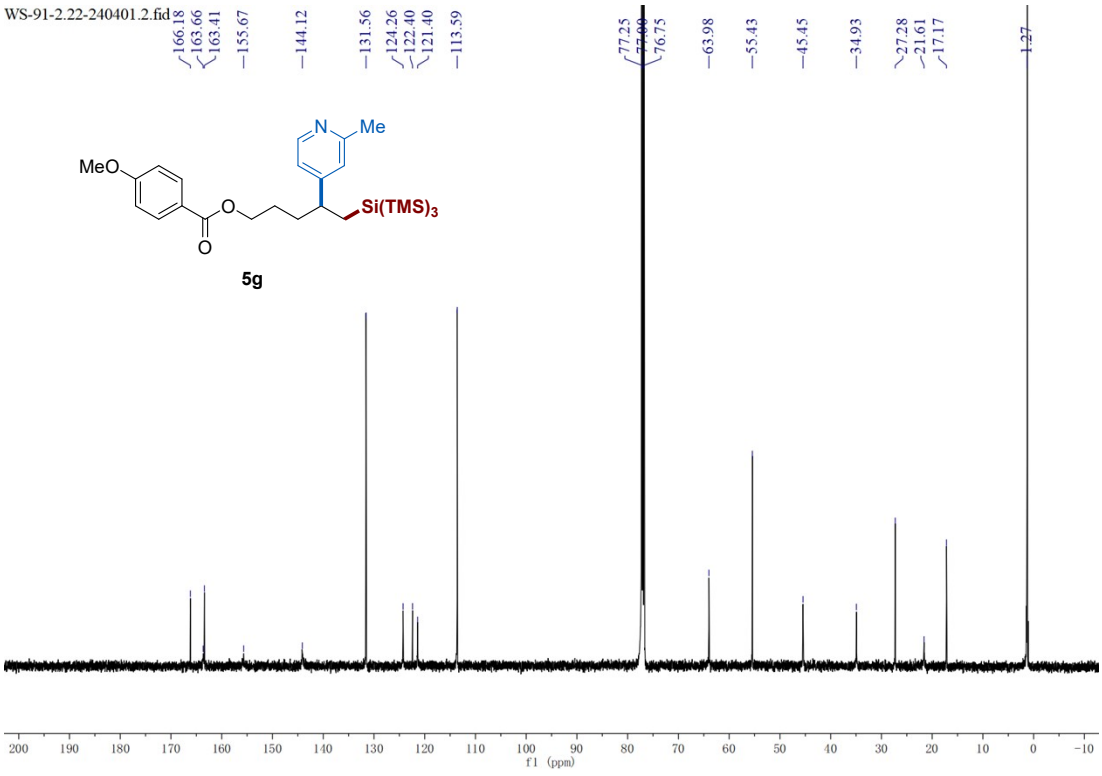


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-methylpyridin-4-yl)pentyl 4-methoxybenzoate (5g)

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

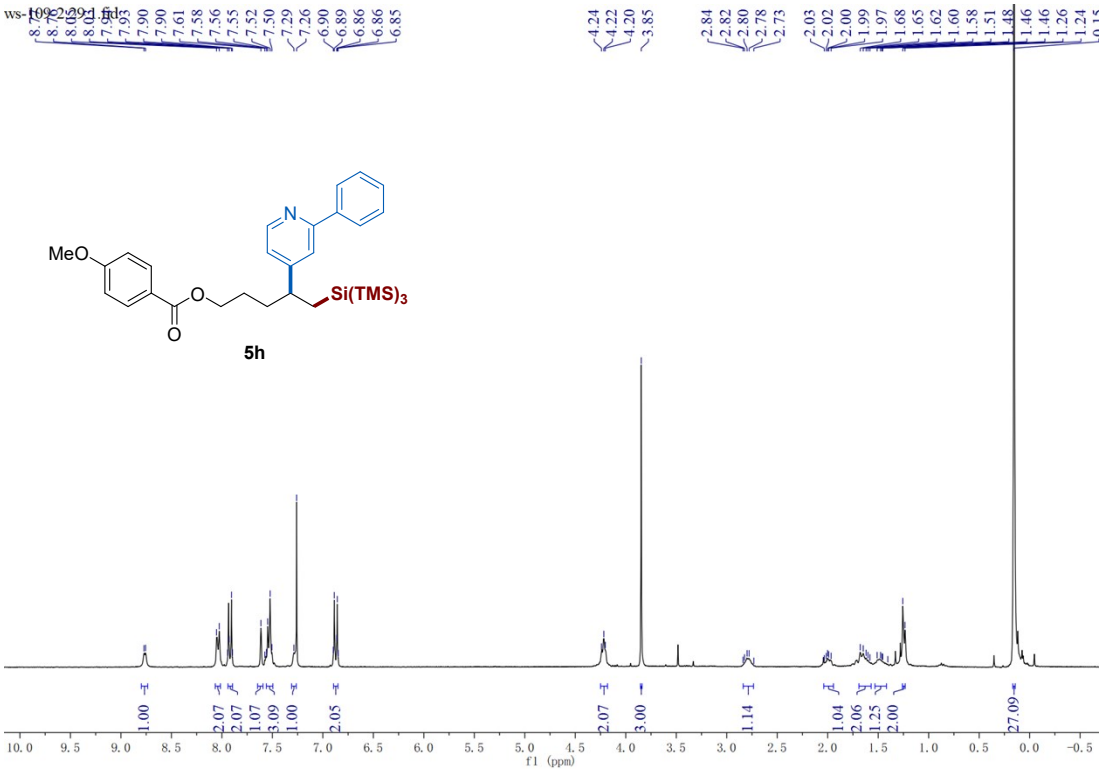


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

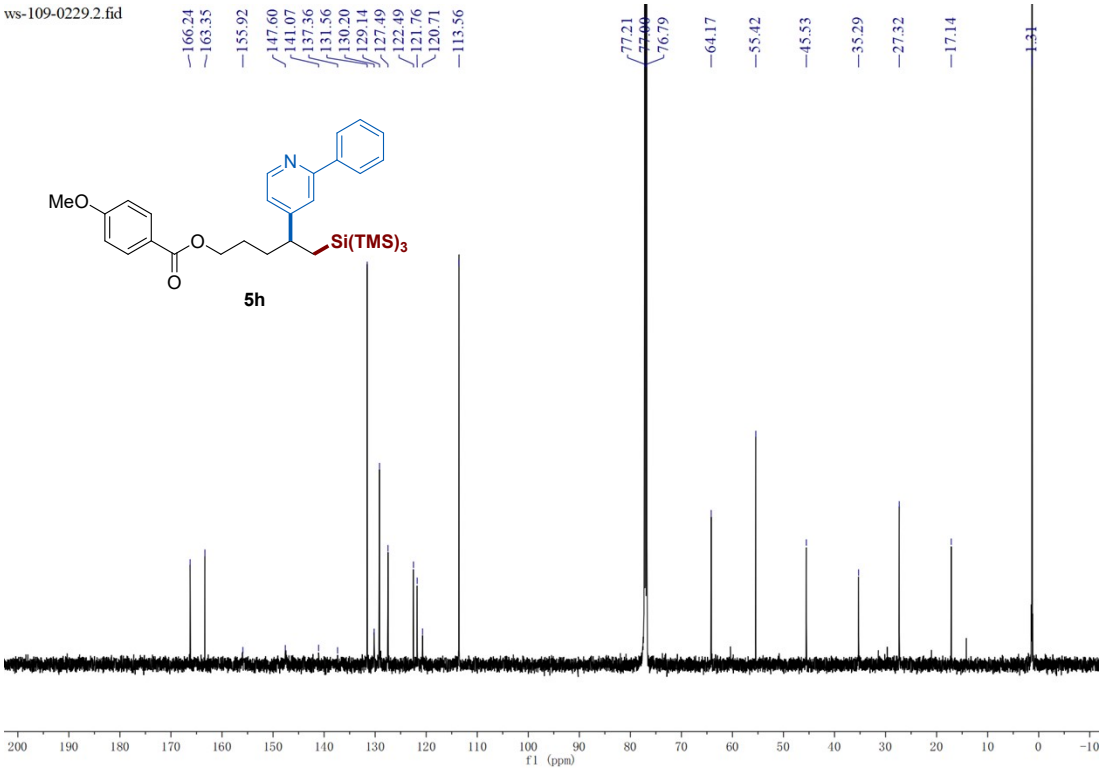


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-phenylpyridin-4-yl)pentyl 4-methoxybenzoate (5h)

300 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

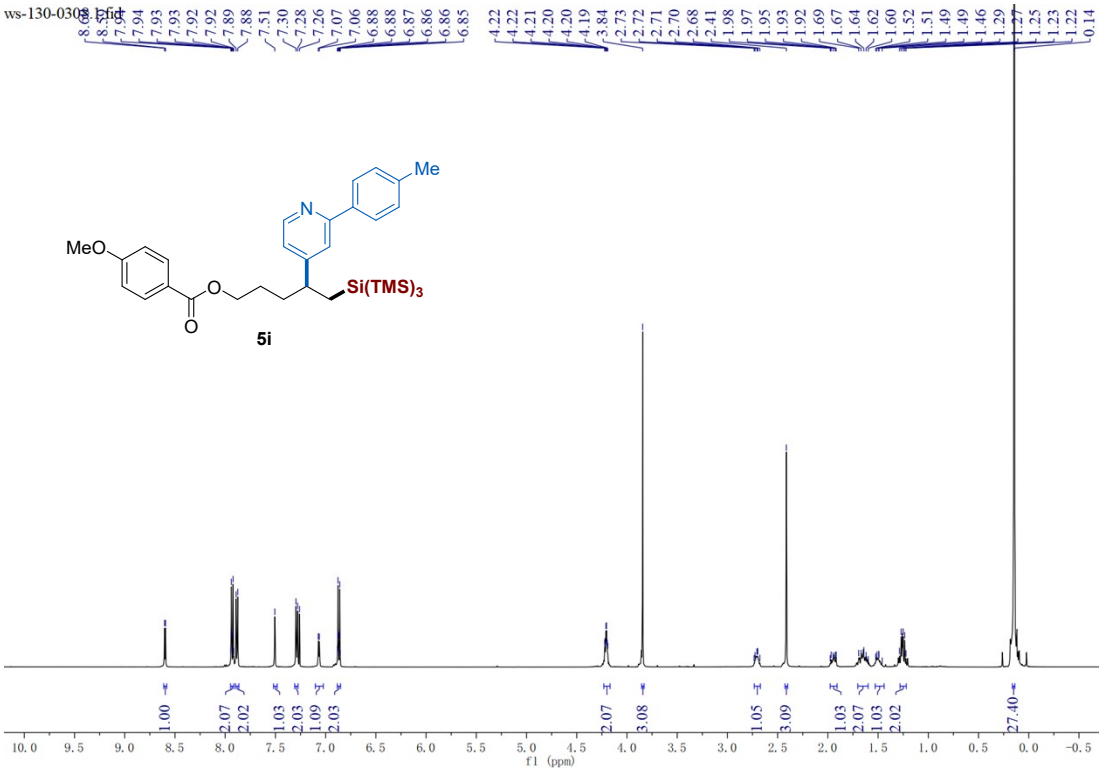


151 Hz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

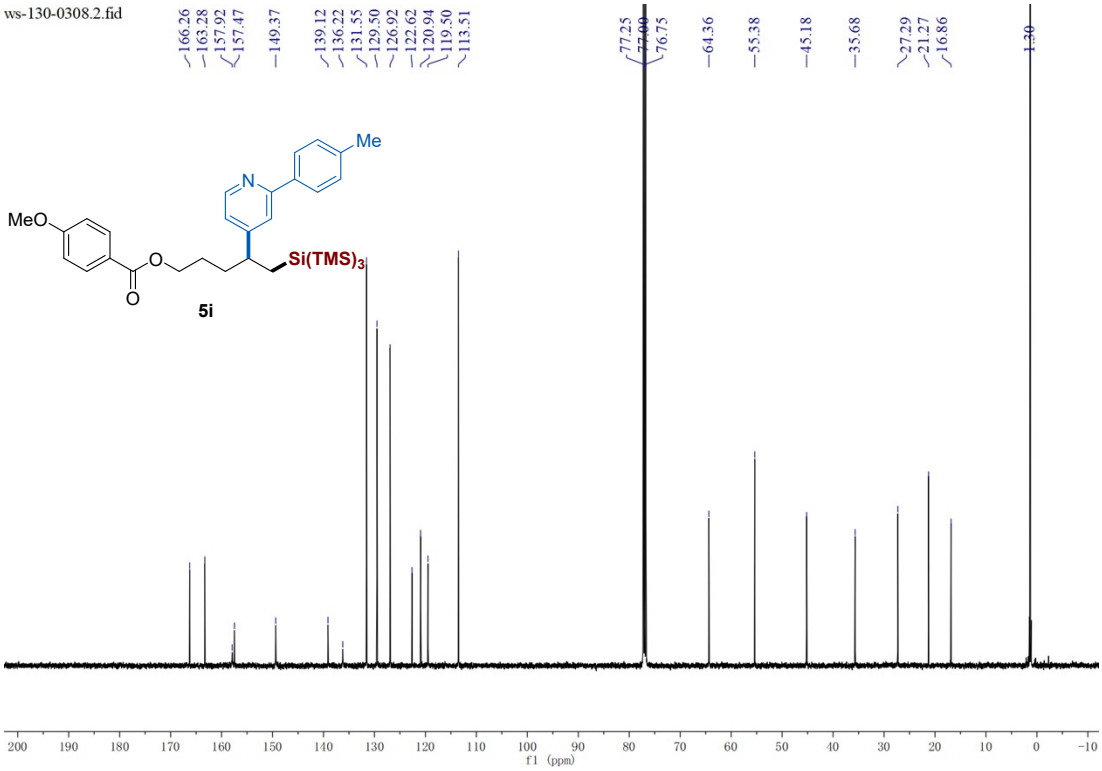


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-(p-tolyl)pyridin-4-yl)pentyl 4-methoxybenzoate (5i)

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

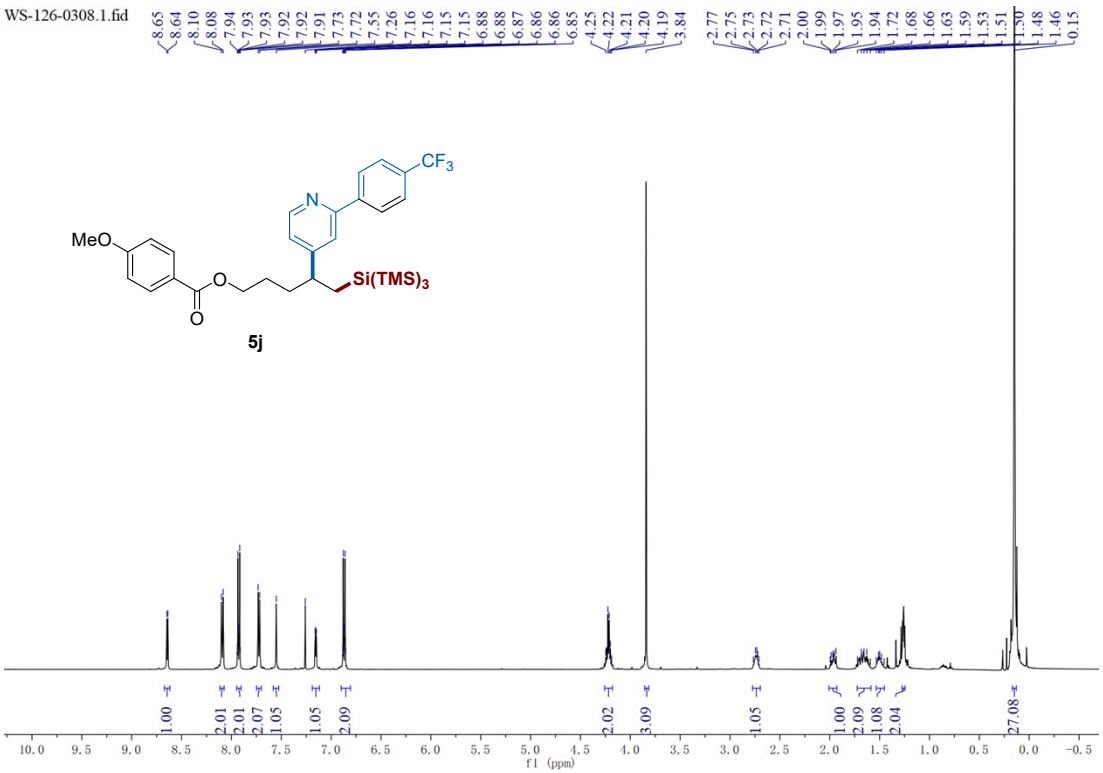


126 Hz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

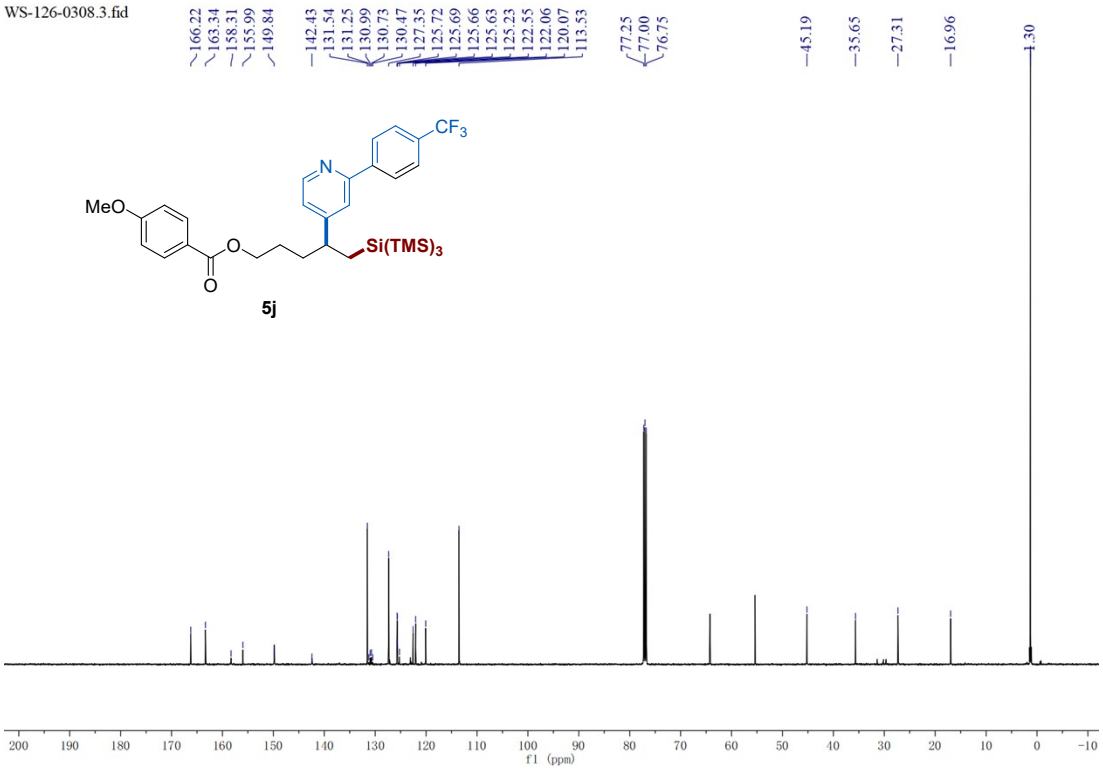


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl) trisilan-2-yl)-4-(2-(4-(trifluoromethyl) phenyl) pyridin-4-yl) pentyl 4-methoxybenzoate (5j)

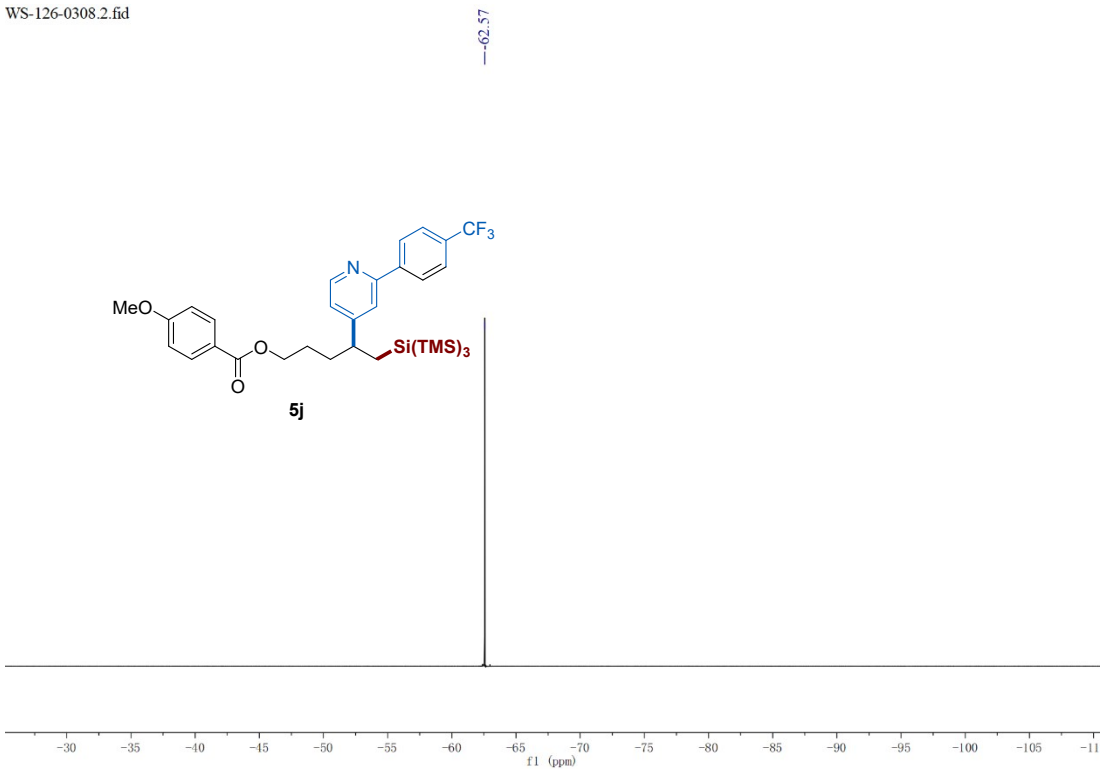
500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)



126 Hz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

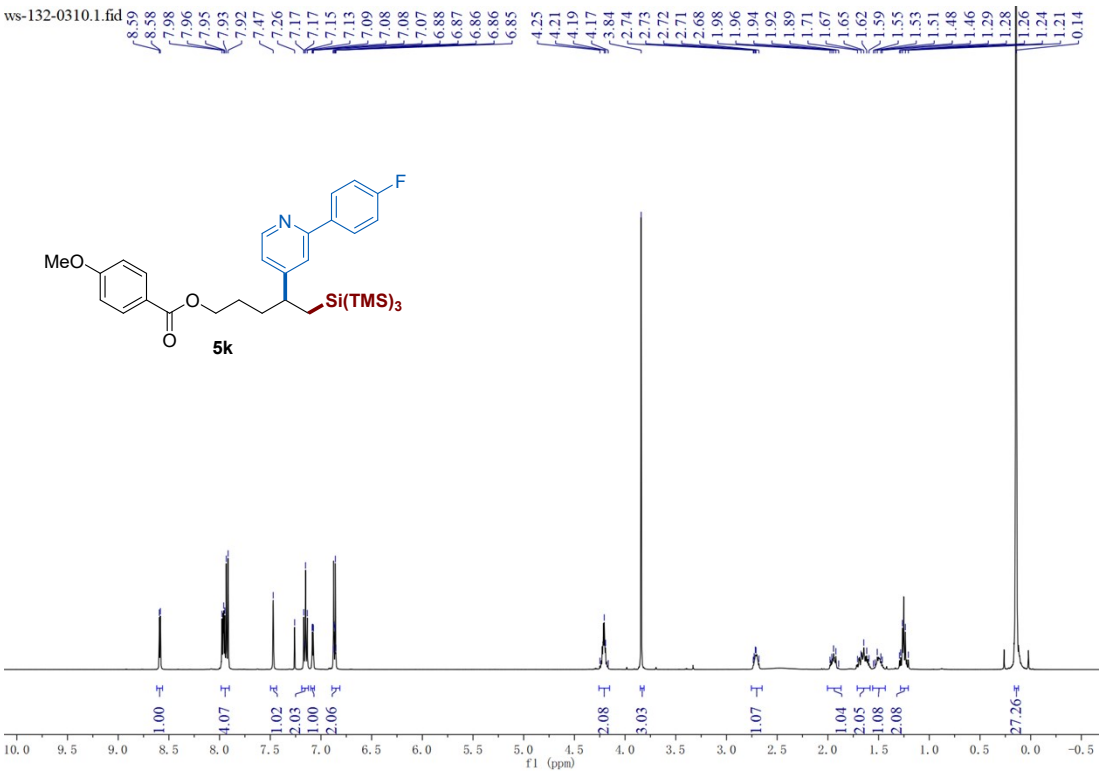


565 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$).

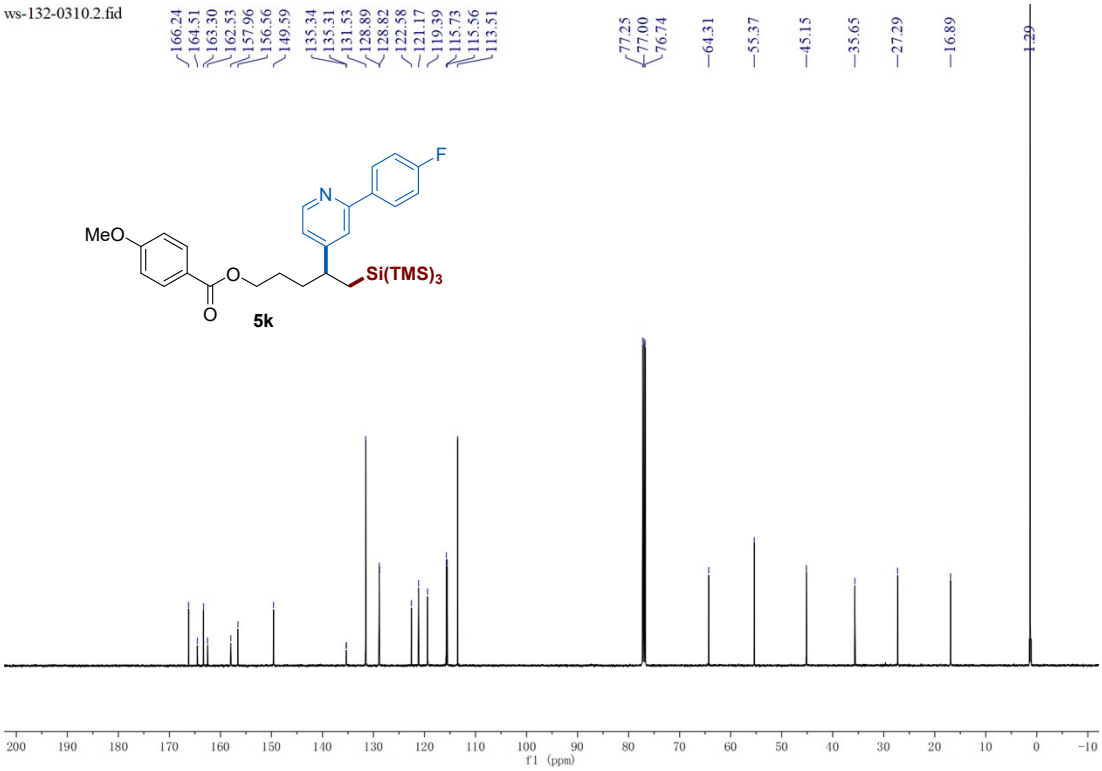


4-(2-(4-Fluorophenyl)pyridin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate. (5k)

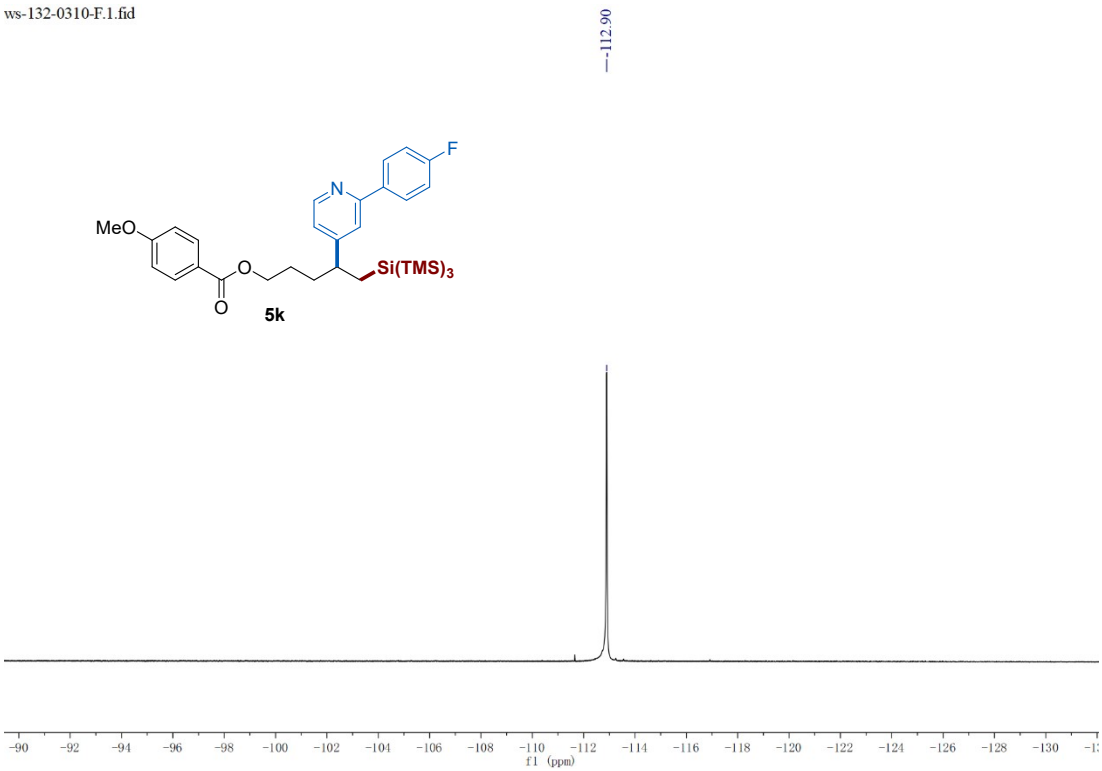
500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)



126 Hz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

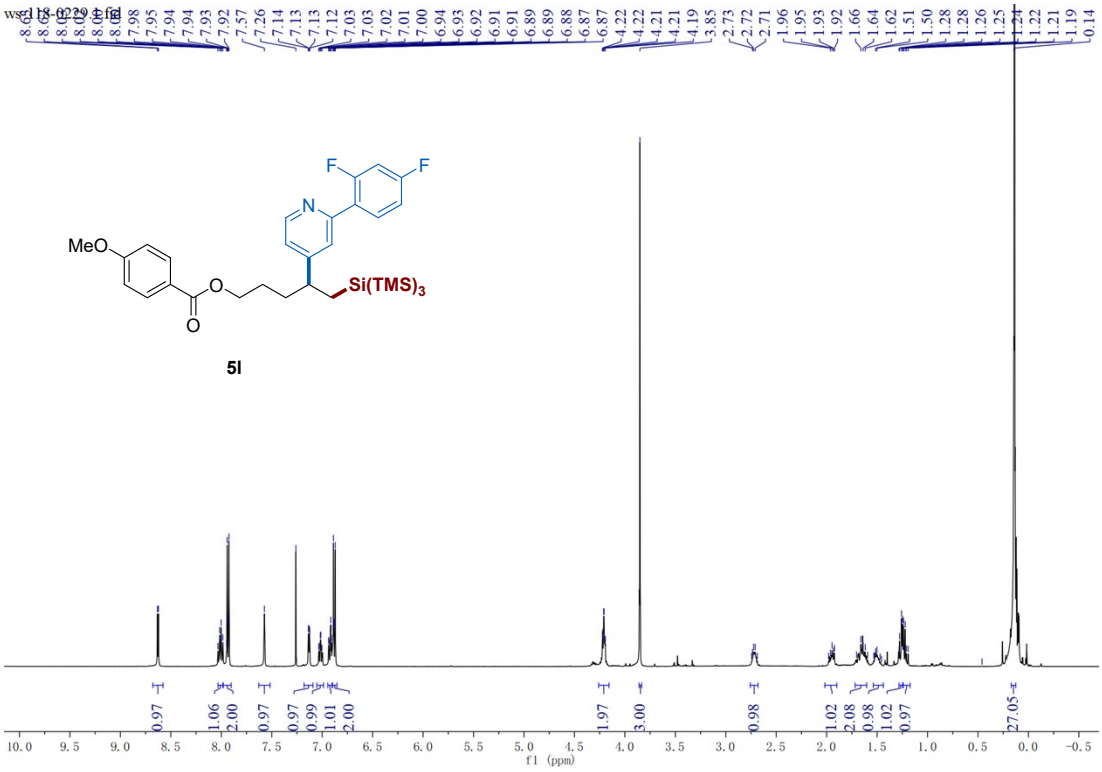


471 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$).

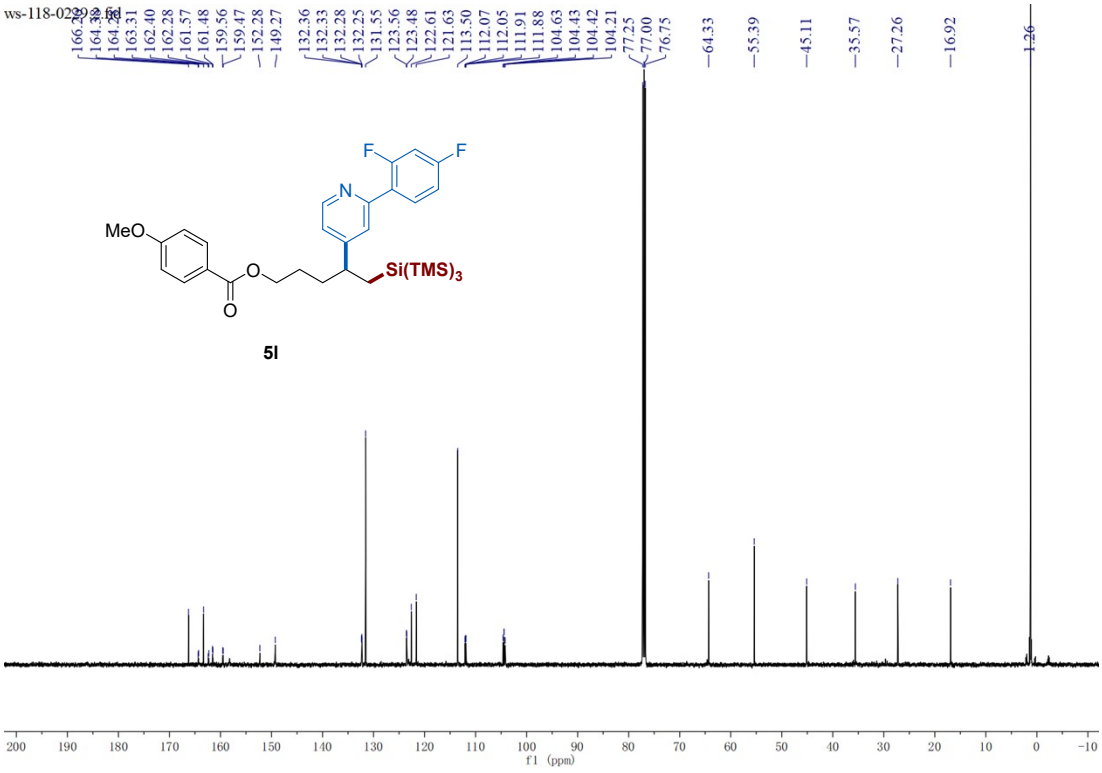


5-Azido-4-(2-phenylquinolin-4-yl) pentyl 4-methoxybenzoate (5l)

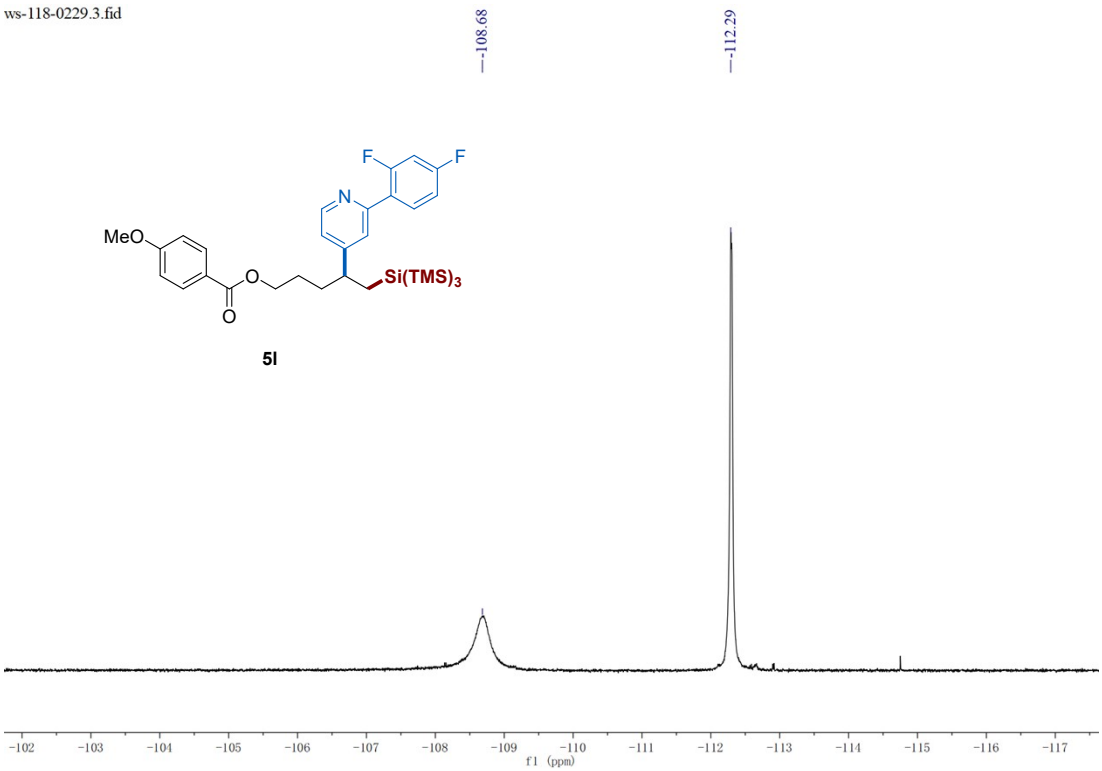
300 MHz 1H NMR Spectrum (recorded in $CDCl_3$)



151 Hz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

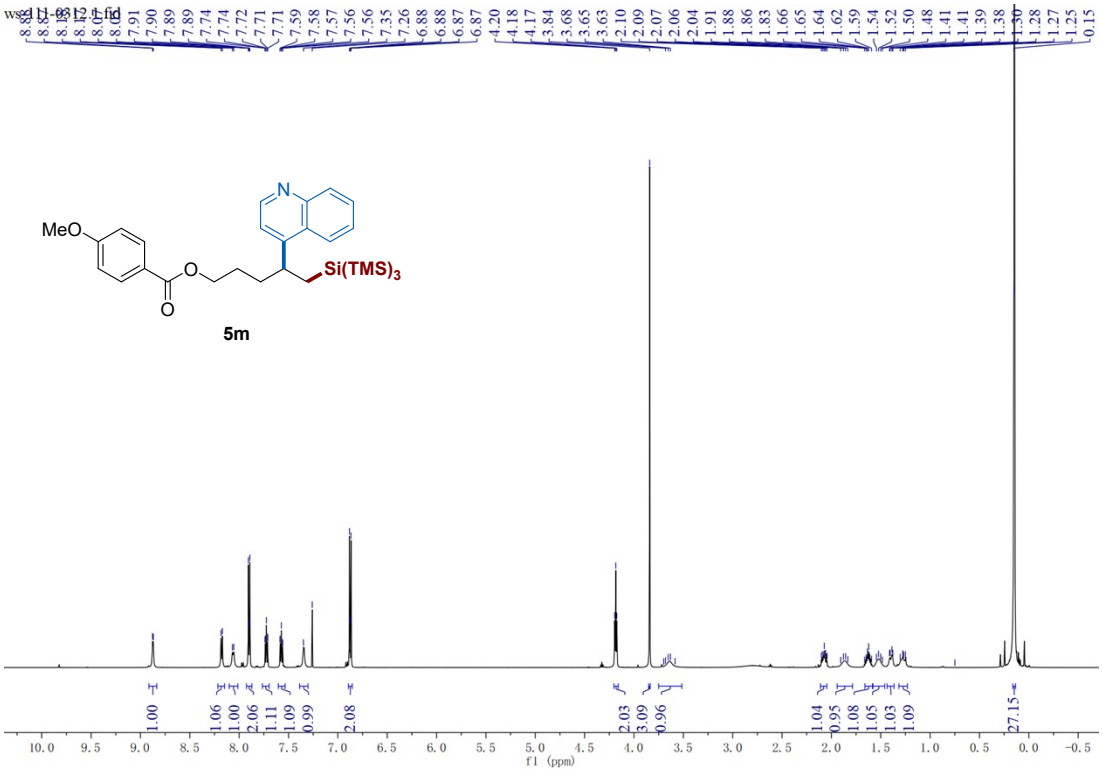


471 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$).

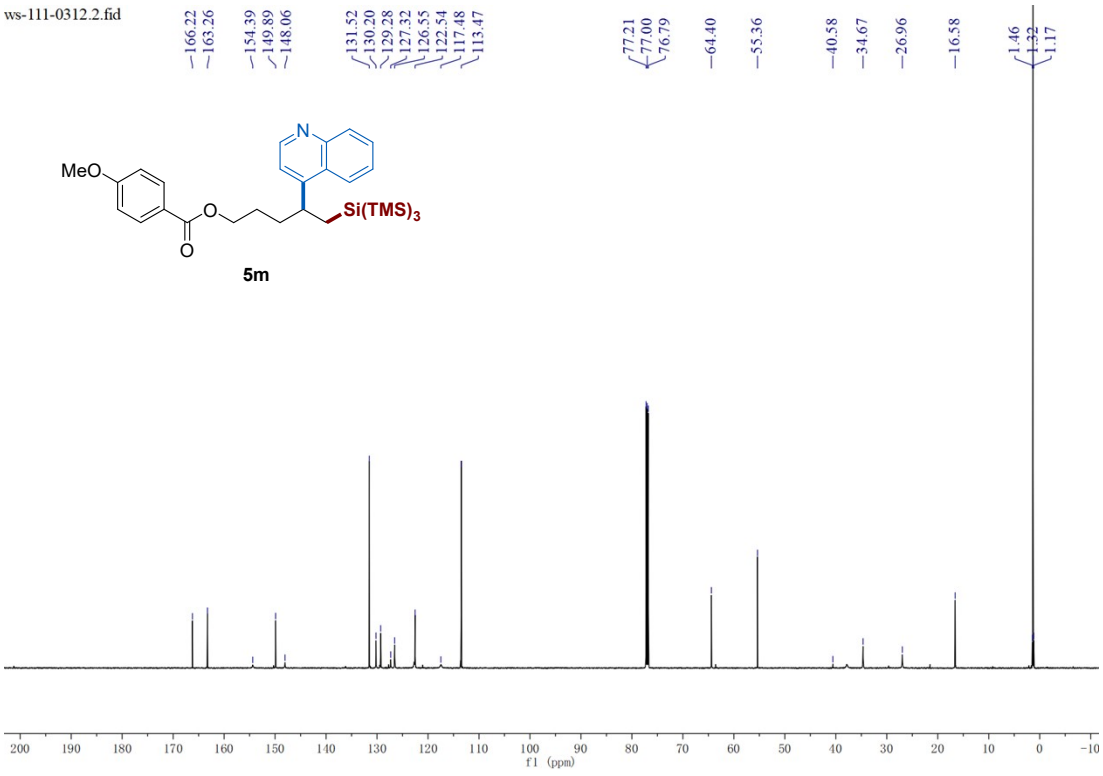


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(quinolin-4-yl)pentyl 4-methoxybenzoate (5m)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

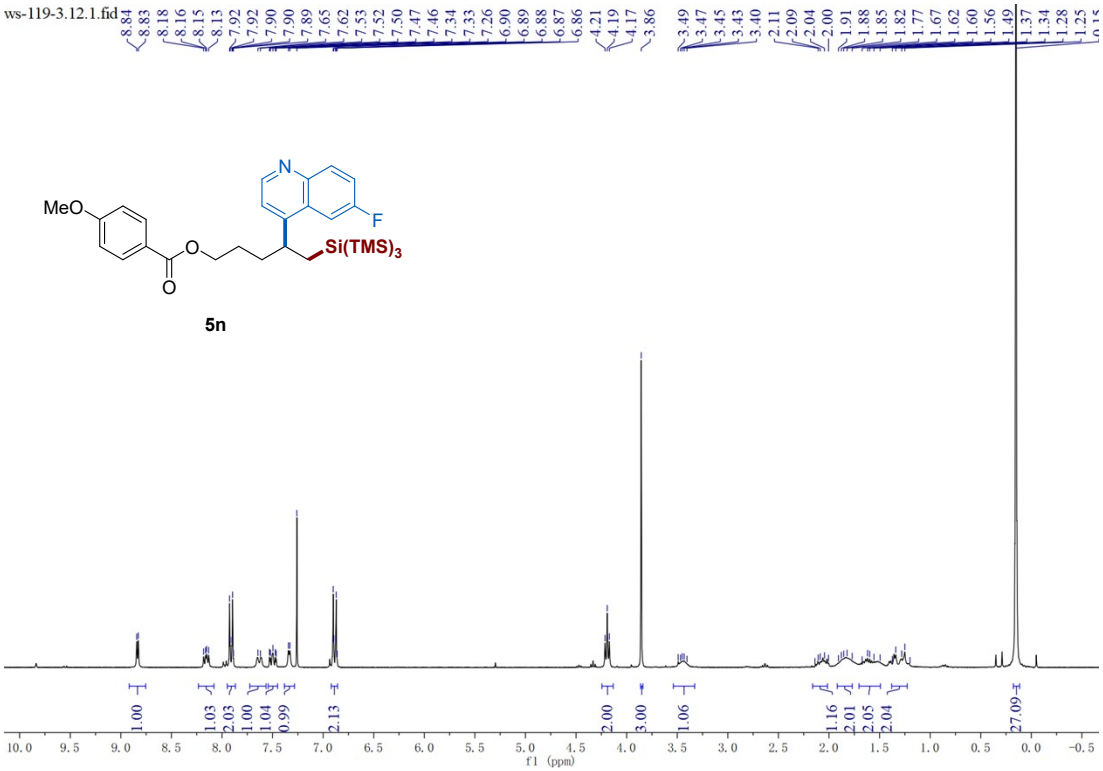


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

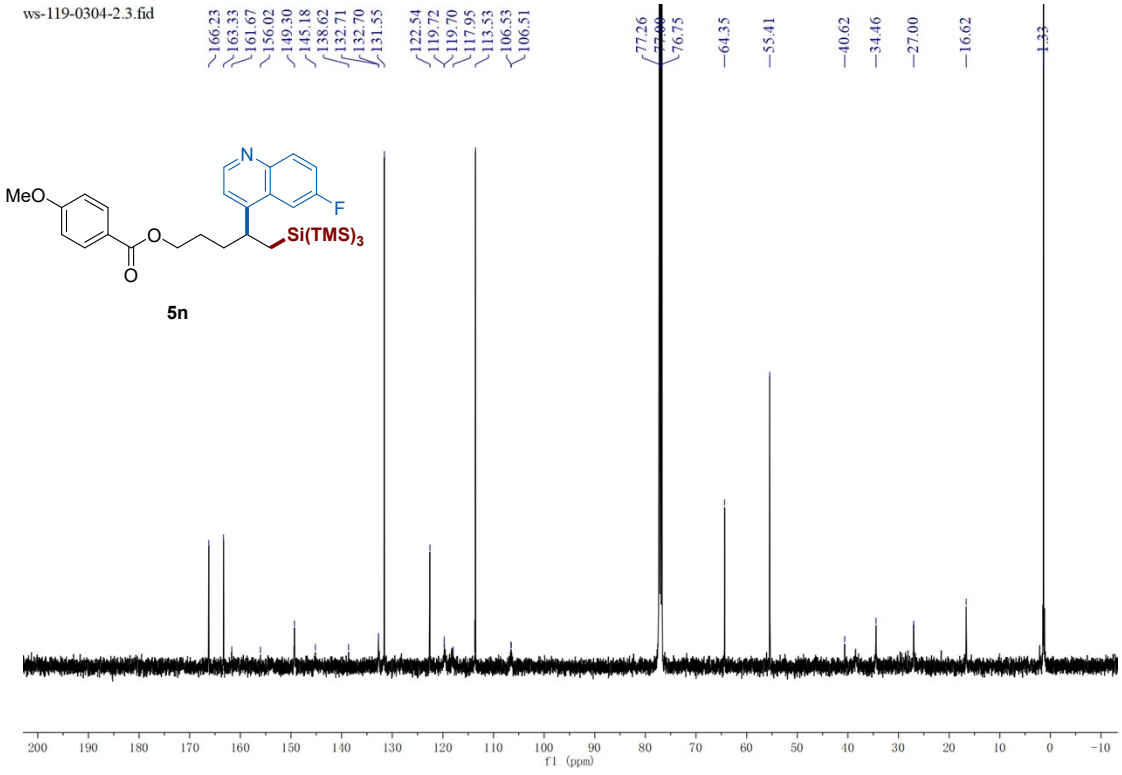


4-(6-Fluoroquinolin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5n)

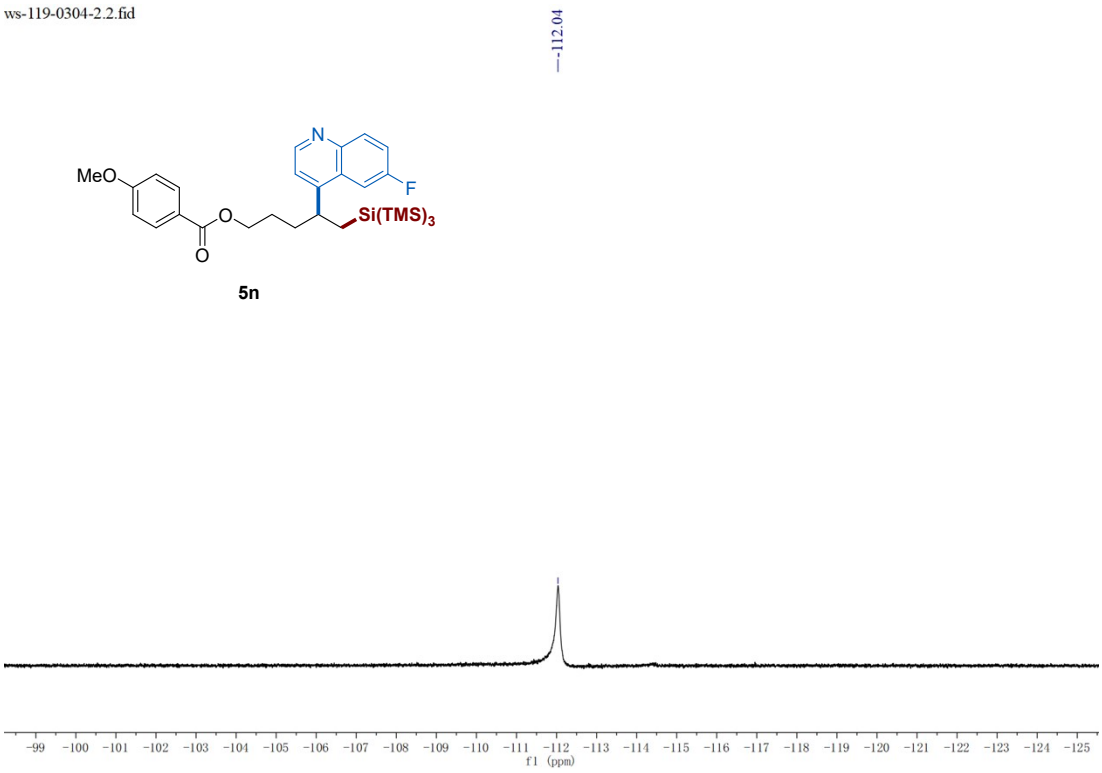
300 MHz 1H NMR Spectrum (recorded in $CDCl_3$)



126 Hz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

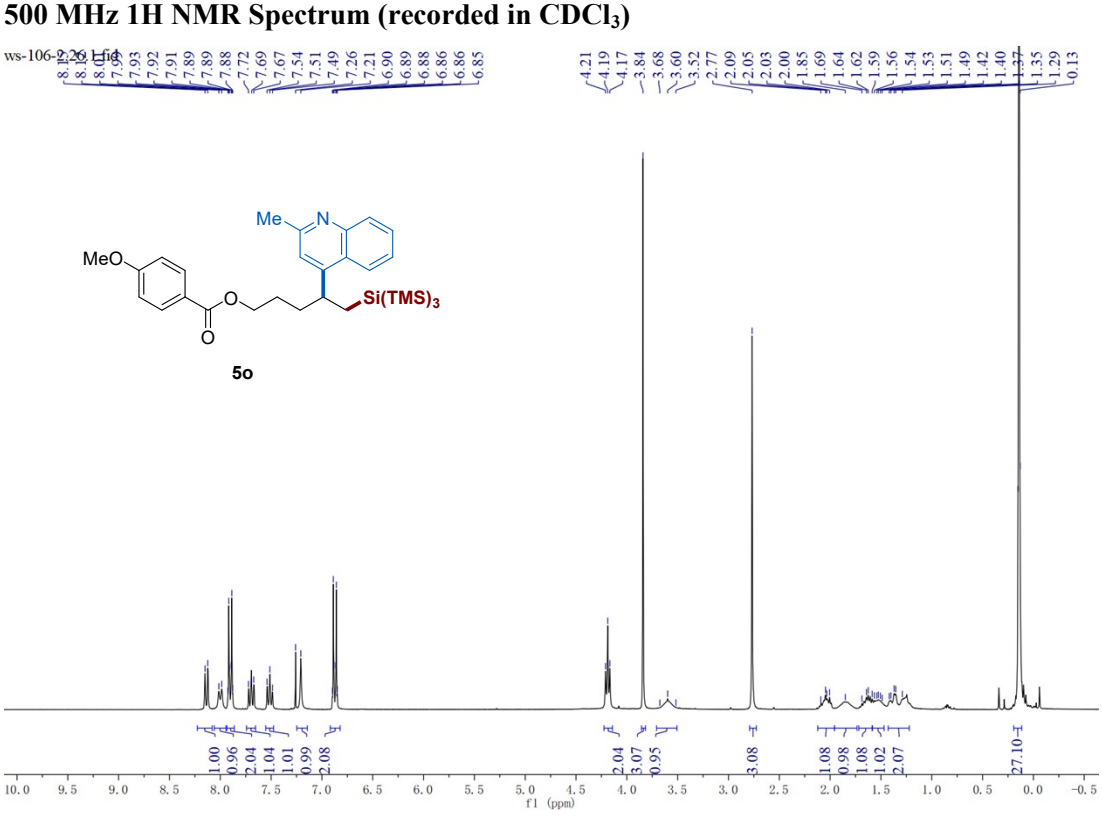


471 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$).

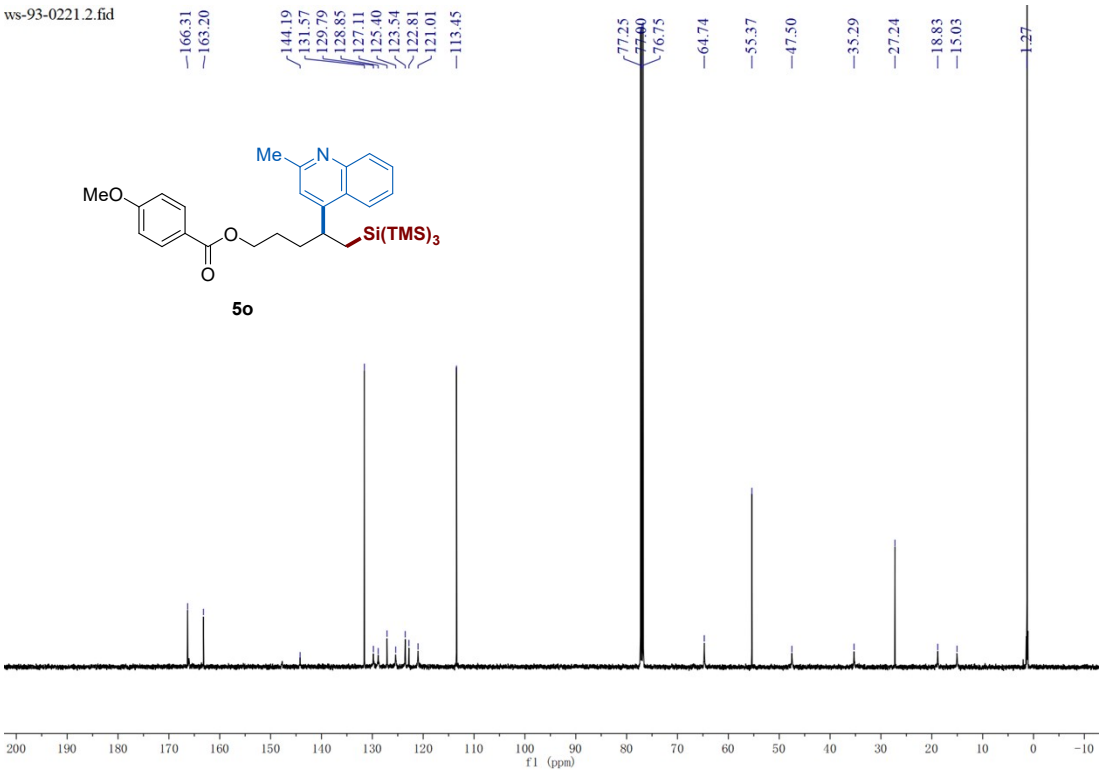


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-methylquinolin-4-yl)pentyl 4-methoxybenzoate (5o)

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

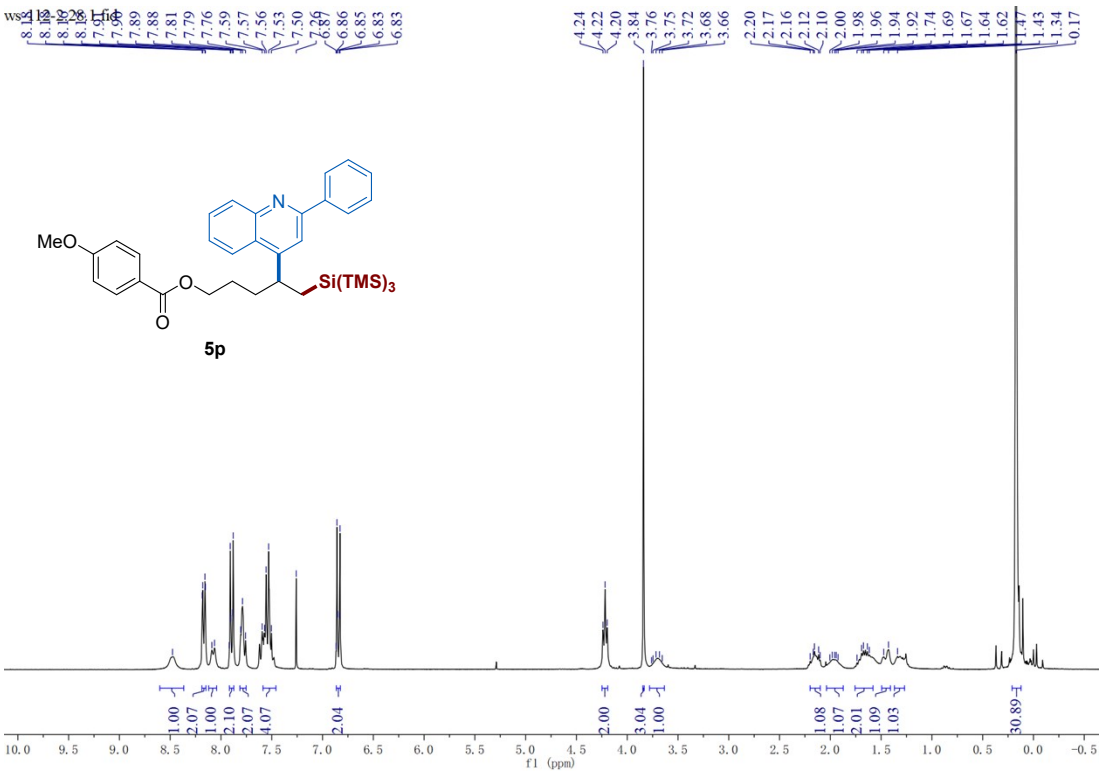


126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)

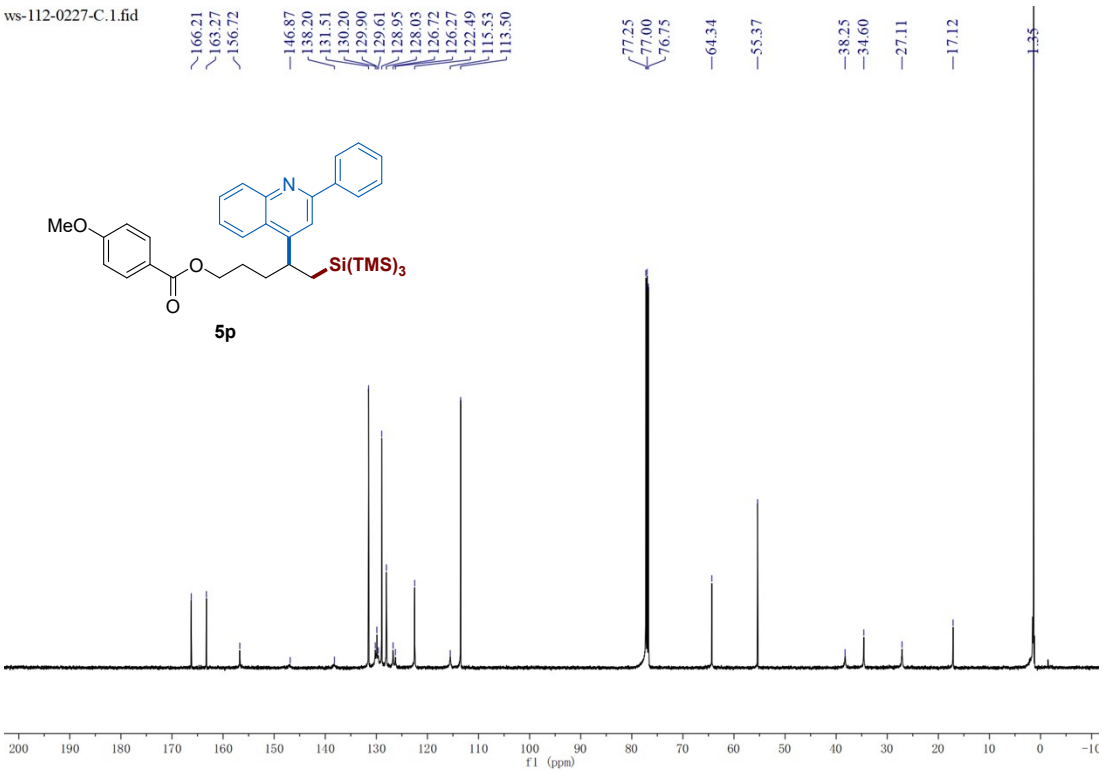


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(2-phenylquinolin-4-yl)pentyl 4-methoxybenzoatee (5p)

300 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

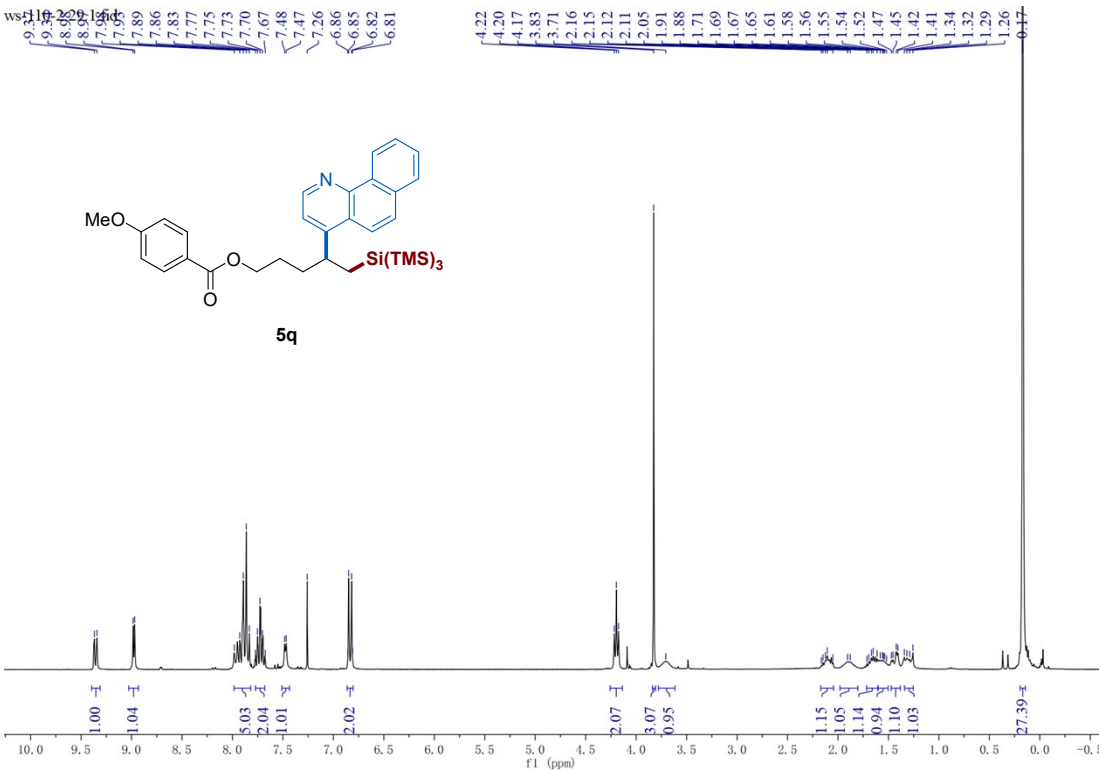


126 Hz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

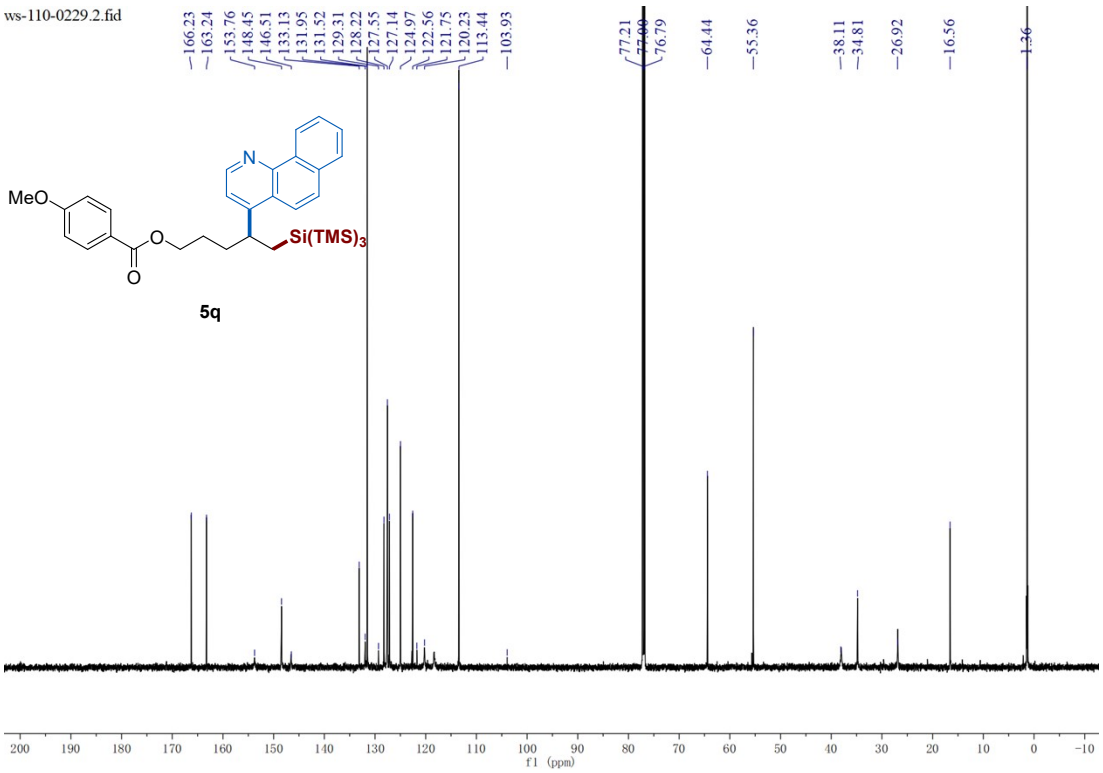


4-(Benzo[h]quinolin-4-yl)-5-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pentyl 4-methoxybenzoate (5q)

500 MHz 1H NMR Spectrum (recorded in $CDCl_3$)

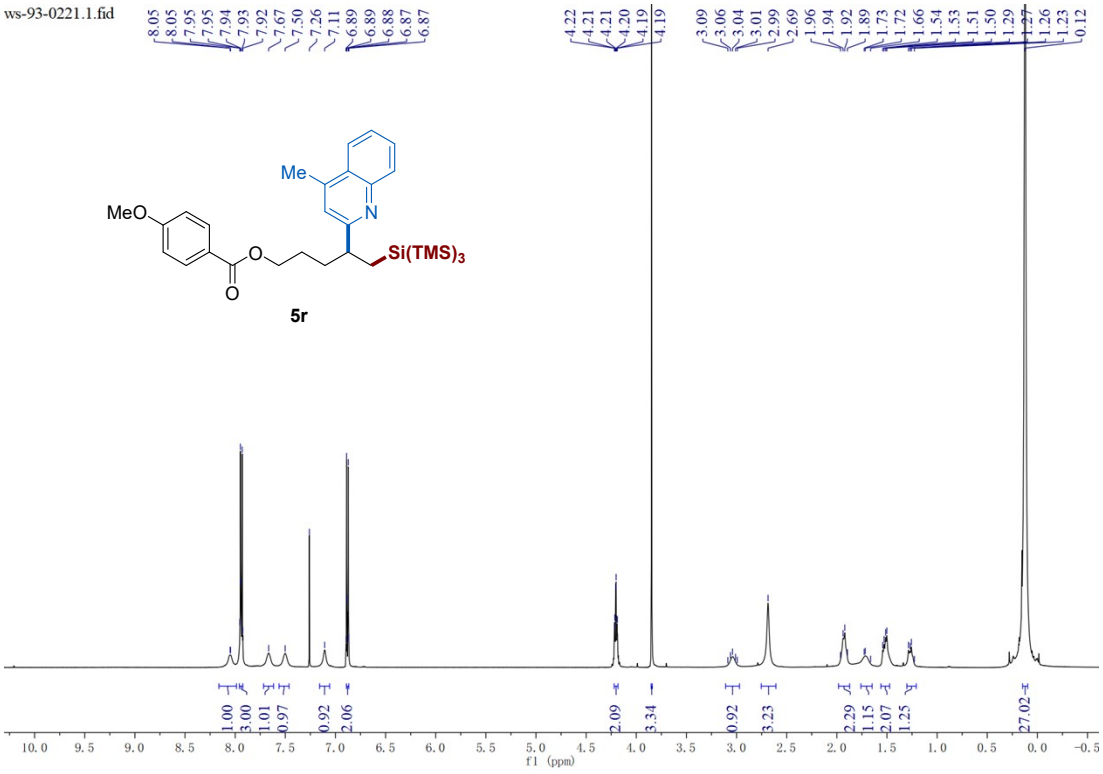


151 Hz ^{13}C {^1H} NMR Spectrum (recorded in $CDCl_3$)

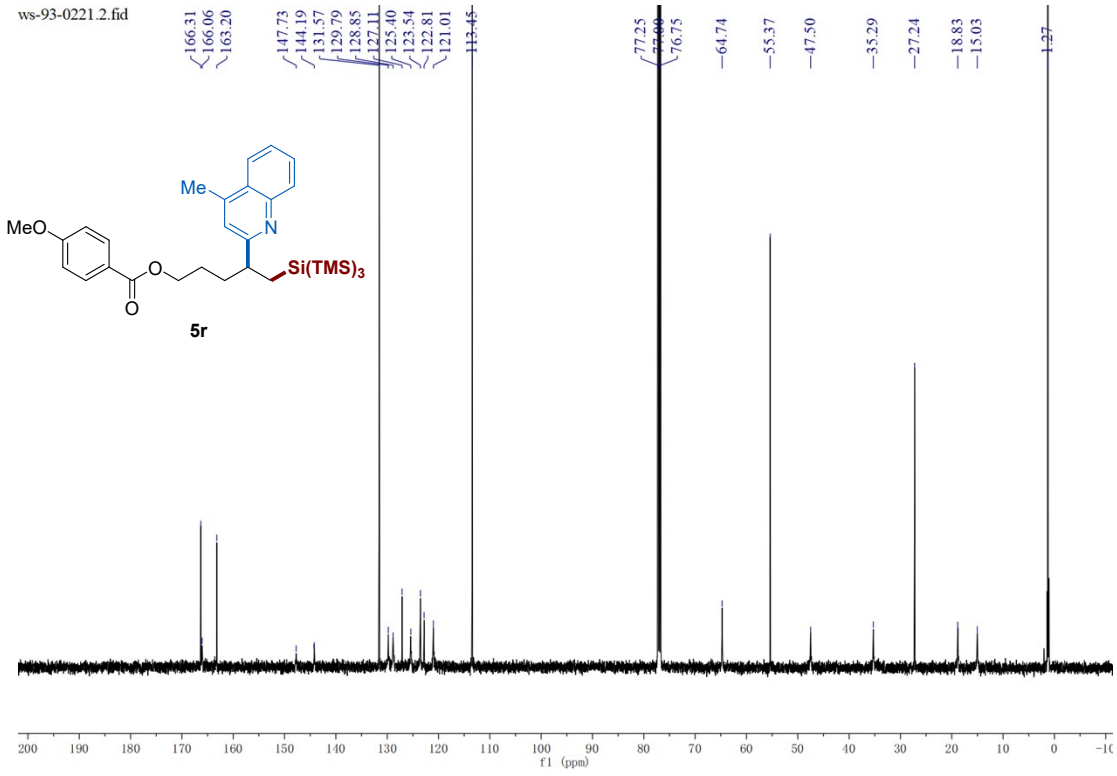


5-(1,1,1,3,3,3-Hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-4-(4-methylquinolin-2-yl)pentyl 4-methoxybenzoate (5r)

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

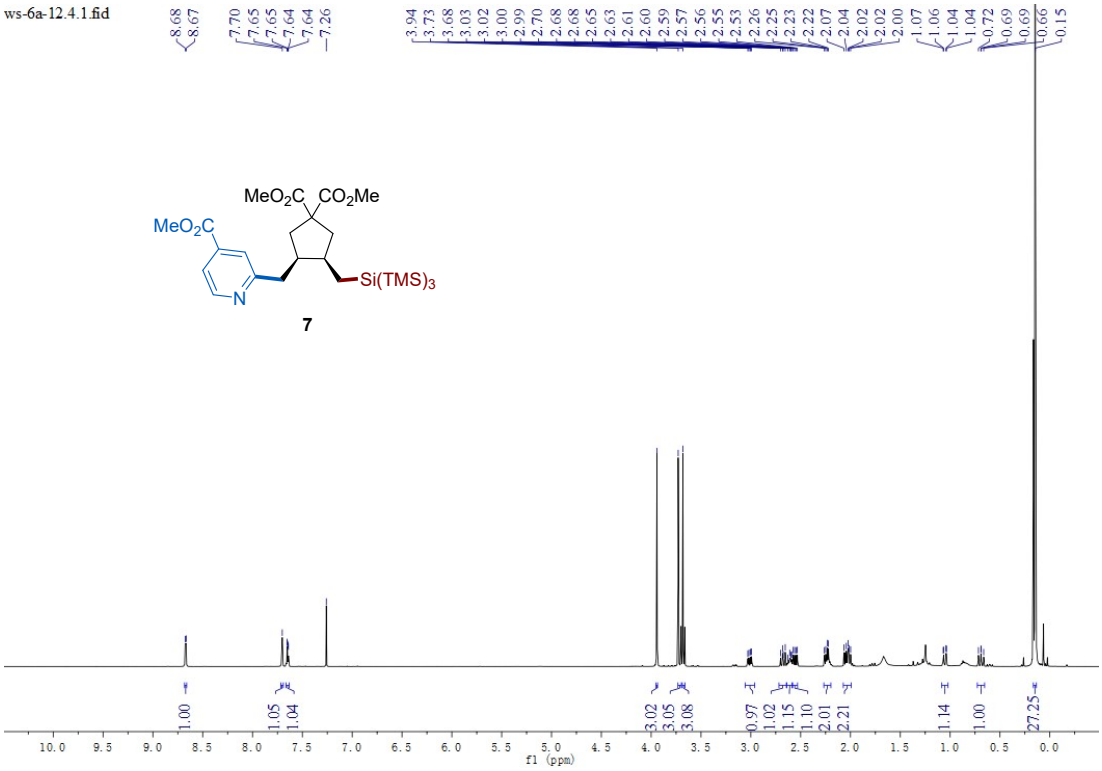


151 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)



Dimethyl (3R,4R)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-4-((4-(methoxycarbonyl)pyridin-2-yl)methyl)cyclopentane-1,1-dicarboxylate (7)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



126 MHz ^{13}C {^{1}H} NMR Spectrum (recorded in $CDCl_3$)