Supplementary Information

Conversion of 1-alkenes into 1,4-diols through an auxiliary-mediated formal homoallylic C-H oxidation

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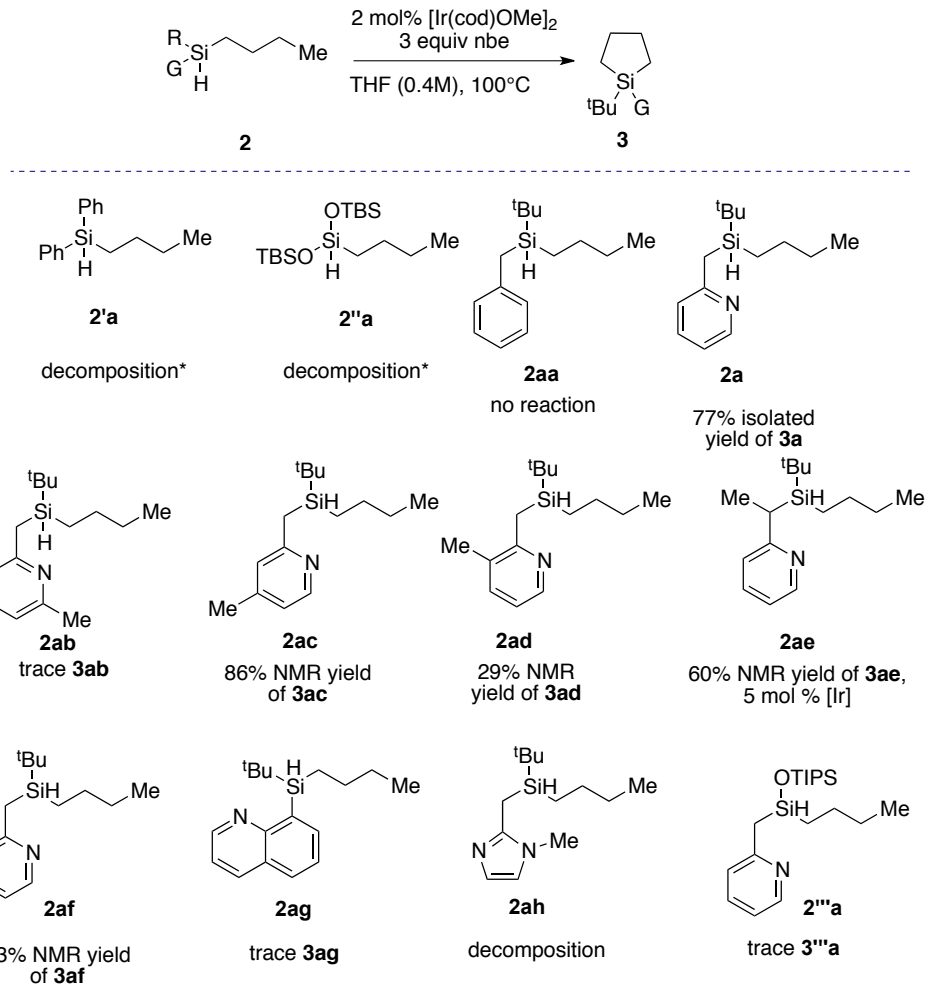
General Information

GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. ^{1}H signals are referenced to residual $CHCl_3$ at 7.27 ppm. ^{13}C signals are referenced to $CDCl_3$ at 77.0 ppm. HRMS analyses were performed on Micromass 70 VSE mass spectrometer. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques unless otherwise noted. Anhydrous solvents purchased from Sigma-Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. The starting materials were purchased from Sigma-Aldrich, Alfa Aesar, Strem Chemicals, AK Scientific, Gelest Inc., and TCI. Butene-1 and 3-methyl-1-butene were supplied in Sure-Pack^{TM} cylinders (Sigma-Aldrich).

The Design of Si,N-Type Chelating Directing Group

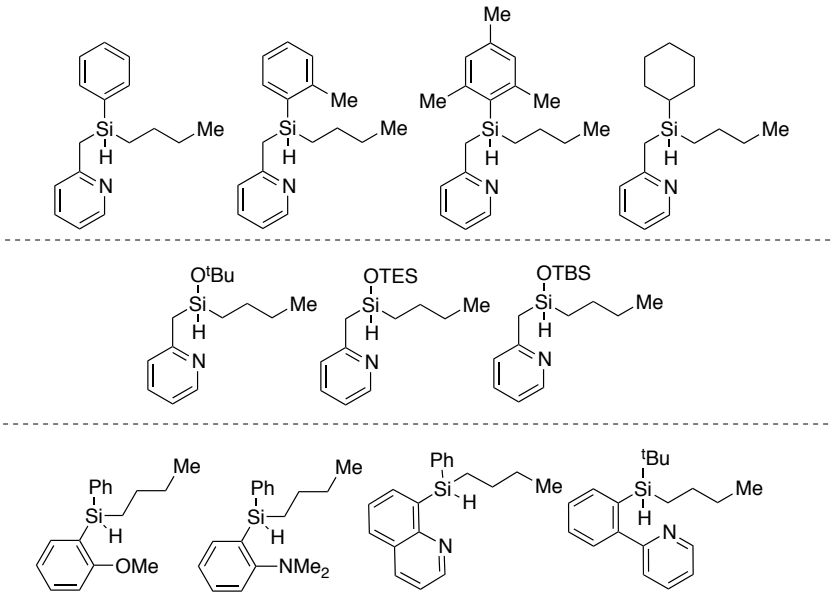
Fist, we screened different groups at silicon to build efficient chelating directing group. We synthesized a number of stable silyl derivatives **2**. With compound **2a** in hand we established conditions for dehydrogenative silylation and compared the efficiency of different silyl derivatives **2** under partially optimized Ir-catalyzed C-H silylation reaction (Supplementary Figure S1). The compounds **2a** and **2ac**, **2ae** were the most efficient in dehydrogenative silylation reaction. Taking into account both the straightforward preparation of the starting materials and efficiency of the dehydrogenative cyclization step, we decided to use picolyl substituent as a coordinating ligand at the silicon. The control experiment with **2aa** (benzyl group instead of picolyl) did not show any conversion of starting material.



* In the presence of 4 mol% 3,4,7,8-tetramethylphenanthroline ligand the formation of the trace of product was observed by GC-MS.

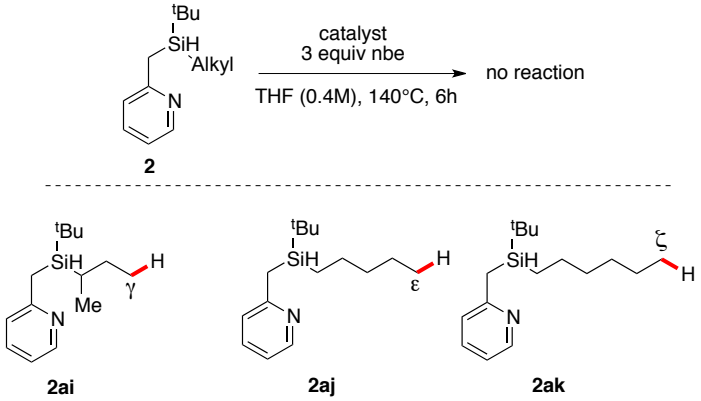
Supplementary Figure S1. Optimization of directing group.

Optimization reveled that the presence of bulky *tert*-butyl substituent is critical for stability of substrates containing chelating directing group. Thus, the formation of compounds lacking tert-butyl group depicted on Supplementary Figure S2 was detected by GC/MS method. However, these molecules decomposed during preparation or isolation.



Supplementary Figure S2. Unstable substrates.

Additional experiments demonstrated that only primary δ-C–H bond can be silylated. Compounds **2ai**, **2aj**, **2ak** were unreactive under reaction condition.

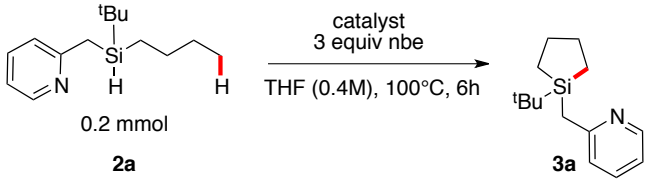


Supplementary Figure S3. Attempted γ-, ε-, ζ-C–H bond silylation.

Optimization of Dehydrogenative Silylation Reaction

1mL Wheaton V-vial was charged with 0.2 mmol of starting material, catalyst, 2-norbornene and solvent (0.5 mL, 0.4M). The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminum block. The reaction mixture was stirred either until full consumption of starting material or for period of time indicated below. The reported yields for screening experiments, unless otherwise indicated, are determined by GC-MS using icosane as internal standard.

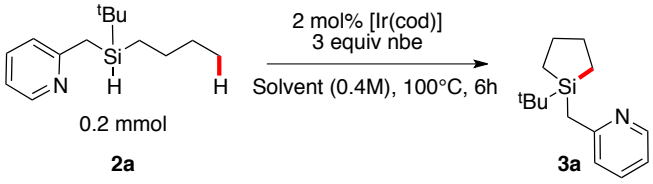
Supplementary Table S1. Optimization of the catalyst for *δ*-C−H dehydrogenative silylation reaction.



entry	Catalyst	catalyst mol %	product %	Recovered starting material %
1	**$[Ir(cod)OMe]_2$**	**2**	**77**	**0**
2	$[Ir(cod)Cl]_2$	2	58	0
3	$[Ir(Cy_3P)(Pyridine)(cod)]PF_6$	4	6	60
4	$IrCl(CO)(PPh_3)_2$, Vaska's complex	4	0	80
5	$[Ir(cod)_2]BF_4$	4	64	0
6	$[Ir(cod)_2][B(C_8H_3F_6)_4]$	4	trace	57
7	$[Ir(coe)_2Cl]_2$	2	57	0
8	Ir(cod)(acac)	4	62	0
9	Tris(norbornadiene)(acetylacetonato)iridium(III)	4	0	87
10	Dichloro(pentamethylcyclopentadienyl)iridium(III) dimer	2	0	69
11[a]	$[Rh(nbd)Cl]_2$	2	0	0
12	$[Rh(cod)Cl]_2$	2	0	0
13[b]	$[Rh(cod)Cl]_2$	1.5	0	0

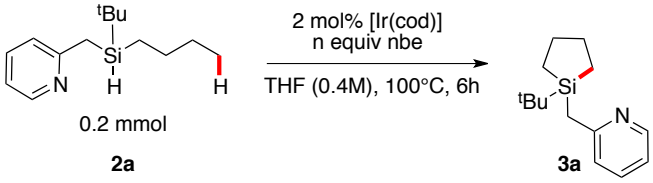
[a] Reactions were carried out for 16h, GC-MS data indicates hydrosilylation of norbornene with substrate as a major reaction pathway. [b] Reaction conditions: dppp (4.5 mol%), dioxane (1 M), 180 °C, 3 h (*25*); no difference observed in ligandless conditions.

Supplementary Table S2. Optimization of the solvent for Ir-catalyzed *δ*-C−H dehydrogenative silylation reaction.



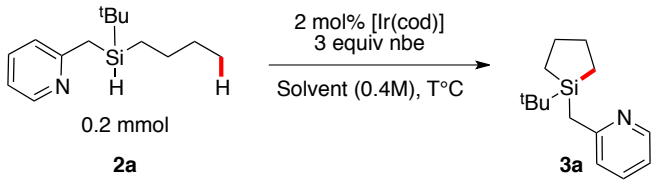
entry	solvent	product %	recovered starting material %
1	**THF**	**77**	**0**
2	Dioxane	trace	71
3	Diglyme	trace	73
4	DMF	0	80
5	BuCN	0	32
6	Toluene	26	0
7	Hexane	46	0
8	DCE	2	7

Supplementary Table S3. Optimization of the amount of norbornene (hydrogen acceptor) for Ir-catalyzed *δ*-C−H dehydrogenative silylation reaction.



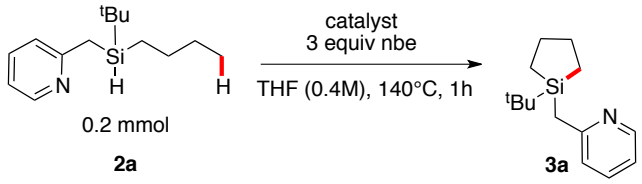
entry	nbe, equiv	product %	recovered starting material %
1	0	trace	64
2	1	58	4
3	2	74	0
4	**3**	**77**	**0**
5	5	72	0

Supplementary Table S4. Optimization of the temperature for Ir-catalyzed *δ*-C−H dehydrogenative silylation reaction.



entry	t °C	reaction time, h	product %	recovered starting material %
1	80	16	56	0
2	100	6	77	0
3	**140**	**1**	**89**	**0**

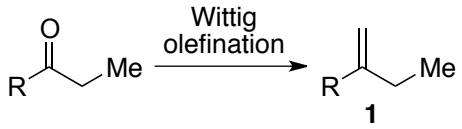
Supplementary Table S5. Optimization of the Ir-catalyst for *δ*-C−H dehydrogenative silylation reaction at 140°C.



entry	catalyst	catalyst, mol %	product %	recovered starting material %
1	**$[Ir(cod)OMe]_2$**	**2**	**89**	**0**
2	$[Ir(cod)Cl]_2$	2	57	0
5	$[Ir(cod)_2]BF_4$	4	60	0
7	$[Ir(coe)_2Cl]_2$	2	46	23
8	Ir(cod)(acac)	4	77	0

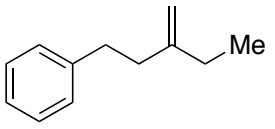
Preparation of Starting Materials

General Procedure for Preparation of 1-alkenes 1



1

Methyltriphenylphosphonium bromide (5.71 g, 16 mmol) was suspended in dry THF (20 mL) and ^{n}BuLi (2.5M in hexanes, 6.4 mL, 16 mmol) was added at -78°C. The reaction mixture was stirred for 1h at RT and ketone (*21*) (10 mmol) in dry THF (20 mL) was added. The reaction mixture was stirred for 4 h at RT. Then, the reaction was quenched with water; olefin was extracted (pentane) and washed 3 times with water, dried over $MgSO_4$, concentrated and purified by flash column chromatography (hexanes).



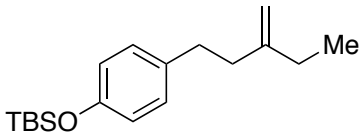
1i

(3-Methylenepentyl)benzene (1i) was obtained according to the general procedure in 66% yield as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29-7.33 (m, 2H), 7.19-7.24 (m, 3H), 4.79 (m, 2H), 2.79 (t, *J* =8.2 Hz, 2H), 2.36 (t, *J* =8.2 Hz, 2H), 2.11 (q, *J* =7.5 Hz, 2H), 1.08 (t, *J* =7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 151.0, 142.3, 128.31, 128.28, 125.7, 107.9, 38.1, 34.5, 29.0, 12.4.

GC/MS (m/z, I%): 160.0 ($[M]^+$, 10.8%), 91.0 (100.0%).



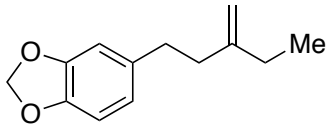
1j

***tert*-Butyldimethyl(4-(3-methylenepentyl)phenoxy)silane (1j)** was obtained according to the general procedure in 66% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.08 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 4.78 (d, *J* = 5.5 Hz, 2H), 2.73 (t, *J* =8.2 Hz, 2H), 2.34 (t, *J* =8.2 Hz, 2H), 2.10 (q, *J* =7.3 Hz, 2H), 1.09 (t, *J* =7.5 Hz, 3H), 1.03 (s, 9H), 0.23 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 153.6, 151.0, 135.0, 129.1, 119.8, 107.9, 38.3, 33.7, 29.0, 25.7, 18.2, 12.4, 4.4.

GC/MS (m/z, I%): 290.2 ($[M]^+$, 5.7%), 221.1 (100.0%), 163.0 (65.3%), 73 (34.0%).



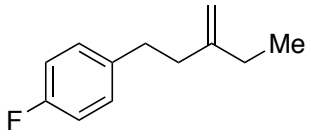
1k

5-(3-Methylenepentyl)benzo[*d*][1,3]dioxole (1k) was obtained according to the general procedure in 48% yield as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.74 (d, *J* = 7.9 Hz, 1H), 6.71 (m, 1H), 6.64-6.67 (m, 1H), 5.93 (s, 2H), 4.76 (d, *J* = 7.0 Hz, 2H), 2.69 (t, *J* =8.2 Hz, 2H), 2.30 (t, *J* =8.2 Hz, 2H), 2.07 (q, *J* =7.3 Hz, 2H), 1.06 (t, *J* =7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.8, 147.5, 145.5, 136.2, 121.0, 108.8, 108.1, 108.0, 100.7, 38.3, 34.2, 29.0, 12.3.

GC/MS (m/z, I%): 204.1 ($[M]^+$, 9.5%), 135.0 (100.0%).



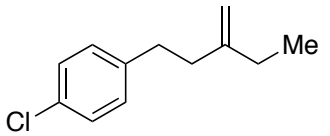
1l

1-Fluoro-4-(3-methylenepentyl)benzene (1l) was obtained according to the general procedure in 55% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.10-7.17 (m, 2H), 6.92-6.97 (m, 2H), 4.74 (d, *J* = 16.0 Hz, 2H), 2.72 (t, *J* = 7.9 Hz, 2H), 2.30 (t, *J* = 7.9 Hz, 2H), 2.06 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.2 (d, *J* = 243.2 Hz), 150.6, 137.9, 129.6 (d, *J* = 7.4 Hz), 115.0 (d, *J* = 21.3 Hz), 108.2, 38.2, 33.6, 28.9, 12.2.

GC/MS (m/z, I%): 178.1 ([M]+, 7.4%), 109.0 (100.0%).



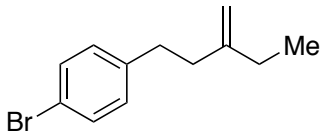
1m

1-Chloro-4-(3-methylenepentyl)benzene (1m) was obtained according to the general procedure in 69% yield as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.25 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 4.75 (dd, *J* = 14.6, 0.9 Hz, 2H), 2.73 (t, *J* =8.2 Hz, 2H), 2.31 (t, *J* =8.2 Hz, 2H), 2.07 (q, *J* =7.5 Hz, 2H), 1.06 (t, *J* =7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.5, 142.2, 140.7, 129.7, 128.3, 108.3, 37.9, 33.7, 28.9, 12.3.

GC/MS (m/z, I%): 196.0 ($[M]^+$, 1.7%), 194.0 ($[M]^+$, 5.7%), 127.0 (33.1%), 125.0 (100.0%).



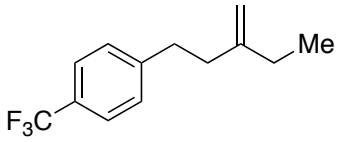
1n

1-Bromo-4-(3-methylenepentyl)benzene (1n) was obtained according to the general procedure in 74% yield as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.76 (dd, *J* = 14.3, 0.7 Hz, 2H), 2.72 (t, *J* =8.2 Hz, 2H), 2.32 (t, *J* =8.2 Hz, 2H), 2.08 (q, *J* =7.3 Hz, 2H), 1.06 (t, *J* =7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 150.4, 141.2, 131.3, 130.1, 119.5, 108.3, 37.8, 33.8, 28.9, 12.3.

GC/MS (m/z, I%): 240.0 ($[M]^+$, 5.0%), 238.0 ($[M]^+$, 4.8%), 170.9 (97.0%), 168.9 (100.0%), 90.0 (22.6%).



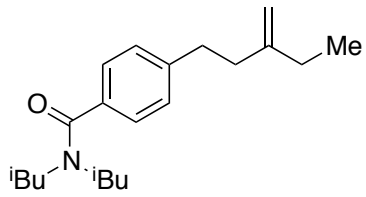
1o

1-(3-Methylenepentyl)-4-(trifluoromethyl)benzene (1o) was obtained according to the general procedure in 88% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.52 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 4.72 (d, *J* = 19.9 Hz, 2H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.33 (t, *J* = 8.1 Hz, 2H), 2.06 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 150.2, 146.4, 133.8 (d, *J* = 19.4 Hz), 128.6, 128.1 (d, *J* = 32.4 Hz), 125.2 (d, *J* = 3.7 Hz), 124.4 (q, *J* = 271.9 Hz), 108.4, 37.6, 34.2, 28.9, 21.3.

GC/MS (m/z, I%): 228.1 ([M]+, 9.9%), 199.0 ([M-Et]+, 23.0%), 159.0 (100.0%).



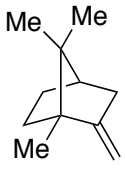
1p

***N*,*N*-Diisobutyl-4-(3-methylenepentyl)benzamide (1p)** was obtained according to the general procedure in 79% yield as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.25 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 4.72 (d, *J* = 13.6 Hz, 2H), 3.3 (br. s, 2H), 3.1 (br. s, 2H), 2.72-2.79 (m, 2H), 2.28-2.35 (m, 2H), 2.1 (br. s, 1H), 2.05 (q, *J* = 7.3 Hz, 2H), 1.8 (br. s, 1H), 1.02 (t, *J* = 7.3 Hz, 3H), 1.0 (br. s, 6H), 0.7 (br. s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 172.6, 150.6, 143.3, 134.9, 128.2, 127.1, 108.2, 56.6, 51.2, 37.8, 34.3, 28.9, 26.8, 26.2, 20.2, 19.8, 12.3.

GC/MS (m/z, I%): 315.3 ($[M]^+$, 3.2%), 187.1 (100.0%).



2-Methylenebornane

(1*S*,4*R*)-1,7,7-trimethyl-2-methylenebicyclo[2.2.1]heptane (2-methylenebornane):

Methyltriphenylphosphonium bromide (5.71 g, 16 mmol) was suspended in dry THF (20 mL) and ^{n}BuLi (2.5M in hexanes, 6.4 mL, 16 mmol) was added at -78°C. The reaction mixture was stirred for 1h at RT and (1*R*)-(+)-Camphor (1.52 g, 10 mmol) in dry THF (20 mL) was added. The reaction mixture was refluxed for 24 h. Then, the reaction was quenched with water; olefin was extracted (pentane) and washed 3 times with water, dried over $MgSO_4$, concentrated and purified by kugelrohr distillation. Product was isolated as a white solid in 74% yield.

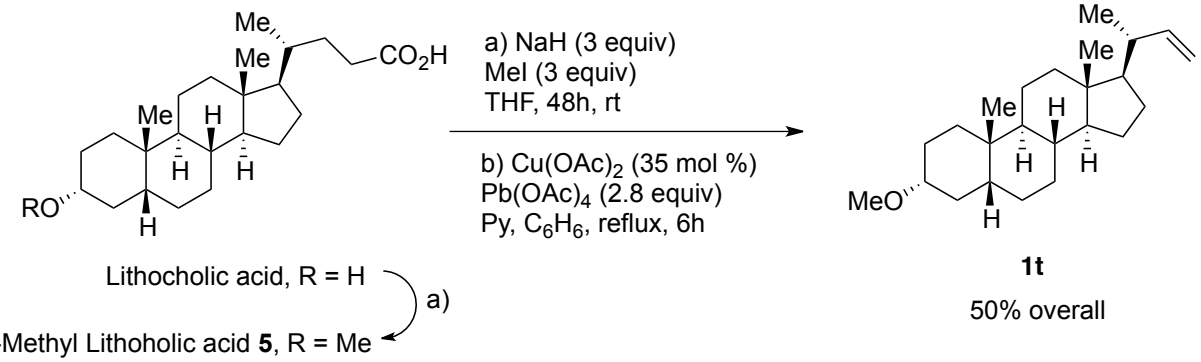
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 4.68 (br. s, 1H), 4.62-4.64 (m, 1H), 2.38 (d, J = 16.2 Hz), 1.88-1.93 (m, 1H), 1.71-1.80 (m, 2H), 1.62 (td, J = 12.0, 3.7 Hz, 1H), 1.15-1.28 (m, 2H), 0.91 (s, 3H), 0.88 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 159.5, 101.0, 51.5, 47.2, 44.7, 37.0, 35.2, 28.0, 19.6, 19.0, 12.5.

GC/MS (m/z, I%): 150.1 ($[M]^+$, 19.5%), 135.1 1 ($[M\text{-}Me]^+$, 50.9%), 121.1 (25.8%), 107.1 (100.0%), 94.0 (46.5%), 93.0 (64.0%), 91.1 (59.0%), 79.0 (79.1%), 77.0 (29.4%).

Synthesis of Lithocholic Acid Derivative 1t

The alkene was prepared from lithocholic acid via methylation of alcoholic OH, followed by an oxidative decarboxylation.



Supplementary Figure S4. Synthesis of lithochilic acid derivatives.

3α-Methyl lithocholic acid (5): To a 250 mL round bottom flask equipped with stirring bar, argon inlet, and septum, NaH (1080 mg, 45 mmol, 3 equiv) was added and the flask was evacuated and refilled with inert gas (3 times). Dry THF (50 mL) was added and the resulting suspension was placed in the ice bath. A solution of lithocholic acid (5.66 g, 15 mmol) in dry

THF (50 ml) was added to the reaction mixture at 0°C. In 30 minutes MeI (2.07 mL, 4.71 g, 30 mmol) was added and the reaction mixture was stirred 12 h at room temperature. After that, another portion of MeI (1 ml, 2.28 g, 15 mmol) in 50 ml of THF was added, and the reaction stirred for 12h at room temperature. The solvent was removed in vacuo (CAUTION, excess of MeI), and the residue was quenched (sat. NH_4Cl_{aq}). To the resulting solution HCl_{aq} (1mL, 36% aqueous solution) was added and the product was extracted (ethyl acetate 3×50 mL). Organic phase was dried (Na_2SO_4) and evaporated in vacuo. The obtained product was used without further purification. Analytical sample was prepared via crystallization from Et_2O as a white solid, m.p. 188-190°C.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 3.34 (s, 3H), 3.10-3.20 (m, 1H), 2.32-2.44 (m, 1H), 2.18-2.29 (m, 1H), 1.86-1.96 (m, 1H), 1.59-1.91 (m, 6H), 1.51-1.65 (m, 2H), 1.19-1.43 (m, 12H), 0.99-1.14 (m, 5H), 0.90 (s, 3H), 0.9 (d, J = 6.4 Hz, 3H), 0.62 (s, 3H).

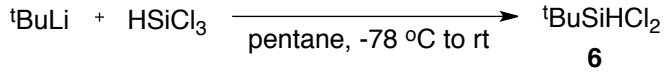
^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 179.9, 80.5, 56.4, 55.9, 55.5, 42.7, 42.0, 40.3, 40.1, 35.8, 35.3, 34.9, 32.7, 31.0, 30.8, 29.7, 28.2, 27.3, 26.7, 26.4, 24.2, 23.4, 20.8, 18.2, 12.0.

3α-Methyl-24-nor-5β-chol-22-ene (1t) was obtained from 3α-methyl lithocholic acid **5** following the literature procedure[32] in 50% yield as a white solid, m.p. 62-64°C.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 5.60-5.70 (m, 1H), 4.87 (dd, J = 17.1, 1.0 Hz, 1H), 4.86 (dd, J = 10.3, 1.8 Hz, 1H), 3.34 (s, 3H), 3.10-3.20 (m, 1H), 2.00-2.08 (m, 1H), 1.90-1.96 (m, 1H), 1.63-1.87 (m, 6H), 1.50-1.60 (m, 3H), 1.31-1.43 (m, 6H), 1.19-1.29 (m, 6H), 1.10-1.16 (m, 2H), 1.00 (d, J = 6.6 Hz, 3H), 0.91 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 145.3, 111.5, 80.4, 56.5, 55.6, 42.7, 42.1, 41.2, 40.4, 40.1, 35.9, 35.3, 34.9, 32.8, 28.5, 27.3, 26.8, 26.4, 24.2, 23.4, 22.6, 20.8, 20.1, 21.2.

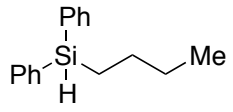
GC/MS (m/z, I%): 344.2 ([M]+, 1.4%), 297.3 (21.2%), 257.2 (100.0%), 215.2 (39.5%).



Supplementary Figure S5. Synthesis of ^{t}BuSiHCl$_2$.

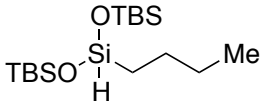
***tert*-Butyldichlorosilane (6)** was prepared according to the modified literature procedure.[33] To a 250 mL round bottom flask equipped with stirring bar, argon inlet, and septum, $HSiCl_3$ (50 mmol) and pentane (50 mL) were added. The mixture was cooled down to -78°C and then ^{t}BuLi (1.7M in pentane, 50 mmol) was added dropwise at this temperature during 2 h (syringe pump). The mixture stirred 30 min at RT and then the precipitate was quickly filtered through ceramic filter (with layer of celite). The pentane was carefully evaporated in vacuo. Then, the product was distilled out from the residue under ~ 20-30 torr vacuum, at rt to 40°C into a cold receiver flask (- 78 °C). The product was isolated in 30% yield as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 5.26 (s, 1H), 1.09 (s. 9H).

Preparation of Hydrosilanes 2



2'a

Diphenylbutylsilane 2'a was prepared according to the reported procedure.[34]

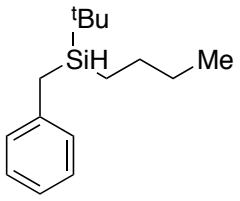


2''a

1,5-di-*tert*-Butyl-3-butyl-1,1,5,5-tetramethyltrisiloxane (2''a): to a solution of *n*-butyldichlorosilane[35] (314 mg, 2 mmol) in 4 mL of anhydrous Et_2O TBSOLi (prepared from 4 mmol of TBSOH and 4 mmol of ^{n}BuLi) in 4 mL of anhydrous Et_2O was slowly added at 0°C under inert atmosphere. The reaction was kept at this temperature for 2h. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and used for the next step without column chromatography purification (hexanes/ethyl acetate = 10:1). 1,5-di-*tert*-Butyl-3-butyl-1,1,5,5-tetramethyltrisiloxane was obtained in 30 % yield as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.61 (s, 1H), 1.31-1.39 (m, 4H), 0.92 (t, J = 7.7 Hz, 3H), 0.64 (t, J = 8.0 Hz), 0.06 (s, 12H).

GC/MS (m/z, I%): 333.0 ($[M]^+$-Me, 6.8%), 291.0 ($[M-^tBu]^+$, 100.0%).



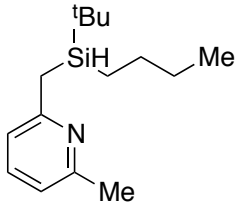
2aa

Benzyl(*tert*-butyl)(butyl)silane (2aa): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, the reaction mixture was transferred into another flask filled with a mixture of magnesium powder (72 mg, 3 mmol) and a crystal of iodine in anhydrous THF (6 mL). Benzylbromide (0.24 mL, 2 mmol) in dry THF (0.2M) was added dropwise to the reaction vessel over 1h at RT. After stirring for 1h at RT, the reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). Benzyl(*tert*-butyl)(butyl)silane was obtained in 45% yield as a colorless oil. R_f (hexanes/EtOAc = 6/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.23-7.26 (m, 2H), 7.09-7.14 (m, 3H), 3.64-3.67 (m, 1H), 2.29 (dd, J = 11.4, 2.6 Hz, 1H), 2.14 (dd, J = 13.9, 4.8 Hz, 1H), 1.23-1.32 (m, 4H), 0.97 (s, 9H), 0.85 (t, J = 7.3 Hz, 3H), 0.60-0.65 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 140.5, 128.5, 128.3, 124.1, 27.5, 27.2, 26.3, 19.5, 17.1, 13.6, 9.0.

GC/MS (m/z, I%): 234.2 ($[M]^+$, 7.7%), 177.1 ($[M-^tBu]^+$, 38.4%), 121.0 (100.0%).



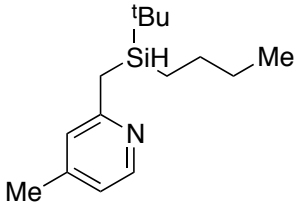
2ab

2-((*tert*-Butyl(butyl)silyl)methyl)-6-methylpyridine (2ab): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, ((6-methylpyridin-2-yl)methyl)lithium (prepared from 3 mmol of 2,6-lutidine and 2 mmol of ^{n}BuLi at -40°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-((*tert*-Butyl(butyl)silyl)methyl)-6-methylpyridine was obtained in 28% yield as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38 (t, J = 7.7 Hz, 1H), 6.83-6.87 (m, 2H), 3.66-3.68 (m, 1H), 2.48 (s, 3H), 2.47 (dd, J = 13.4, 2.6 Hz, 1H), 2.36 (dd, J = 13.6, 4.8 Hz, 1H), 1.12-1.27 (m, 4H), 0.94 (s, 9H), 0.81 (t, J = 7.0 Hz, 3H), 0.59-0.64 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 160.5, 157.5, 136.1, 122.7, 119.5, 118.7, 27.4, 27.1, 26.3, 24.4, 23.2, 17.0, 13.6, 9.1.

GC/MS (m/z, I%): 249.2 ($[M]^+$, 0.2%), 248.2 ($[M-H]^+$, 0.7%), 192.1 ($[M-^tBu]^+$, 100.0%), 136.0 (25.8%), 134.0 (30.5%).



2ac

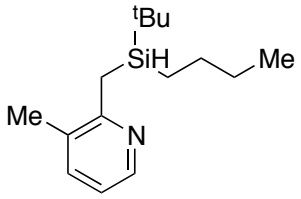
2-((*tert*-Butyl(butyl)silyl)methyl)-4-methylpyridine (2ac): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, ((4-methylpyridin-2-yl)methyl)lithium (prepared from 3 mmol of 2,4-lutidine and 2 mmol of ^{n}BuLi at -40°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-((*tert*-Butyl(butyl)silyl)methyl)-4-methylpyridine was obtained in 50% yield as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.30 (d, J = 5.1 Hz, 1H), 6.89 (s, 1H), 6.82 (d, J = 4.8 Hz, 1H), 3.67-3.70 (m, 1H), 2.46 (dd, J = 13.2, 2.9 Hz, 1H), 2.34 (dd, J = 13.2, 4.4 Hz, 1H), 2.29 (s,

3H), 1.22-1.28 (m, 3H), 1.14-1.16 (m, 1H), 0.95 (s, 9H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.62 (td, *J* = 8.0, 3.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.4, 149.1, 147.3, 123.9, 121.0, 27.8, 27.5, 26.7, 23.4, 21.3, 17.4, 14.0, 9.5.

GC/MS (m/z, I%): 249.2 ($[M]^+$, 0.2%), 248.2 ($[M-H]^+$, 0.7%), 192.1 ($[M-^tBu]^+$, 100.0%), 190.1 (14.2%), 136.0 (32.9%), 134.0 (33.4%).



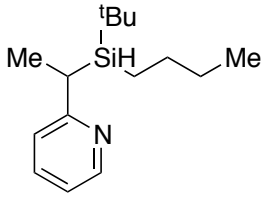
2ad

2-((*tert*-Butyl(butyl)silyl)methyl)-3-methylpyridine (2ad): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, ((3-methylpyridin-2-yl)methyl)lithium (prepared from 3 mmol of 2,3-lutidine and 2 mmol of ^{n}BuLi at -40°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-((*tert*-Butyl(butyl)silyl)methyl)-3-methylpyridine was obtained in 32% yield as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.28 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.35 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.93 (dd, *J* = 7.5, 5.0 Hz, 1H), 3.69-3.71 (m, 1H), 2.52 (dd, *J* = 13.2, 2.6 Hz, 1H), 2.38 (dd, *J* = 13.2, 5.1 Hz, 1H), 2.30 (s, 3H), 1.18-1.22 (m, 3H), 1.02-1.06 (m, 1H), 0.99 (s, 9H), 0.77 (t, *J* = 7.3 Hz, 3H), 0.61-0.65 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.9, 146.4, 137.2, 130.0, 119.8, 27.3, 27.2, 26.2, 20.9, 19.5, 17.0, 13.6, 9.2.

GC/MS (m/z, I%): 249.2 ($[M]^+$, 0.2%), 248.2 ($[M-H]^+$, 0.8%), 192.1 ($[M-^tBu]^+$, 100.0%), 136.0 (30.9%), 134.0 (31.8%).



2ae

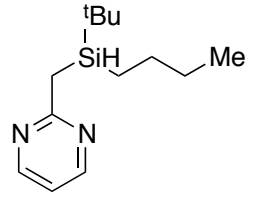
2-(1-(*tert*-Butyl(butyl)silyl)ethyl)pyridine (2ae): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, (1-(pyridin-2-yl)ethyl)lithium (prepared from 3 mmol of 2-ethylpyridine and 2 mmol of ^{n}BuLi at -40°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-(1-(*tert*-Butyl(butyl)silyl)ethyl)pyridine was

obtained in 51% yield as a colorless oil; 10:1 mixture of diastereomers. Chemical shifts are reported for a major diastereomer. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.47-8.48 (m, 1H), 7.53 (td, *J* = 7.6, 1.8 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 7.0 (ddd, J = 7.4, 4.9, 0.9 Hz, 1H), 3.61-3.62 (m, 1H), 2.69-2.74 (m, 1H), 1.54 (d, *J* = 7.5 Hz, 3H), 1.10-1.24 (m, 4H), 0.91 (s, 9H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.47-0.59 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.0, 148.8, 135.9, 121.7, 119.7, 28.8, 27.9, 27.5, 26.4, 17.8, 16.6, 13.6, 8.6.

GC/MS (m/z, I%): 249.2 ($[M]^+$, 0.4%), 248.2 ($[M-H]^+$, 1.3%), 192.1 ($[M-^tBu]^+$, 100.0%), 136.0 (34.6%).

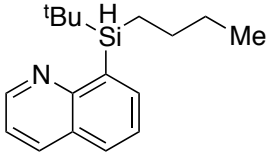


2af

2-((*tert*-Butyl(butyl)silyl)methyl)pyrimidine (2af): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, 2-methylpyrimidyllithium (prepared from 2 mmol of 2-methypyrimidine and 2 mmol of LDA at -78°C in 10 mL THF) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-((*tert*-Butyl(butyl)silyl)methyl)pyrimidine was obtained in 14% yield as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.85.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.55 (d, *J* = 4.8 Hz, 2H), 6.98 (t, *J* = 4.8 Hz, 2H), 3.70-3.75 (m, 1H), 2.55-2.73 (m, 2H), 1.20-1.30 (m, 4H), 0.93 (s, 9H), 0.80 (t, *J* = 7.0 Hz, 3H), 0.62-0.66 (m, 2H).

GC/MS (m/z, I%): 235.2 ($[M-H]^+$, 0.3%), 179.1 ($[M-^tBu]^+$, 100.0%).



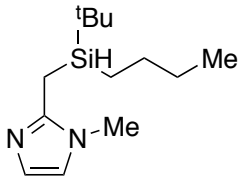
2ag

8-(*tert*-Butyl(butyl)silyl)quinolone (2ag): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, quinolin-8-yllithium (prepared from 2 mmol of 8-bromoquinoline and 2 mmol of ^{sec}BuLi at -78°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 8-(*tert*-Butyl(butyl)silyl)quinoline was obtained in 24% yield as a orange oil. R_f (hexanes/EtOAc = 4/1): 0.65.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.90 (dd, *J* = 4.0, 1.8 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.99 (dd, *J* = 6.6, 1.5 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.52 (dd, *J* = 8.0, 6.7 Hz, 1H), 7.37 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.33-4.35 (m, 1H), 1.23-1.38 (m, 4H), 1.01 (s, 9H), 0.93-0.96 (m, 2H), 0.81 (t, *J* = 7.0 Hz, 3H). R_f (hexanes/EtOAc = 4/1): 0.75.

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 152.7, 149.2, 138.7, 138.1, 135.9, 129.2, 127.6, 125.9, 120.7, 28.4, 27.5, 26.3, 17.8, 13.7, 10.4.

GC/MS (m/z, I%): 271.1 ($[M]^+$, 0.6%), 270.2 ($[M-H]^+$, 2.2%), 214.1 ($[M-^tBu]^+$, 87.1%), 212.1 (51.5%), 158.0 (59.0%), 156.0 (100%), 130.0 (20.9%).



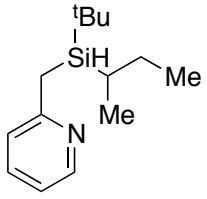
2ah

2-((*tert*-Butyl(butyl)silyl)methyl)-1-methyl-1*H*-imidazole (2ah): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, ((1-methyl-1*H*-imidazol-2-yl)methyl)lithium (prepared from 2 mmol of 1,2-dimethyl-1*H*-imidazole and 2 mmol of ^{n}BuLi at -30°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-((*tert*-Butyl(butyl)silyl)methyl)-1-methyl-1*H*-imidazole was obtained in 34% yield as a pale yellow oil. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.86 (d, *J* = 1.3 Hz, 2H), 6.73 (d, *J* = 1.5 Hz, 2H), 3.75-3.78 (m, 1H), 3.55 (s, 3H), 2.26 (dd, J = 14.9, 3.1 Hz, 1H), 2.20 (dd, *J* = 14.9, 4.8 Hz, 1H), 1.25-1.29 (m, 3H), 1.13-1.19 (m, 1H), 0.96 (s, 9H), 0.83 (t, *J* = 7.3 Hz, 3H), 0.66-0.69 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 146.8, 126.8, 119.7, 32.9, 27.2, 26.9, 26.3, 16.7, 13.6, 10.4, 9.3.

GC/MS (m/z, I%): 238.2 ($[M]^+$, 0.4%), 237.2 ($[M-H]^+$, 0.5%), 181.1 ($[M-^tBu]^+$, 100.0%), 125.0 (25.1%).



2ai

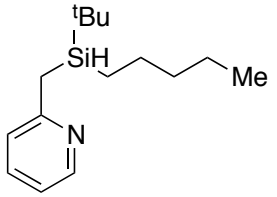
2-((*sec*-Butyl(*tert*-butyl)silyl)methyl)pyridine (2ai): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and 2 mmol 1.6 M ^{sec}BuLi diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, picolyl lithium (prepared from 3 mmol of picoline and 2 mmol of ^{n}BuLi at -78°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-

((*sec*-Butyl(*tert*-butyl)silyl)methyl)pyridine was obtained in 60% yield as a colorless oil; 1:1 mixure of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.44 (d, *J* = 4.2 Hz, 1H), 7.49 (m, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.97 (t, *J* = 6.1 Hz, 1H), 3.70 and 3.67 (two m, 1H, 1:1 ratio), 2.42-2.50 (m, 2H), 1.45-1.63 (m, 1H), 1.09-1.31 (m, 1H), 0.95-0.97 (m, 9H), 1.05-0.80 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.7, 148.9, 135.9, 122.9, 119.4, 28.1, 28.0, 26.6, 25.8, 22.1, 21.6, 18.6, 18.4, 18.0, 17.7, 15.4, 15.2, 13.5, 13.4.

GC/MS (m/z, I%): 235.0 ($[M]^+$, 0.2%), 234.2 ($[M-H]^+$, 0.5%), 178.2 ($[M-^tBu]^+$, 100.0%), 122.0 (34.1%), 120.0 (26.5%).



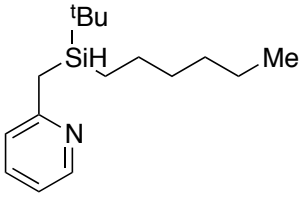
2aj

2-((*tert*-Butyl(pentyl)silyl)methyl)pyridine (2aj) was obtained from 1-bromopentane according to the method II in 71% yield as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.41-8.43 (m, 1H), 7.48 (td, *J* = 7.7, 1.8 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.95-6.97 (m, 1H), 3.68-3.70 (m, 1H), 2.49 (dd, *J* = 13.2, 2.9 Hz, 1H), 2.37 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.15-1.25 (m, 6H), 0.93 (s, 9H), 0.79-0.83 (m, 3H), 0.58-0.62 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.3, 149.0, 135.9, 122.6, 119.4, 35.5, 27.3, 24.5, 23.3, 22.1, 17.0, 13.9, 9.3.

GC/MS: m/z 249.2 ($[M]^+$, 0.1%), 248.1 ($[M-H]^+$, 0.9%), 192.1 ($[M-^tBu]^+$, 100.0%), 122.0 (38.2%), 120.0 (38.3%).



2ak

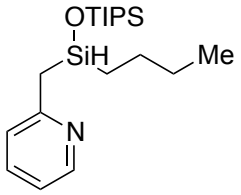
2-((*tert*-Butyl(hexyl)silyl)methyl)pyridine (2ak): *tert*-butyldichlorosilane (408 mg, 2.6 mmol) was dissolved in dry 2 mL of anhydrous Et_2O and 2 mmol 2.2 M hexyl lithium diluted in 10 mL Et_2O was added dropwise to the reaction vessel at -78°C. After stirring for 30 min at -78°C, 2-picolyl lithium (prepared from 3 mmol of 2-picoline and 2 mmol of ^{n}BuLi at -40°C in 10 mL Et_2O) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using flash column chromatography (hexanes/ethyl acetate = 10:1). 2-((*tert*-Butyl(hexyl)silyl)methyl)pyridine was obtained in 77% yield as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.44 (m, 1H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.97-6.99 (m, 1H), 3.68-3.71 (m, 1H), 2.50 (dd, *J* = 13.2, 2.6 Hz, 1H), 2.38 (dd, *J*

= 13.2, 4.4 Hz, 1H), 1.14-1.26 (m, 8H), 0.94 (s, 9H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.62 (td, *J* = 7.7, 2.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.4, 149.0, 135.9, 122.6, 119.4, 32.9, 31.4, 27.4, 24.8, 23.3, 22.5, 17.0, 14.1, 9.4.

GC/MS: m/z 263.2 ($[M]^+$, 0.2%), 262.2 ($[M-H]^+$, 0.7%), 206.1 ($[M-^tBu]^+$, 100.0%), 122.0 (43.2%), 120.0 (42.0%).



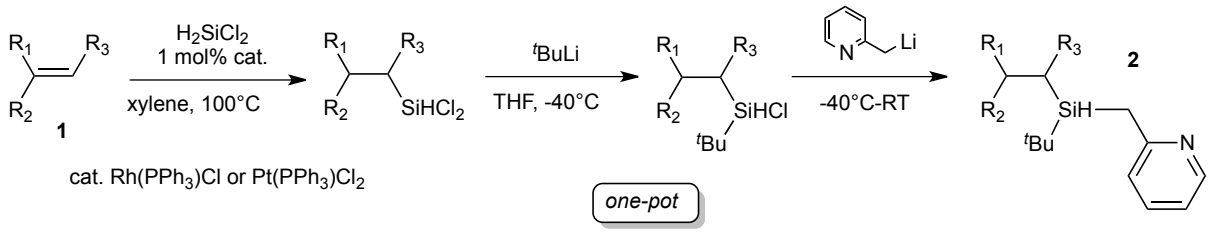
2'''a

2-[(1-Butyl-3,3,3-triisopropyldisiloxanyl)methyl]pyridine (2'a): to a solution of *n*-butyldichlorosilane (314 mg, 2 mmol) in 4 mL of anhydrous Et_2O TIPSOLi (prepared from 2 mmol of TIPSOH and 2 mmol of ^{n}BuLi) in 4 mL of anhydrous Et_2O was slowly added at 0°C under inert atmosphere. The reaction was kept at this temperature for 2h, cooled down to -40°C and 2-picolyllithium (prepared from 3 mmol of 2-picoline and 2.1 mmol of PhLi at 35°C in 10 mL Et_2O) was added. The reaction was stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and used for the next step without column chromatography purification (hexanes/ethyl acetate = 10:1). 2-[(1-Butyl-3,3,3-triisopropyldisiloxanyl)methyl]pyridine was obtained in 77 % yield as a yellow oil. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.44 (d, *J* = 5.1 Hz, 1H), 7.50 (td, *J* = 7.8, 1.9 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.96-7.01 (m, 1H), 4.80 (bs, 1H), 2.48 (dd, *J* = 13.3, 2.8 Hz, 1H), 2.35 (dd, *J* = 13.3, 2.4 Hz, 1H), 1.14-1.23 (m, 4H), 0.89-1.06 (m, 21H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.63 – 0.70 (m, 2H).

GC/MS: m/z (I, %) 322 (M^+-H, 3.8%), 266 (M^+-^{t}Bu, 94%), 178 (97%), 120 (100%).

Method I:

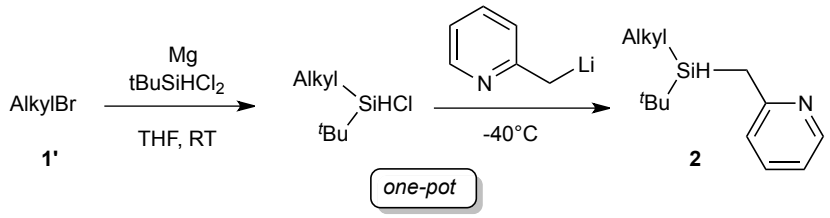


Supplementary Figure S6. Preparation of hydrosilanes, **Method I**.

An oven dried 5 mL Wheaton V-vial, containing a stirring bar, was charged with alkene (2 mmol) and $Rh(PPh_3)_3Cl$ (1 mol %) for mono- and 1,1-disubstituted alkenes or $Pt(PPh_3)_2Cl_2$ (1 mol %) for trisubstituted alkene under N_2 atmosphere (glovebox). H_2SiCl_2 (2 equiv, 25%

solution in xylene) was added, and the reaction was heated at 100°C until full consumption of starting alkene (GC control). The obtained $RSiHCl_2$ was transferred to the 50 mL flask via syringe, an the excess of H_2SiCl_2 was removed under reduced pressure. The residue was dissolved in 8 mL of dry THF and cooled down to -40°C. ^{t}BuLi (0.8M in pentane, 2.5 mL, 2 mmol, 1 equiv) was added slowly to the reaction mixture at -40°C. The reaction mixture was stirred under -40 ^{0}C for 30 minutes and then 2-picolyl lithium [prepared from 2-picoline (0.25 mL, 2.5 mmol, 1.25 equiv) and 2.4 mmol of PhLi (1.8M in dibutyl ether, 1.33 mL, 2.4 mmol, 1.2 equiv) in 10 mL Et_2O at 35°C] was added at -40°C. The reaction was stirred for 30 min at -40°C and then quenched with 5 ml of saturated NH_4Cl, extracted (Et_2O), and washed with water, dried over $MgSO_4$, concentrated, and purified by flash column chromatography (hexanes/ethyl acetate 10:1).

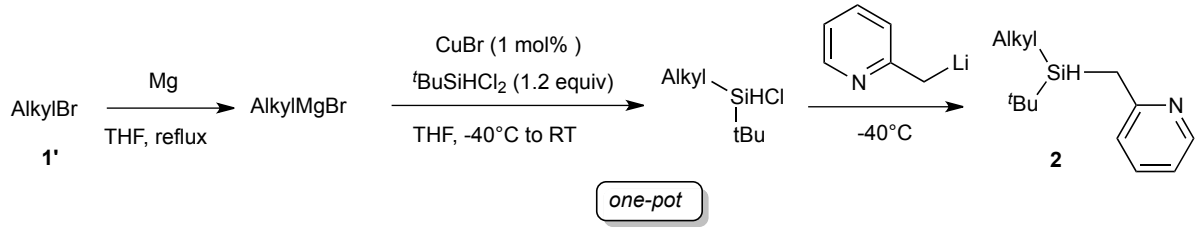
Method II:



Supplementary Figure S7. Preparation of hydrosilanes, **Method II**.

To a mixture of magnesium powder (72 mg, 3 mmol) and a crystal of iodine, anhydrous THF (6 mL) was added and stirred at RT for 10 min under argon atmosphere. *tert*-Butyldichlorosilane (408 mg, 2.6 mmol) was added to a reaction mixture and alkylhalide (2 mmol) in dry THF (0.2M) was added dropwise to the reaction vessel over 1h. After stirring for 2h at RT, 2-picolyl lithium [prepared from 2-picoline (0.3 mL, 3 mmol, 1.5 equiv) and ^{n}BuLi (2.5M in hexanes, 0.96 mL, 2.4 mmol, 1.2 equiv) at -40°C in 10 mL Et_2O] was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with saturated NH_4Cl, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified by flash column chromatography (hexanes/ethyl acetate 10:1).

Method III:

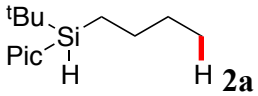


Supplementary Figure S8. Preparation of hydrosilanes, **Method III**.

An oven dried 5 mL Wheaton V-vial, containing a stirring bar, was charged with RBr (2 mmol) and Mg (53 mg, 1.1 equiv, 2.2 mmol) under N_2 atmosphere (glovebox). Dry THF (3

mL) containing 1 drop of dibromoethane was added, and the reaction was refluxed for 12 h. The obtained RMgBr was transferred to the 25 mL flask containing CuBr (3 mg, 1 mol %) and stirred 10 min. To the obtained mixture a solution of $^{t}BuSiHCl_2$ (2.4 mmol) in 0.5 mL of THF was added dropwise at -40°C. The mixture was warmed up to RT and stirred for 30 min.

In the separate 25 mL flask the solution of MeLi (1.7M in ether, 3 mmol) was added to a solution of 2-picoline (3 mmol) in 3 mL of THF at -40 °C. The mixture allowed to warm to -20 °C and stirred 10 min at this temperature. The solution of picolyllithium was cooled down to -40 °C and the solution of R_2SiHCl was added dropwise. The reaction was stirred at -40 °C for ~2-4 h (GC monitoring). The reaction allowed to warm to room temperature, quenched (sat. NH_4Cl_{aq}), and extracted (ethyl acetate, 3×10 mL). The combined organic extracts were dried (Na_2SO_4), and concentrated under a reduced pressure. The residue was purified by column chromatography (hexanes/ethyl acetate = 10:1).



2a

2-((*tert*-Butyl(butyl)silyl)methyl)pyridine (2a): An oven dried 25 mL flask, containing a stirring bar, 1 ml of o-xylene, was capped with rubber septum, filled with argon and pre-weighted. The flask was placed into pre-cooled bath (-20 °C) and connected via needle to a household rubber balloon filled with 1-Butene. After stirring for 30 minutes at -20 °C, the temperature was gently increased up to room temperature and the amount of 1-Butene condensed into the flask was calculated (364 mg). 2 equiv of H_2SiCl_2 (13 mmol, 5252 mg of 25% solution in xylene), 1 mol % of $Rh(PPh_3)_3Cl$ (60 mg suspended in 1 ml of xylene) were added to the flask. The reaction mixture was placed into pre-heated oil bath (100 °C) and stirred for 2 hours. Then, the reaction mixture was cooled down to room temperature and the volatile material was removed under reduced pressure. The residue was dissolved into 30 ml of dry THF and cooled down to -40 °C. $^{t}BuLi$ (0.8M in pentane, 7.5 mL, 6 mmol, 0.92 equiv) was added slowly to the reaction mixture at -40°C. The reaction mixture was stirred under -40 °C for 30 minutes and then 2-picolyl lithium [prepared from 2-picoline (0.95 mL, 9.5 mmol, 1.5 equiv) and 6.5 mmol of PhLi (2.0M in dibutyl ether, 3.25 mL, 1.2 equiv) at 35°C] in 15 mL Et_2O was added at -40°C. The reaction was stirred for 30 min at -40°C and then quenched with 15 ml of saturated aqueous NH_4Cl, extracted (Et_2O), and washed with water, dried over $MgSO_4$, concentrated, and purified by flash column chromatography (hexanes/ethyl acetate 10:1). **2a** was obtained as colorless oil. Yield is 61 %. R_f (hexanes/EtOAc = 4/1): 0.8.

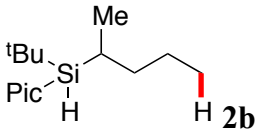
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.45 (m, 1H), 7.51 (td, *J* = 7.7, 1.8 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.99 (dd, *J* = 7.0, 5.1 Hz, 1H), 3.69-3.71 (m, 1H), 2.51 (dd, *J* = 13.4, 2.8 Hz, 1H), 2.39 (dd, *J* = 13.2, 4.4 Hz, 1H), 1.07-1.28 (m, 4H), 0.95 (s, 9H), 0.81 (t, *J* = 7.0 Hz, 3H), 0.62 (td, *J* = 8.4, 3.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.4, 149.0, 136.0, 122.7, 119.4, 27.4, 27.1, 26.3, 23.3, 17.0, 13.6, 9.1.

GC/MS: m/z (I, %): 235.3 ($[M]^+$, 0.2%), 178.2 ($[M-^{t}Bu]^+$, 100.0%), 122.1 (31.9%), 120.1 (29.0%).

Alternatively, **2a** can be synthesized via the following procedure:

To the solution of *tert*-butyldichlorosilane (408 mg, 2.6 mmol) dry Et_2O (2 mL) ^{n}BuLi (2.5M in hexanes, 0.8 mL, 2 mmol) diluted in 10 mL Et_2O was added dropwise at -78°C. After stirring for 30 min at RT, 2-picolyl lithium (prepared in 10 mL of Et_2O from 3 mmol of 2-picoline and 2 mmol of ^{n}BuLi at -40°C) was added to the reaction mixture at -78°C and stirred for 30 min at this temperature. The reaction was quenched with water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified using column chromatography (hexanes/ethyl acetate = 10:1). **2a** was obtained in 87% yield as colorless oil.



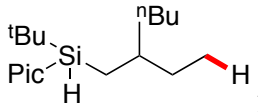
2b

2-((*sec*-Butyl(*tert*-butyl)silyl)methyl)pyridine (2b) was obtained from 2-bromopentane according to the **Method III** in 40% yield as a colorless oil; 1.35:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.40-8.43 (m, 1H), 7.45-7.52 (m, 1H), 7.05-7.09 (m, 1H), 6.93-7.01 (m, 1H), 3.68 and 3.65 (two t, *J* = 4.0 Hz, 1H, ratio 1.35:1), 2.40-2.51 (m, 2H), 1.33-1.40 (m, 2H), 1.16-1.22 (m, 2H), 0.96 and 0.95 (two s, 9H, 1.35:1 ratio), 0.93-0.97 (m, 3H), 0.86-0.90 (m, 1H), 0.76-0.84 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.7, 149.0, 135.9, 122.9, 119.4, 35.9, 35.1, 28.2, 28.0, 22.0, 21.6, 16.2, 16.0, 15.8, 15.6, 14.0.

GC/MS: m/z (I, %): 248.2 ($[M-H]^+$, 0.6%), 234.1 ($[M-Me]^+$, 0.7%), 192.1 ($[M-^{t}Bu]^+$, 100.0%).



2c

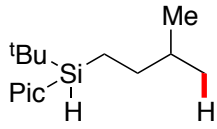
2-((*tert*-Butyl(2-ethylhexyl)silyl)methyl)pyridine (2c) was obtained from 2-ethyl-1-hexene according to the **Method I** in 62% yield as a pale yellow oil, 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.85.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40-8.43 (m, 1H), 7.48-7.52 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.97-6.99 (m, 1H), 3.77-3.80 (m, 1H), 2.50-2.53 (m, 1H), 2.35-2.39 (m, 1H), 1.06-1.25 (m, 9H), 0.92 (s, 9H), 0.82-0.87 (m, 3H), 0.76 (t, *J* =7.2 Hz, 1.5H), 0.70 (t, *J* =7.2 Hz, 1.5H), 0.60-0.62 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.4, 149.1, 135.9, 122.7, 119.4, 35.7, 35.6, 35.4, 35.1, 28.7, 28.5, 28.1, 27.3, 25.7, 23.8, 23.0, 17.0, 17.2, 14.2, 14.1, 10.7, 10.6.

GC/MS: m/z (I, %): 290.2 ($[M-H]^+$, 1.0%), 234.2 ($[M-^{t}Bu]^+$, 100.0%), 178.1 (20.5%), 122.0 (85.3%).

Alternatively, **2c** can be prepared from commercially available (2-ethylhexyl)magnesium bromide by **Method III**. Yield is 75%.



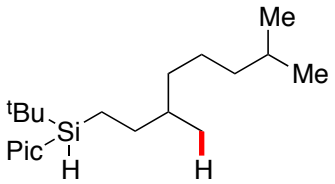
2d

2-((*tert*-Butyl(isopentyl)silyl)methyl)pyridine (2d) An oven dried 25 mL flask, containing a stirring bar, 1 ml of o-xylene, was capped with rubber septa, filled with argon and pre-weighted. The flask was placed into pre-cooled bath (-20 ^{o}C) and connected via needle to a household rubber balloon filled with 3-methyl-1-butene. After stirring for 30 minutes at -20 ^{o}C, the temperature was gently increased up to room temperature and the amount of 3-methyl-1-butene condensed into the flask was calculated (455 mg). 2 equiv of H_2SiCl_2 (13 mmol, 5252 mg of 25% solution in xylene), 1 mol % of $Rh(PPh_3)_3Cl$ (60 mg suspended in 1 ml of xylene) were added to the flask. The reaction mixture was placed into pre-heated oil bath (100 ^{o}C) and stirred for 2 hours. Then, the reaction mixture was cooled down to room temperature and the volatile material was removed under reduced pressure. The residue was dissolved into 30 ml of dry THF and cooled down t -40 ^{o}C. ^{t}BuLi (0.8M in pentane, 7.5 mL, 6 mmol, 0.92 equiv) was added slowly to the reaction mixture at -40°C. The reaction mixture was stirred under -40 ^{0}C for 30 minutes and then 2-picolyl lithium [prepared from 2-picoline (0.95 mL, 9.5 mmol, 1.5 equiv) and 6.5 mmol of PhLi (2.0M in dibutyl ether, 3.25 mL, 1.2 equiv) at 35°C] in 15 mL Et_2O was added at -40°C. The reaction was stirred for 30 min at -40°C and then quenched with 15 ml of saturated aqueous NH_4Cl, extracted (Et_2O), and washed with water, dried over $MgSO_4$, concentrated, and purified by flash column chromatography (hexanes/ethyl acetate 10:1). **2d** was obtained as colorless oil. Yield is 64 %. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.44-8.45 (m, 1H), 7.57 (t, *J* = 6.9, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.03-7.05 (m, 1H), 3.68-3.72 (m, 1H), 2.56 (dd, *J* = 13.4, 2.8 Hz, 1H), 2.45 (dd, *J* = 13.2, 4.6 Hz, 1H), 1.35-1.40 (m, 1H), 1.12-1.18 (m, 1H), 0.98-1.03 (m, 1H), 0.96 (s, 9H), 0.79 (d, *J* = 6.6 Hz, 6H), 0.60-0.63 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 148.1, 136.7, 123.0, 119.6, 33.9, 30.8, 27.4, 22.9, 22.0, 21.9, 17.1, 6.8.

Alternatively, **2d** can be prepared from commercially available 1-bromo-3-methylbutane by **Method II**. Yield is 36%.



2e

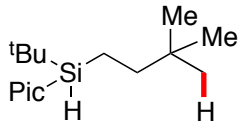
2-((*tert*-Butyl(3,7-dimethyloctyl)silyl)methyl)pyridine (2e) was obtained from 3,7-dimethyl-1-octene according to the **Method I** in 64% yield as a pale yellow oil, 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.85.

Alternatively **2e** can be prepared from commercially available 1-bromo-3,7-dimethyloctane via formation of Grignard reagent according to the **Method III** in 58%.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.44-8.45 (m, 1H), 7.49-7.52 (m, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.99 (m, 1H), 3.70 (m, 1H), 2.52 (dd, *J* = 13.2, 2.8 Hz, 1H), 2.37-2.41 (m, 1H), 1.48-1.52 (m, 1H), 1.10-1.31 (m, 8H), 0.92-0.99 (m, 1H), 0.95 and 0.96 (two s, 9H), 0.86 (d, *J* = 6.6 Hz, 6H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.53-0.64 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.4, 149.1, 135.9, 122.6, 119.4, 39.3, 36.6, 36.5, 35.5, 31.94, 31.89, 27.9, 27.4, 24.7, 23.3, 23.2, 22.7, 22.6, 19.1, 19.0, 17.1, 6.3.

GC/MS: m/z (I, %): 319.2 ($[M]^+$, 0.3%), 262.2 ($[M-^tBu]^+$, 100.0%), 122.0 (31.2%), 120.0 (29.1%).



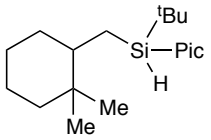
2f

2-((*tert*-Butyl(3,3-dimethylbutyl)silyl)methyl)pyridine (2f) was obtained from commercially available 3,3-dimethylbut-1-ene according to the **Method I** in 60% yield as a pale yellow oil. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.45 (m, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.02 (dd, *J* = 6.8, 5.3 Hz, 1H), 3.67-3.70 (m, 1H), 2.55 (dd, *J* = 13.2, 2.9 Hz, 1H), 2.43 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.13-1.17 (m, 1H), 0.96 (s, 9H), 0.94-1.02 (m, 1H), 0.77 (s, 9H), 0.53-0.57 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 148.5, 136.4, 122.9, 119.6, 38.9, 37.4, 31.2, 28.7, 28.6, 27.4, 25.8, 22.9, 17.2, 6.7, 3.5.

GC/MS: m/z (I, %): 262.0 (M^+-H, 0.9%), 206.0 (M^+-^{t}Bu, 100%), 120.0 (40%).



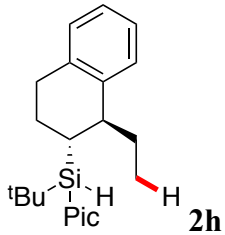
2g

2-((*tert*-Butyl((2,2-dimethylcyclohexyl)methyl)silyl)methyl)pyridine (2g) was obtained from 1,1-dimethyl-2-methylenecyclohexane[36] according to the **Method I** in 62% yield as a pale yellow oil; 6:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.85.

^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer): δ ppm 8.42-8.46 (m, 1H), 7.50 (td, *J* = 7.5, 1.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.95 (m, 1H), 3.72 (br. s, 1H), 2.50 (dd, *J* = 13.2, 2.8 Hz, 1H), 2.32 (dd, *J* = 13.1, 4.9 Hz, 1H), 1.45-1.52 (m, 1H), 1.23-1.41 (m, 4H), 1.00-1.28 (m, 4H), 0.95 (s, 9H), 0.85 (s, 3H), 0.69 (s, 3H), 0.64-0.73 (m, 1H), 0.09-0.19 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, major diastereomer): δ ppm 161.3, 149.1, 135.9, 122.7, 119.4, 43.6, 41.4, 34.3, 30.5, 29.7, 27.3, 26.8, 24.2, 22.4, 18.8, 17.4, 10.3.

GC/MS: m/z (I, %): 302.0 (M^+-H, 0.8%), 246.0 (M^+-^{t}Bu, 100%), 122.0 (43%).



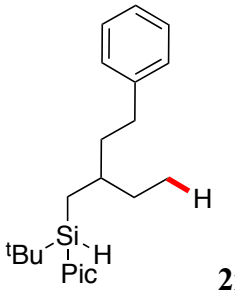
2h

2-((*tert*-Butyl(1-ethyl-1,2,3,4-tetrahydronaphthalen-2-yl)silyl)methyl)pyridine (2h) was obtained from 4-ethyl-1,2-dihydronaphthalene[37] according to the **Method I** in 41% yield as a pale yellow oil; 1.5:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.34-8.40 (m, 1H), 7.37-7.47 (m, 1H), 6.79-7.12 (m, 6H), 3.79 and 3.76 (two br. s, 1H, 1.5:1 ratio), 2.59-2.89 (m, 3H), 2.22-2.48 (m, 2H), 2.05-2.20 (m, 1H), 1.58-1.75 (m, 3H), 1.37-1.47 (m, 1H), 0.98 and 0.97 (two s, 9H, 1:1.5 ratio), 0.76-0.82 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.4, 149.0, 148.9, 140.6, 140.4, 138.1, 137.7, 135.9, 135.8, 129.2, 129.0, 125.6, 125.4, 125.2, 122.9, 122.8, 119.5, 119.4, 41.1, 41.0, 31.1, 30.7, 30.1, 29.2, 28.1, 23.4, 23.1, 22.5, 22.0, 21.6, 20.8, 18.2, 17.8, 11.3, 10.7.

GC/MS: m/z (I, %): 337.0 (M^+-H, 1.3%), 280.0 (M^+-^{t}Bu, 47%), 178.0 (78%), 122.0 (100%).



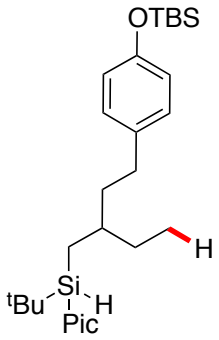
2i

2-((*tert*-Butyl(2-ethyl-4-phenylbutyl)silyl)methyl)pyridine (2i) was obtained from compound **1i** according to the **Method I** in 59% yield as a colorless oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.45 (m, 1H), 7.44-7.50 (m, 1H), 7.26-7.29 (m, 2H), 7.12-7.18 (m, 3H), 6.93-7.06 (m, 2H), 3.84 (m, 1H), 2.39-2.55 (m, 4H), 1.27-1.55 (m, 5H), 0.95-0.97 (m, 9H), 0.82 and 0.76 (two td, J = 7.2, 2.2 Hz, 3H, 1:1 ratio), 0.68-0.72 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 149.0, 143.0, 142.9, 135.9, 128.3, 128.2, 128.1, 125.43, 125.41, 122.6, 119.4, 37.6, 37.3, 35.5, 35.3, 32.9, 28.3, 27.9, 23.7, 23.6, 16.9, 14.1, 10.4.

GC/MS: m/z (I, %): 339.1 ($[M]^+$, 0.5%), 338.2 ($[M-H]^+$, 1.8%), 282.2 ($[M-^tBu]^+$, 100.0%), 122.0 (46.3%), 120.0 (47.9%).

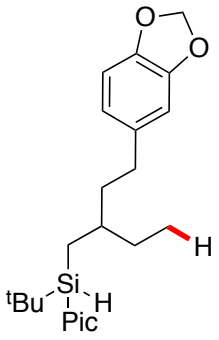


2j

2-((*tert*-Butyl(4-(4-(*tert*-butyldimethylsilyloxy)phenyl)-2-ethylbutyl)silyl)methyl)pyridine (2j) was obtained from compound **1j** according to the **Method I** in 30% yield as a colorless oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.85.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.44 (m, 1H), 7.45-7.0 (m, 1H), 6.94-7.06 (m, 4H), 6.73-6.74 (m, 2H), 3.82 (m, 1H), 2.34-2.50 (m, 4H), 1.26-1.50 (m, 5H), 0.95-0.99 (m, 18H), 0.81 and 0.74 (two t, J = 7.2 Hz, 3H, 1:1 ratio), 0.67-0.69 (m, 2H), 0.18 and 0.19 (two s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 153.4, 149.1, 135.9, 135.7, 135.6, 129.1, 122.7, 119.71, 119.68, 119.4, 37.8, 37.4, 35.4, 35.3, 32.0, 28.3, 28.0, 27.3, 25.7, 23.8, 23.7, 18.2, 16.9, 14.1, 10.5, 4.5.



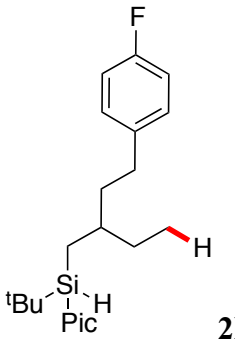
2k

2-(((4-(Benzo[*d*][1,3]dioxol-5-yl)-2-ethylbutyl)(*tert*-butyl)silyl)methyl)pyridine (2k) was obtained from compound **1k** according to the **Method I** in 26% yield as a colorless oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.75.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.44 (m, 1H), 7.47-7.50 (m, 1H), 6.95-7.06 (m, 2H), 6.55-6.72 (m, 3H), 5.91-5.92 (m, 2H), 3.81 (m, 1H), 2.32-2.53 (m, 4H), 1.22-1.48 (m, 5H), 0.95 (two s, 9H), 0.79 and 0.74 (two t, J = 7.2 and 6.8 Hz, 3H, 1:1 ratio), 0.66-0.68 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 149.1, 147.4, 145.3, 137.0, 136.9, 136.0, 122.7, 120.9, 119.5, 108.8, 108.0, 100.6, 38.0, 37.6, 35.4, 35.3, 32.6, 28.4, 27.9, 27.3, 23.74, 23.71, 16.9, 14.1, 10.5.

GC/MS: m/z (I, %): 383.2 ($[M]^+$, 12.8%), 382.3 ($[M-H]^+$, 25.0%), 326.2 ($[M-^tBu]^+$, 87.0%), 324.2 (73.8%), 178.1 (88.8%), 135.0 (79.8%), 122.0 (100.0%), 120.1 (92.1%).



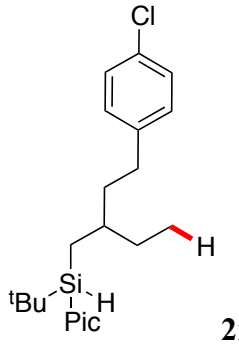
2l

2-((*tert*-Butyl(2-ethyl-4-(4-fluorophenyl)butyl)silyl)methyl)pyridine (2l) was obtained from compound **1l** according to the **Method I** in 69% yield as a pale yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.75.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.39-8.41 (m, 1H), 7.42-7.50 (m, 1H), 7.01-7.09 (m, 3H), 6.89-6.97 (m, 3H), 3.80 (br. s, 1H), 2.31-2.54 (m, 4H), 1.16-1.51 (m, 5H), 0.95 and 0.94 (two s, 9H, ratio 1:1), 0.79 and 0.73 (two t, J = 7.0 Hz, J = 7.0 Hz, 3H, ratio 1:1), 0.61-0.63 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.3, 161.1, 159.9, 149.1, 138.5, 135.9, 129.6, 129.5, 122.7, 119.4, 114.9, 114.8, 37.8, 37.4, 35.5, 35.3, 32.1, 28.3, 27.9, 27.3, 23.7, 16.9, 14.1, 10.5.

GC/MS: m/z (I, %): 356.0 (M^+-H, 0.64%), 300.0 (M^+-^{t}Bu, 100%), 122.0 (60%).



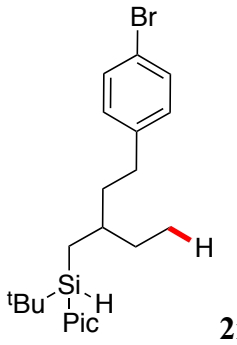
2m

2-((*tert*-Butyl(4-(4-chlorophenyl)-2-ethylbutyl)silyl)methyl)pyridine (2m) was obtained from compound **1m** according to the **Method I** in 57% yield as a colorless oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.75.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40-8.43 (m, 1H), 7.44-7.49 (m, 1H), 7.20-7.22 (m, 2H), 7.01-7.05(m, 3H), 6.92-6.97 (m, 1H), 3.81 (m, 1H), 2.33-2.54 (m, 4H), 1.19-1.50 (m, 5H), 0.95 (two s, 9H), 0.79 and 0.74 (two t, J = 7.2 Hz, 3H, 1:1 ratio), 0.61-0.71 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.1, 149.0, 141.4, 141.3, 135.9, 131.1, 129.6, 128.21, 128.18, 122.6, 119.4, 37.5, 37.1, 35.4, 35.2, 32.2, 28.2, 27.8, 27.2, 23.7, 23.6, 16.8, 14.1, 14.0, 10.4.

GC/MS: m/z (I, %): 375.2 ($[M]^+$, 0.4%), 373.1 ($[M]^+$, 0.7%), 318.2 ($[M-^tBu]^+$, 36.3%), 316.2 ($[M-^tBu]^+$, 100.0%), 324.2 (73.8%), 122.0 (51.0%), 120.0 (55.7%).



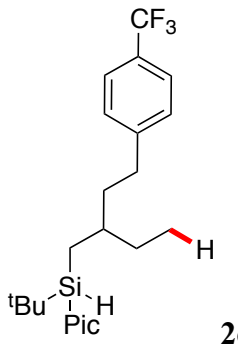
2n

2-(((4-(4-Bromophenyl)-2-ethylbutyl)(*tert*-butyl)silyl)methyl)pyridine (2n) was obtained from compound **1n** according to the **Method I** in 32% yield (second step in pentane) as a pale yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.75.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.38-8.44 (m, 1H), 7.44-7.50 (m, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.92-7.07 (m, 4H), 3.79 (br. s, 1H), 2.31-2.55 (m, 4H), 1.16-1.51 (m, 5H), 0.94 (two s, 9H, ratio 1:1), 0.78 and 0.73 (two t, *J* = 7.1 Hz, *J* = 7.1 Hz, 3H, ratio 1:1), 0.59-0.69 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.1, 149.1, 142.0, 141.9, 136.0, 131.2, 130.1, 122.7, 119.5, 119.1, 37.5, 37.0, 35.5, 35.2, 32.3, 28.3, 27.9, 23.7, 16.9, 14.1, 10.4.

GC/MS: m/z (I, %): 418.0 (M^+, 0.8%), 362.0, 360.0 (M^+-^{t}Bu, 100%, 99%), 178 (37%), 122, 120 (67%, 73%).



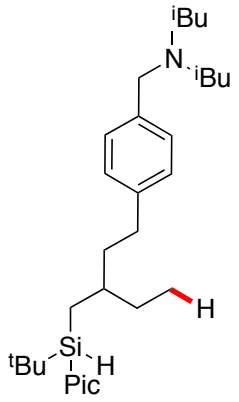
2o

2-((*tert*-Butyl(2-ethyl-4-(4-(trifluoromethyl)phenyl)butyl)silyl)methyl)pyridine (2o) was obtained from compound **1o** according to the **Method I** in 45% yield as a pale yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.36-8.45 (m, 1H), 7.41-7.54 (m, 3H), 7.17-7.25 (m, 2H), 7.00-7.07 (m, 1H), 6.89-6.98 (m, 1H), 3.80 (br. s, 1H), 2.41-2.64 (m, 3H), 2.31-2.39 (m, 1H), 1.17-1.57 (m, 5H), 0.95 and 0.94 (two s, 9H, 1:1 ratio), 0.80 and 0.74 (two t, *J* = 7.0 Hz, *J* = 7.0 Hz, 3H, 1:1 ratio), 0.59-0.71 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.1, 149.1, 147.3, 147.1, 135.9, 128.6, 130.1, 125.1, 122.7, 119.5, 37.4, 36.9, 35.5, 35.3, 32.8, 27.9, 27.3, 23.7, 16.9, 14.1, 10.4.

GC/MS: m/z (I, %): 406.0 (M^+-H, 0.8%), 350.0 (M^+-^{t}Bu, 100%), 178.0 (28%), 120.0 (92%).



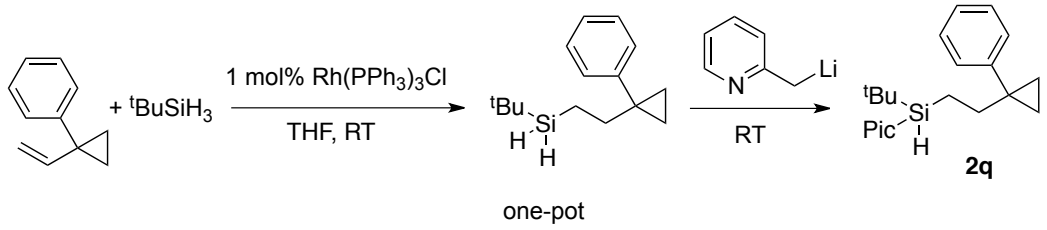
2p

***N*-(4-(3-((*tert*-Butyl(pyridin-2-ylmethyl)silyl)methyl)pentyl)benzyl)-*N*-isobutyl-2-methylpropan-1-amine (2p)** was obtained from compound **1p** according to the **Method I** in 40% yield as a pale yellow oil; 1:1 mixture of diastereomers. Hydrosilylation was accompanied with reduction of amide. R_f (hexanes/EtOAc = 4/1): 0.45.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.39-8.47 (m, 1H), 7.44-7.50 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.01-7.08 (m, 3H), 6.92-7.00 (m, 1H), 3.82 (bs, 1H), 3.44 (d, *J* = 2.8 Hz, 2H) 2.33-2.55 (m, 4H), 2.07 (dd, *J* = 7.2, 3.3 Hz, 4H), 1.72-1.82 (m, 2H), 1.18-1.54 (m, 5H), 0.95 and 0.94 (two s, 9H, 1:1 ratio), 0.87 (dd, *J* = 6.4, 2.8 Hz, 12H), 0.80 and 0.74 (two t, *J* = 7.2 Hz, *J* = 7.2 Hz, 3H, 1:1 ratio), 0.65-0.70 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.3, 149.1, 141.1, 137.6, 135.9, 128.7, 127.9, 122.7, 119.4, 63.3, 59.5, 37.7, 37.3, 35.6, 35.4, 32.6, 28.4, 28.0, 27.3, 26.3, 25.7, 23.7, 20.9, 16.9, 14.1, 10.5.

GC/MS: m/z (I, %): 480.0 (M^+, 1.3%), 437.0 (M^+-^{i}Pr, 100%), 423.0 (M^+-^{t}Bu, 29%), 352.0 (38%), 148.0 (60%).



Supplementary Figure S9. Synthesis of compound **2q**.

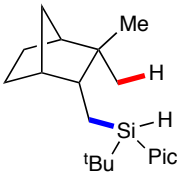
2-((*tert*-Butyl(2-(1-phenylcyclopropyl)ethyl)silyl)methyl)pyridine (2q): An oven dried 5 mL Wheaton V-vial, containing a stirring bar, was charged with (1-vinylcyclopropyl)benzene[38] (2 mmol), 1 mol % Wilkinson's Catalyst $Rh(PPh_3)_3Cl$ under N_2 atmosphere (glovebox). 1 Equiv. of ^{t}BuSiH$_3$[39] in THF (1M) was added, and the reaction was stirred at RT until full consumption of starting alkene. The obtained intermediate was transferred to the 50 mL flask via syringe and the solution of 1.2 equiv of picolyl lithium (2.5 mmol of picoline and 2.4 mmol of PhLi at 35°C in

Et_2O) in Et_2O was added at RT. The reaction was stirred for 12h and then quenched with 5 ml of water, extracted (Et_2O) and washed with water, dried over $MgSO_4$, concentrated and purified by flash column chromatography (hexanes/ethyl acetate 10:1) to afford **2q** as a light yellow oil in 49% yield. R_f (hexanes/EtOAc = 4/1): 0.75.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.40 (d, *J* = 5.1 Hz, 1H), 7.44 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13-7.22 (m, 5H), 6.91-6.99 (m, 2H), 3.63 (br. s, 1H), 2.46 (dd, *J* = 13.5, 2.9 Hz, 1H), 2.32 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.48-1.56 (m, 1H), 1.32-1.40 (m, 1H), 0.90 (s, 9H), 0.71-0.75 (m, 2H), 0.51-0.63 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.1, 149.1, 144.9, 135.9, 129.0, 128.0, 125.7, 122.6, 119.4, 35.5, 27.9, 29.3, 25.7, 23.0, 17.0, 13.0, 6.4.

GC/MS: m/z (I, %): 322.0 (M^+-H, 3.8%), 266.0 (M^+-^{t}Bu, 94%), 178.0 (97%), 120.0 (100%).



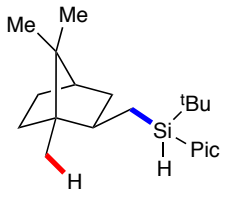
2r

2-((*tert*-Butyl((3,3-dimethylbicyclo[2.2.1]heptan-2-yl)methyl)silyl)methyl)pyridine (2r) was obtained from commercially available camphene according to the **Method I** in 64% yield as a pale yellow oil; 1.5:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.40-8.44 (m, 1H), 7.44-7.52 (m, 1H), 7.03-7.08 (m, 1H), 6.93-6.99 (m, 1H), 3.73 (br. s, 1H), 2.47-2.53 (m, 1H), 2.31-2.38 (m, 3H), 1.95-1.99 and 1.87-1.91 (two multiplets, 1H, 1:1.5 ratio), 1.62-1.65 (m, 1H), 0.97-1.51 (m, 6H), 0.94 and 0.93 (two s, 9H, 1:1.5 ratio), 0.81 and 0.73 (two s, 3H, 2:3 ratio), 0.72 and 0.64 (two s, 3H, 1:1.5 ratio), 0.44-0.62 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.4, 149.1, 135.9, 122.7, 119.4, 49.2, 48.9, 46.8, 46.1, 43.5, 42.3, 37.3, 36.8, 32.2, 31.9, 27.3, 24.7, 23.8, 23.5, 21.8, 21.7, 19.6, 19.4, 17.2, 16.9, 6.16, 5.74.

GC/MS: m/z (I, %): 314.0 (M^+-H, 2%), 258.0 (M^+-^{t}Bu, 100%), 178.0 (48%), 122.0 (57%).



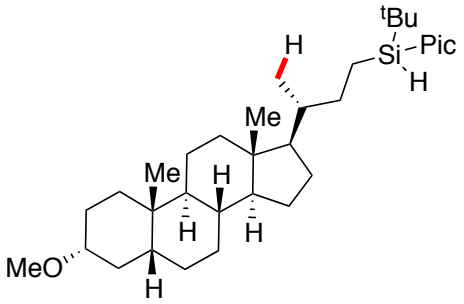
2s

2-((*tert*-Butyl((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)methyl)silyl)methyl)pyridine (2s) was obtained from compound **1i** according to the **Method I** in 57% yield as a colorless oil; mixture of isomers. R_f (hexanes/EtOAc = 4/1): 0.8.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.45 (m, 1H), 7.49-7.52 (m, 1H), 7.05-7.10 (m, 1H), 6.96-7.01 (m, 1H), 2.48-2.55 (m, 1H), 2.31-2.40 (m, 1H), 0.45-1.62 (m, 29H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.3, 149.1, 149.0, 135.9, 135.8, 122.8, 119.4, 47.7, 47.3, 47.1, 45.5, 45.4, 45.3, 44.1, 43.0, 40.0, 39.5, 39.3, 38.6, 38.5, 38.2, 37.8, 28.6, 28.4, 27.6, 27.4, 27.3, 27.2, 24.0, 23.9, 23.4, 21.0, 20.6, 20.4, 20.0, 18.41, 18.38, 17.2, 16.6, 14.5, 14.4, 13.8, 13.7, 13.2, 12.9, 10.3, 10.2.

GC/MS: m/z (I, %): 328.3([M-H]$^+$, 1.0%), 272.2 ([M-^{t}Bu]$^+$, 100.0%), 324.2 (73.8%), 178.1 (66.9%), 136.1 (22.9%), 122.0 (66.0%), 120.0 (47.1%).



2t

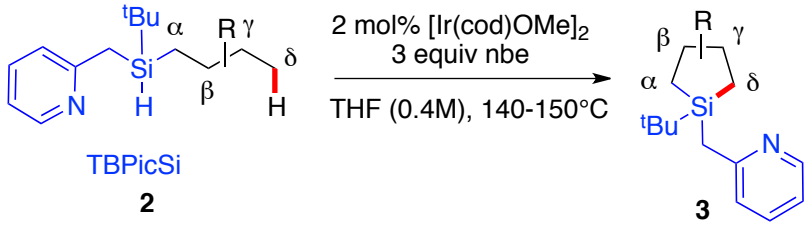
2-((*tert*-Butyl((*R*)-3-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)butyl)silyl)methyl)pyridine (2t) was obtained from compound **1t** according to the **Method I** in 38% yield as a colorless oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.85.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.44 (m, 1H), 7.51 (td, *J* = 7.6, 1.8 Hz, 1H), 7.07 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.98-7.01 (m, 1H), 3.66-3.69 (m, 1H), 3.35 (two s, 3H, 1:1 ratio), 3.13-3.19 (m, 1H), 2.49-2.53 (m, 1H), 2.36-2.41 (m, 1H), 1.52-1.93 (m, 8H), 1.19-1.38 (m, 11H), 1.00-1.11 (m, 5H), 0.95 and 0.96 (two s, 9H), 0.91 (s, 3H), 0.81 (two d, *J* = 6.7 Hz, 3H, 1:1 ratio), 0.64-0.72 (m, 2H), 0.59-0.60 (two s, 3H, 1:1 ratio), 0.37-0.45 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.3, 149.0, 136.0, 122.7, 119.4, 80.4, 56.4, 55.5, 42.6, 42.0, 40.3, 40.1, 38.1, 38.0, 35.8, 35.3, 34.9, 32.8, 30.8, 30.7, 28.14, 28.09, 27.44, 27.41, 27.3, 26.8, 26.4, 25.8, 24.2, 23.4, 23.3, 23.2, 20.8, 17.83, 17.81, 17.1, 17.0, 12.1, 5.0, 4.9.

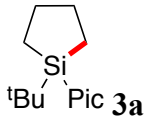
GC/MS: m/z (I, %): 522.5 ([M-H]$^+$, 0.8%), 508.3 ([M-Me]$^+$, 0.9%), 466.4 ([M-^{t}Bu]$^+$, 100.0%), 178.1 (32.0%), 122.0 (43.1%), 120.0 (21.2%).

Optimized Procedure for the Ir-Catalyzed C−H Silylation Reaction:



Supplementary Figure S10. Ir-catalyzed *δ*-C−H dehydrogenative silylation reaction.

1mL Wheaton V-vial was charged with 0.3 mmol of starting material, $[Ir(cod)OMe]_2$ or $[Ir(cod)Cl]_2$ (4.0 mg, 2 mol%), 2-norbornene (84.6 mg, 3 equiv), and THF (0.75 mL, 0.4M). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (140-150°C) aluminum block. The reaction mixture was stirred until full consumption of starting material. After completion of the reaction (as determined by GC-MS analysis), Wheaton V-vial containing cyclic product was cooled down. The product was purified by flash silica gel column chromatography (hexanes/ethyl acetate = 10:1).



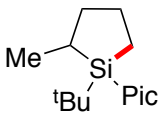
3a

2-((1-*tert*-Butylsilolan-1-yl)methyl)pyridine (3a) was obtained from compound **2a** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 1h. Product was isolated in 84% yield (average of two runs) as a yellow oil. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.43 (m, 1H), 7.49 (td, *J* = 7.6, 1.8 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.96 (ddd, *J* = 7.3, 5.0, 0.7 Hz, 1H), 2.46 (s, 2H), 1.37-1.40 (m, 2H), 1.09-1.13 (m, 2H), 0.96 (s, 9H), 0.56-0.59 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 149.0, 135.8, 122.5, 119.1, 27.3, 26.9, 24.5, 16.8, 7.7.

HRMS (EI) calcd. for $C_{14}H_{23}NSi$ $[M]^+$: 233.15998. Found: 233.15925.



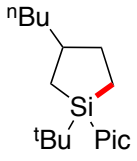
3b

2-((1-*tert*-Butyl-2-methylsilolan-1-yl)methyl)pyridine (3b) was obtained from compound **2b** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 1h. Product was isolated in 74% yield as a yellow oil; 1.3:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.43 (d, *J* = 4.8 Hz, 1H), 7.45-7.49 (m, 1H), 6.94-7.05 (m, 2H), 2.46-2.47 (m, 2H), 1.60-1.80 (m, 2H), 1.19-1.29 (m, 1H), 1.18 and 1.14 (two d, *J* = 7.3 Hz, 3H, 1.3:1 ratio), 0.94-1.07 (m, 2H), 1.0 and 0.91 (two s, 9H), 0.57-0.76 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.8, 161.5, 149.0, 148.9, 135.7, 135.6, 122.9, 122.5, 119.2, 119.1, 37.9, 37.4, 27.2, 26.9, 25.4, 24.7, 24.6, 22.6, 19.9, 18.2, 18.0, 17.4, 15.8, 15.3, 8.6, 8.3.

HRMS (EI) calcd. for $C_{15}H_{25}NSi$ $[M]^+$: 247.17563. Found: 247.17530.



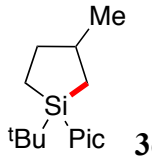
3c

2-((1-*tert*-Butyl-3-butylsilolan-1-yl)methyl)pyridine (3c) was obtained from compound **2c** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 1h. Product was isolated in 100% yield (average of two runs) as a brown oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.44 (m, 1H), 7.49 (td, *J* = 7.3, 1.8 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.96-6.98 (m, 1H), 2.42-2.48 (m, 2H), 1.66-1.70 (m, 1H), 1.36-1.37 (m, 0.5 H), 1.06-1.26 (m, 6H), 0.95 (s, 9H), 0.71-92 (m, 6H), 0.44-0.51 (m, 1H), 0.23-0.26 (m, 0.5H), 0.00-0.10 (dd, *J* = 14.9, 11.4, 0.5H), 0.02 (dd, *J* = 14.5, 11.7, 0.5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 148.9, 135.8, 122.54, 122.51, 119.12, 119.08, 41.3, 40.6, 38.0, 37.9, 34.2, 33.4, 30.3, 30.2, 26.8, 24.8, 24.7, 22.9, 22.6, 16.9, 16.8, 15.0, 14.3, 14.2, 14.1, 7.9, 7.5.

HRMS (EI) calcd. for $C_{18}H_{31}SiN$ $[M]^+$: 289.22258. Found: 289.22199.



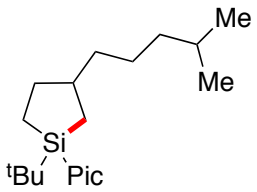
3d

2-((1-*tert*-Butyl-3-methylsilolan-1-yl)methyl)pyridine (3d) was obtained from compound **2d** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 1h. Product was isolated in 73% yield as a yellow oil. R_f (hexanes/EtOAc = 4/1): 0.65.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.44 (m, 1H), 7.49 (td, *J* = 7.7, 1.8 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.96-6.98 (m, 1H), 2.47 (d, *J* = 12.8 Hz, 1H), 2.43 (d, *J* = 12.8 Hz, 1H), 1.63-1.69 (m, 1H), 0.95 (s, 9H), 0.90 (d, *J* = 5.5 Hz, 3H), 0.74-0.86 (m, 3H), 0.49-0.56 (m, 1H), 0.11 (dd, *J* = 14.5, 10.8).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.3, 149.0, 135.8, 122.5, 119.1, 36.1, 35.5, 26.8, 24.8, 23.5, 17.5, 16.8, 8.1.

HRMS (EI) calcd. for $C_{15}H_{25}NSi$ $[M-H]^+$: 246.16780. Found: 246.16738.



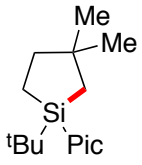
3e

2-((1-*tert*-Butyl-3-(4-methylpentyl)silolan-1-yl)methyl)pyridine (3e) was obtained from compound **2e** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 3h. Product was isolated in 46% (average of two runs) yield as a yellow oil; 3:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.45 (m, 1H), 7.47-7.50 (m, 1H), 6.95-7.02 (m, 2H), 2.42-2.49 (m, 2H), 1.70-1.73 (m, 1H), 1.43-1.50 (m, 1H), 1.00-1.25 (m, 6H), 0.95 (s, 9H), 0.83-0.92 (m, 6.75H), 0.73-0.79 (m, 3H), 0.45-0.54 (m, 1H), 0.21-0.29 (m, 0.25H), 0.12 and 0.02 (two dd, J = 14.9, 11.4 and J = 14.1, 11.4 Hz, 1H, 3:1 ratio).

^{13}C NMR (126 MHz, $CDCl_3$, major diastereomer) δ ppm 161.3, 149.0, 135.7, 122.5, 119.1, 40.6, 38.9, 38.5, 34.2, 27.9, 26.8, 25.7, 24.8, 22.7, 22.6, 16.8, 14.9, 7.5.

HRMS (TOF MS ES+) calcd. for $C_{20}H_{36}NSi$ $[M+H]^+$: 318.2617. Found: 318.2620.



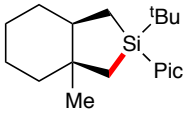
3f

2-((1-*tert*-Butyl-3,3-dimethylsilolan-1-yl)methyl)pyridine (3f) was obtained from compound **2f** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 2h. Product was isolated in 61% yield (average of two runs) as a yellow oil. R_f (hexanes/EtOAc = 4/1): 0.65.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.44 (m, 1H), 7.49 (td, J = 7.7, 1.8 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 6.96-6.98 (m, 1H), 2.50 (d, J = 12.8 Hz, 1H), 2.47 (d, J = 12.8 Hz, 1H), 1.20-1.26 (m, 1H), 0.91 -1.01(m, 1H), 0.96 (s, 9H), 0.92 (s, 3H), 0.68-0.71 (m, 2H), 0.46-0.60 (m, 2H), 0.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.3, 149.0, 135.7, 122.8, 119.2, 41.0, 38.5, 31.5, 29.8, 27.0, 25.1, 22.1, 16.9, 7.1.

HRMS (EI) calcd. for $C_{16}H_{27}NSi$ $[M]^+$: 261.19128. Found: 261.19189.



3g

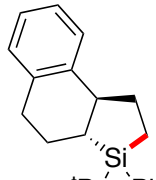
2-((2-*tert*-Butyl-3a-methyloctahydro-1*H*-benzo[*c*]silol-2-yl)methyl)pyridine (3g) was obtained from compound **2g** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$

as catalyst. The reaction was carried out at 140°C for 1h. Product was isolated in 93% yield as a yellow oil; Mixture of isomers. R_f (hexanes/EtOAc = 4/1): 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.43 (m, 1H), 7.47-7.49 (m, 1H), 7.01-7.05 (m, 1H), 6.93-6.97 (m, 1H), 2.41-2.53 (m, 2H), 0.21-1.63 (m, 25H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.6, 161.5, 149.1, 149.0, 148.9, 148.8, 135.8, 135.7, 123.0, 122.9, 122.6, 119.3, 119.2, 119.1, 48.0, 46.3, 44.9, 43.6, 43.5, 40.1, 39.8, 39.6, 39.5, 35.4, 34.1, 30.5, 30.2, 28.5, 27.9, 27.7, 27.6, 27.0, 26.6, 26.0, 25.8, 25.6, 25.5, 25.3, 25.1, 24.2, 22.8, 22.6, 22.5, 20.4, 19.8, 19.0,17.9, 17.1, 17.0, 16.7, 13.7, 12.3, 11.8.

HRMS (TOF MS ES+) calcd. for $C_{19}H_{32}NSi$ $[M+H]^+$: 302.2304. Found: 302.2307.



3h

2-(((3a*R*(*S*),9b*R*(*S*))-3-*tert*-Butyl-2,3,3a,4,5,9b-hexahydro-1*H*-naphtho[2,1-*b*]silol-3-yl)methyl)pyridine (3h) was obtained from compound **2h** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 4h. Product was isolated in 77% yield (average of two runs) as a brown oil; 2.5:1 ratio of diastereomers.[40]

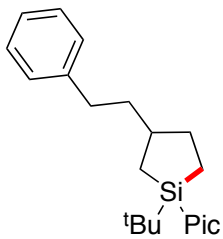
Major diastereomer, R_f (hexanes/EtOAc = 4/1): 0.65. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.43-8.45 (m, 1H), 7.49 (td, *J* = 7.6, 1.8 Hz, 1H), 7.08-7.17 (m, 5H), 6.95-6.98 (m, 1H), 2.84-2.90 (m, 2H), 2.61 (d, *J* = 13.2Hz, 1H), 2.55 (m, 1H), 2.54 (d, *J* = 13.2Hz, 1H), 2.11-2.22 (m, 2H), 1.99-2.03 (m, 1H), 1.18-1.31 (m, 1H), 0.96 (s, 9H), 0.82-0.92 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.3, 149.1, 142.9, 137.4, 135.9, 128.8, 125.5, 125.2, 125.0, 122.9, 119.4, 45.5, 30.9, 29.6, 27.8, 26.9, 24.0, 22.8, 17.4, 6.3.

Minor diastereomer, R_f (hexanes/EtOAc = 4/1): 0.55. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.39-8.40 (m, 1H), 7.46 (td, *J* = 7.6, 1.8 Hz, 1H), 7.14-7.16 (m, 1H), 7.06-7.10 (m, 3H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.92-6.95 (m, 1H), 2.82-2.86 (m, 2H), 2.50-2.61 (m, 4H), 2.25-2.29 (m, 1H), 1.91-1.96 (m, 1H), 1.05 (s, 9H), 0.89-0.94 (m, 1H), 0.72-0.82 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.1, 149.1, 142.1, 137.2, 135.9, 129.1, 125.5, 125.4, 125.3, 122.5, 119.3, 46.1, 31.6, 29.4, 29.3, 27.2, 24.3, 24.1, 18.4, 6.9.

HRMS (TOF MS ES+) calcd. for $C_{22}H_{30}NSi$ $[M+H]^+$: 336.2148. Found: 336.2154.



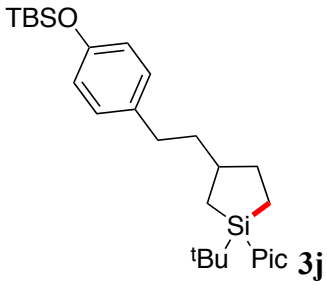
3i

2-((1-*tert*-Butyl-3-phenethylsilolan-1-yl)methyl)pyridine (3i) was obtained from compound **2i** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 2h. Product was isolated in 64% yield as a red oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.5.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.44-8.45 (m, 1H), 7.43-7.51 (m, 1H), 7.24-7.26 (m, 2H), 7.10-7.18 (m, 3H), 6.93-7.03 (m, 2H), 2.43-2.62 (m, 4H), 1.70-1.78 (m, 1H), 1.27-1.66 (m, 2.5H), 0.97 and 0.98 (two s, 9H), 0.74-0.93 (m, 3H), 0.47-0.54 (m, 1H), 0.30-0.34 (0.5H), 0.22 and 0.13 (dd, *J* = 14.7, 11.0 and 14.3, 11.2, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.1, 149.0, 143.1, 143.0, 135.8, 128.3, 128.2, 125.43, 125.39, 122.6, 122.5, 119.2, 119.1, 40.9, 40.4, 40.2, 34.4, 34.1, 33.4, 27.3, 26.8, 26.6, 24.7, 16.9, 14.9, 14.2, 7.9, 7.4.

HRMS (EI+) calcd. for $C_{22}H_{31}NSi$ $[M]^+$: 337.22258. Found: 337.22211.



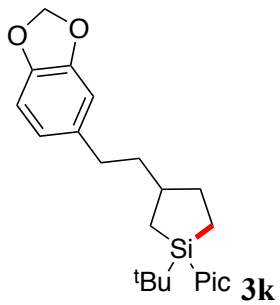
3j

2-((1-*tert*-Butyl-3-(4-(*tert*-butyldimethylsilyloxy)phenethyl)silolan-1-yl)methyl)pyridine (3j) was obtained from compound **2j** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 3h. Product was isolated in 67% yield as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.41-8.44 (m, 1H), 7.46-7.49 (m, 1H), 6.94-7.03 (m, 4H), 6.71-6.73 (m, 2H), 2.42-2.51 (m, 4H), 1.27-1.75 (m, 4H), 0.95, 0.97, 0.98 and 0.99 (four s, 18H), 0.74-0.91 (m, 3H), 0.46-0.54 (m, 1H), 0.18 and 0.19 (two s. 6H), 0.06-0.34 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 153.3, 149.0, 135.8, 135.7, 129.0, 122.6, 122.5, 119.7, 119.2, 119.1, 40.8, 40.4, 40.3, 40.2, 34.1, 33.5, 33.4, 26.8, 25.7, 24.8, 24.7, 18.2, 16.9, 14.9, 14.2, 7.8, 7.5, 4.5.

HRMS (TOF MS ES+) calcd. for $C_{28}H_{46}NOSi_2$ $[M+H]^+$: 468.3118. Found: 468.3121.



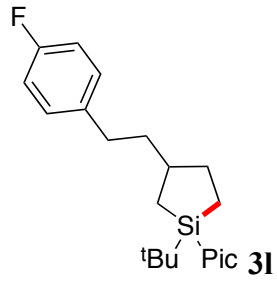
3k

2-((3-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-1-*tert*-butylsilolan-1-yl)methyl)pyridine (3k) was obtained from compound **2k** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 3h. Product was isolated in 75% yield as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.5.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.41-8.44 (m, 1H), 7.45-7.51 (m, 1H), 6.95-7.03 (m, 2H), 6.69-6.71 (m, 1H), 6.54-6.62 (m, 2H), 5.90 and 5.92 (two s, 2H), 2.38-2.50 (m, 4H), 1.68-1.75 (m, 1H), 1.24-1.45 (m, 2.5H), 0.96 and 0.97 (two s. 9H), 0.73-0.85 (m, 2H), 0.46-0.53 (m, 1H), 0.25-0.34 (m, 0.5H), 0.18 and 0.10 (dd, *J* = 14.7, 10.8 and 14.5, 11.6, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.1, 149.0, 147.4, 147.3, 145.3, 137.0, 136.9, 135.79, 135.76, 122.6, 122.5, 120.9, 120.8, 119.2, 119.1, 108.8, 108.7, 108.0, 107.9, 100.6, 40.8, 40.40, 40.39, 40.1, 34.1, 34.0, 33.3, 26.8, 24.69, 24.66, 16.88, 16.85, 14.9, 14.1, 7.8, 7.4.

HRMS (EI+) calcd. for $C_{23}H_{31}NO_2Si$ $[M]^+$: 381.21241. Found: 381.21317.



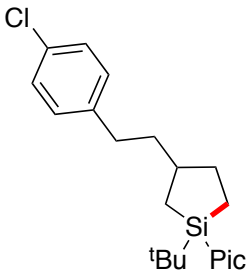
3l

2-((1-*tert*-Butyl-3-(4-fluorophenethyl)silolan-1-yl)methyl)pyridine (3l) was obtained from compound **2l** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 2h. Product was isolated in 53% yield as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40-8.44 (m, 1H), 7.44-7.49 (m, 1H), 7.01-7.08 (m, 3H), 6.91-6.98 (m, 3H), 2.39-2.60 (m, 4H), 1.69-1.77 (m, 1H), 1.24-1.63 (m, 3H), 0.96 and 0.97 (two s. 9H), 0.73-0.93 (m, 2.5H), 0.47-0.54 (m, 1H), 0.27-0.35 (m, 0.5H), 0.20 and 0.11 (dd, *J* = 14.9, 11.0 and 14.3, 11.6, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.13, 161.10, 161.03 (d, *J* =243.2 Hz), 161.01 (d, *J* =242.3 Hz), 149.0, 138.62, 138.59, 138.50, 138.48, 135.8, 135.7, 129.5 (d, *J* = 8.3 Hz), 122.6, 122.5, 119.2, 119.1, 114.8 (d, *J* = 21.3 Hz), 40.8, 40.20, 40.17, 40.1, 39.8, 34.1, 33.54, 33.47, 33.3, 26.8, 24.66, 24.65, 16.9, 16.8, 14.9, 14.1, 7.8, 7.4.

HRMS (TOF MS ES+) calcd. for $C_{22}H_{31}NSiF$ $[M+H]^+$: 356.2210. Found: 356.2205.



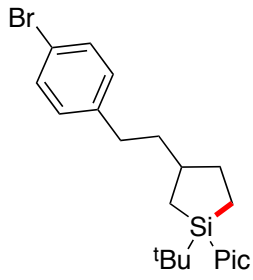
3m

2-((1-*tert*-Butyl-3-(4-chlorophenethyl)silolan-1-yl)methyl)pyridine (3m) was obtained from compound **2m** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 3h. Product was isolated in 82% yield as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.39-8.44 (m, 1H), 7.42-7.51 (m, 1H), 7.19-7.22 (m, 2H), 6.93-7.07 (m, 4H), 2.41-2.54 (m, 4H), 1.68-1.78 (m, 1H), 1.24-1.62 (m, 2.5H), 0.96 and 0.97 (two s. 9H), 0.72-0.93 (m, 2H), 0.46-0.53 (m, 1H), 0.27-0.35 (m, 0.5H), 0.20 and 0.11 (dd, *J* = 14.7, 11.0 and 14.3, 11.6, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.1, 161.0, 149.0, 141.5, 141.3, 135.8, 135.7, 131.1, 129.6, 128.2, 122.6, 122.5, 119.2, 119.1, 40.8, 40.1, 40.0, 39.8, 34.1, 33.7, 33.6, 33.3, 26.8, 24.6, 16.9, 14.8, 14.1, 7.8, 7.4.

HRMS (EI+) calcd. for $C_{22}H_{30}NClSi$ $[M]^+$: 371.18360. Found: 371.18374.



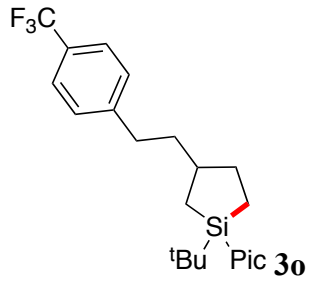
3n

2-((3-(4-Bromophenethyl)-1-*tert*-butylsilolan-1-yl)methyl)pyridine (3n) was obtained from compound **2n** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 2h. Product was isolated in 87% yield as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.38-8.44 (m, 1H), 7.42-7.51 (m, 1H), 7.34-7.37 (m, 2H), 6.94-7.03 (m, 4H), 2.38-2.56 (m, 4H), 1.68-1.84 (m, 1H), 1.24-1.61 (m, 2.5H), 0.96 and 0.97 (two s. 9H), 0.71-0.93 (m, 2H), 0.46-0.53 (m, 1H), 0.27-0.35 (m, 0.5H), 0.20 and 0.10 (dd, *J* = 14.9, 10.8 and 14.3, 11.7, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.1, 161.0, 149.0, 142.0, 141.8, 135.8, 135.7, 131.2, 130.0, 122.6, 122.5, 119.23, 119.15, 119.10, 119.05, 40.8, 40.0, 39.9, 39.8, 34.1, 33.8, 33.6, 33.3, 26.8, 24.6, 16.9, 14.8, 14.1, 7.8, 7.4.

HRMS (TOF MS ES+) calcd. for $C_{22}H_{31}NSiBr$ $[M+H]^+$: 416.1409. Found: 416.1411.



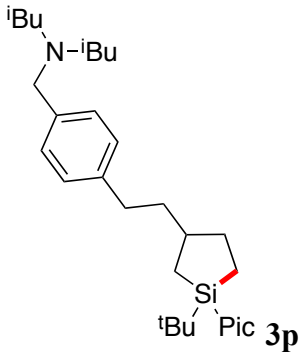
3o

2-((1-*tert*-Butyl-3-(4-(trifluoromethyl)phenethyl)silolan-1-yl)methyl)pyridine (3o) was obtained from compound **2o** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 2h. Product was isolated in 95% yield (average of two runs) as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.6.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.37-8.44 (m, 1H), 7.42-7.51 (m, 3H), 7.19-7.23 (m, 2H), 6.92-7.03 (m, 2H), 2.41-2.67 (m, 4H), 1.69-1.81 (m, 1H), 1.27-1.66 (m, 3.5H), 0.96 and 0.97 (two s. 9H), 0.74-0.93 (m, 2H), 0.48-0.55 (m, 1H), 0.28-0.36 (m, 0.5H), 0.22 and 0.11 (dd, *J* = 14.7, 10.6 and 14.3, 11.7, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.1, 161.0, 149.02, 148.98, 147.2, 147.0, 136.0, 135.8, 128.6, 126.6 (q, *J* = 277.4 Hz), 125.1, 122.6, 122.5, 119.3, 119.2, 40.8, 40.0, 39.8, 39.6, 34.3, 34.1, 34.0, 33.3, 26.8, 24.6, 16.9, 16.8, 14.8, 14.1, 7.8, 7.4.

HRMS (TOF MS ES+) calcd. for $C_{23}H_{31}NSiF_3$ $[M+H]^+$: 406.2178. Found: 406.2172.



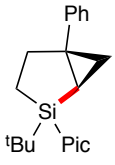
3p

***N*-(4-(2-((1-*tert*-Butyl-1-(pyridin-2-ylmethyl)silolan-3-yl)ethyl)benzyl)-*N*-isobutyl-2-methylpropan-1-amine (3p)** was obtained from compound **2p** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 1h. Product was isolated in 57% yield as a yellow oil; 1:1 mixture of diastereomers. R_f (hexanes/EtOAc = 4/1): 0.4.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42-8.45 (m, 1H), 7.47-7.51 (m, 1H), 7.20-7.22 (m, 2H), 6.95-7.05 (m, 4H), 3.43 and 3.45 (two s, 2H), 2.43-2.58 (m, 4H), 2.06-2.09 (m, 4H), 1.72-1.80 (m, 3H), 1.27-1.64 (m, 3H), 0.96 and 0.97 (two s. 9H), 0.86-0.88 (m, 12H), 0.74-0.81 (m, 1.5H), 0.46-0.53 (m, 1H), 0.26-0.35 (m, 0.5H), 0.20 and 0.12 (dd, *J* = 14.7, 11.0 and 14.3, 11.2, 1:1 ratio, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.20, 161.18, 149.0, 141.2, 137.6, 137.5, 135.8, 128.7, 127.8, 122.6, 122.5, 119.2, 119.1, 83.3, 59.5, 40.9, 40.6, 40.3, 40.1, 34.2, 34.0, 33.4, 26.8, 26.3, 24.8, 24.7, 20.9, 16.9, 14.9, 14.2, 7.9, 7.5.

HRMS (TOF MS ES+) calcd. for $C_{31}H_{51}N_2Si$ $[M+H]^+$: 479.3822. Found: 479.3816.



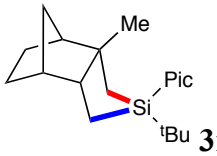
3q

2-((2-*tert*-Butyl-5-phenyl-2-silabicyclo[3.1.0]hexan-2-yl)methyl)pyridine (3q) was obtained from compound **2q** according to the general procedure by using 2 mol% $[Ir(cod)OMe]_2$ as catalyst. The reaction was carried out at 140°C for 3h. Product was isolated in 87% yield (average of two runs) as a yellow oil. R_f (hexanes/EtOAc = 4/1): 0.55.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.45-8.47 (m, 1H), 7.51 (td, *J* = 7.7, 1.8 Hz, 1H), 7.20-7.27 (m, 4H), 7.12-7.16 (m, 2H), 6.99-7.02 (m, 1H), 2.64 (d, *J* = 13.0 Hz, 1H), 2.52 (d, *J* = 13.2 Hz, 1H), 2.25 (dd, *J* = 13.1, 9.3 Hz, 1H), 2.06 (td, *J* = 12.2, 9.1 Hz, 1H), 1.02 (s, 9H), 0.79-0.91 (m, 2H), 0.41-0.45 (m, 2H), 0.10-0.12 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.2, 148.9, 146.5, 135.7, 128.1, 126.6, 125.4, 122.9, 119.3, 32.9, 31.8, 27.2, 24.2, 17.3, 15.4, 8.7, 4.2.

HRMS (TOF MS ES+) calcd. for $C_{21}H_{28}NSi$ $[M+H]^+$: 322.1991. Found: 322.1990.



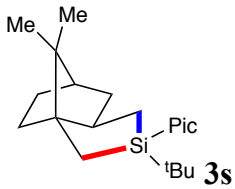
3r

2-[(2-*tert*-Butyl-3a-methyloctahydro-1*H*-4,7-methano-2-benzosilol-2-yl)methyl]pyridine (3r) was obtained from compound **2r** according to the general procedure by using 5 mol% $[Ir(cod)Cl]_2$ as catalyst. The reaction was carried out at 150°C for 20h. Product was isolated in 48% yield (average of two runs) as a red oil; mixture of isomers. R_f (hexanes/EtOAc = 4/1): 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.43-8.45 (m, 1H), 7.47-7.52 (m, 1H), 7.07-7.09 (m, 1H), 6.96-7.00 (m, 1H), 2.53-2.55 (m, 2H), 0.68-2.02 (m, 24H), 0.23-0.27 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.72, 161.70, 149.2, 149.1, 135.9, 135.8, 122.9, 122.7, 119.4, 119.3, 53.2, 52.1, 50.0, 49.8, 48.5, 47.6, 44.0, 43.9, 39.6, 39.5, 33.5, 33.1, 27.6, 27.3, 27.2, 26.3, 25.5, 24.2, 24.0, 20.9, 20.8, 18.6, 17.1, 15.9, 15.2, 7.7, 7.6.

HRMS (EI+) calcd. for $C_{20}H_{31}SiN$ $[M]^+$: 313.22258. Found: 313.22233.



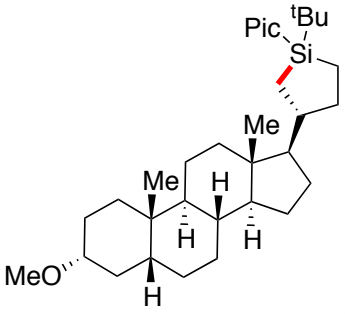
3s

2-[(2-*tert*-butyl-8,8-dimethyloctahydro-3a,6-methano-2-benzosilol-2-yl)methyl]pyridine (3s) was obtained from compound **2s** according to the general procedure by using 5 mol % $[Ir(cod)Cl]_2$ as catalyst. The reaction was carried out at 140°C for 3h. Product was isolated in 40% yield (average of two runs) as a brown oil; mixture of isomers. R_f (hexanes/EtOAc = 4/1): 0.7.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.41-8.44 (m, 1H), 7.47-7.51 (m, 1H), 7.01-7.03 (m, 1H), 6.96-6.99 (m, 1H), 2.42-2.54 (m, 2H), 0.38-1.64 (m, 26H), 0.22 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 161.6, 161.4, 149.0, 135.8, 123.0, 122.6, 119.3, 119.2, 55.7, 54.8, 49.9, 48.4, 47.8, 47.3, 46.6, 40.6, 39.1, 38.9, 27.6, 27.4, 27.3, 26.9, 25.9, 25.2, 21.6, 20.7, 20.1, 18.4, 18.2, 18.1, 17.1, 6.8, 6.3.

HRMS (EI+) calcd. for $C_{21}H_{33}SiN$ $[M]^+$: 327.23823. Found: 327.23864.



3t

2-(((1*R*,3*R*)-1-*tert*-Butyl-3-((3*R*,5*R*,8*R*,9*S*,10*S*,13*S*,14*S*,17*R*)-3-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)silolan-1-yl)methyl)pyridine (3t) was obtained from compound **2t** according to the general procedure by using 5 mol% $[Ir(cod)Cl]_2$ as catalyst. The reaction was carried out at 140°C for 12h. Product was isolated in 48% yield (average of two runs) as a yellow oil; 3:1 mixture of diastereomers (*40*). R_f (hexanes/EtOAc = 4/1): 0.75.

^{1}H NMR (500 MHz, $CDCl_3$, major diastereomer) δ ppm 8.42 (d, *J* = 4.8 Hz, 1H), 7.48 (td, *J* = 7.5, 1.7 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.93-6.96 (m, 1H), 3.34 (s, 3H), 3.12-3.18 (m, 1H), 2.46 (d, *J* = 12.7 Hz, 1H), 2.40 (d, *J* = 12.7 Hz, 1H), 1.96-1.98 (m, 1H), 1.01-1.84 (m, 19H), 0.95 (s, 9H), 0.89-0.94 (m, 7H), 0.62-0.73 (m, 3H), 0.40-0.52 (m, 2H), 0.36 (s, 3H), 0.05 (dd, *J* = 14.3,12.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, major diastereomer) δ ppm 161.3, 149.1, 135.8, 122.5, 119.0, 80.4, 59.0, 56.0, 55.5, 43.5, 42.8, 42.1, 40.4, 40.1, 35.8, 35.3, 34.9, 33.9, 32.7, 28.5, 27.3, 26.8, 26.7, 26.4, 24.6, 24.4, 23.4, 20.6, 16.8, 14.8, 12.2, 6.4.

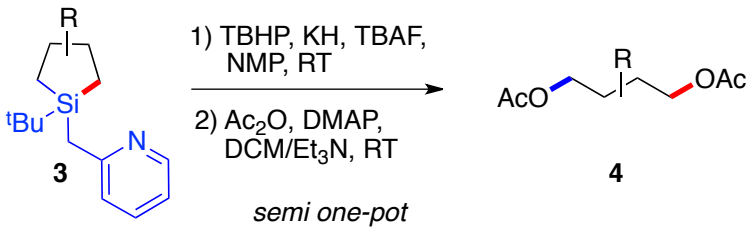
^{1}H NMR (500 MHz, $CDCl_3$, minor diastereomer) δ ppm 8.44 (m, 1H), 7.51 (td, *J* = 7.7, 1.8 Hz, 1H), 6.98-7.01 (m, 2H), 3.36 (s, 3H), 3.13-3.20 (m, 1H), 2.46 (d, *J* = 12.8 Hz, 1H), 2.42 (d, *J* =

12.8 Hz, 1H), 2.00-2.02 (m, 1H), 1.01-1.84 (m, 19H), 0.95 (s, 9H), 0.89-0.94 (m, 6H), 0.61-0.84 (m, 4H), 0.58 (s, 3H), 0.34-0.38 (m, 1H), 0.14 (dd, J = 14.7,11.9 Hz, 1H), 0.01-0.07 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, minor diastereomer) δ ppm 161.2, 149.0, 135.8, 122.5, 119.2, 80.4, 59.2, 56.1, 55.5, 44.0, 42.9, 42.1, 40.4, 40.1, 35.8, 35.3, 34.9, 33.2, 32.8, 28.5, 27.3, 26.8, 26.7, 26.4, 24.6, 24.4, 23.4, 20.7, 16.8, 14.2, 12.4, 7.1.

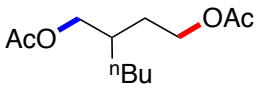
HRMS (TOF MS ES+) calcd. for $C_{34}H_{56}NOSi$ $[M+H]^+$: 522.4131. Found: 522.4127.

Oxidation of Silacycles 3 into Diols 4



Supplementary Figure S11. Oxidation of silacycles **3** into diols **4**.

Oxidation of the C-Si bond was performed similar to the Woerpel's procedure (Supplementary Figure S11). To an ice-cooled (0°C) stirred solution of KH (96 mg, 2.4 mmol, 12 equiv) in 1.0 mL of NMP was added *tert*-butyl hydroperoxide (0.36 mL, 5.0 ~ 6.0 M in decane stored over molecular sieves) dropwise. The mixture was allowed to warm up to RT and kept for 10 min, then was added a solution of silolane (0.2 mmol) in 1.0 mL of NMP. After stirring at RT for 10 min 1.0 mL TBAF (1. mmol, 1.0 M solution in THF) was added. The mixture was stirred overnight at RT and then cooled to 0°C. 1.0 g of $Na_2S_2O_3 \cdot 5H_2O$ and 5 mL DCM was added. The mixture was stirred at RT for 30 min and filtered. DCM was evaporated and to the crude reaction mixture was added 1.2 mL DCM and 0.3 mL triethylamine. To the resulting solution was added DMAP (2.4 mg, 0.02 mmol, 0.1 equiv) and Ac_2O (0.4 mL, 0.4 mmol, 2 equiv). The reaction mixture was stirred at RT for 3h, then neutralized with saturated aqueous solution of $NaHCO_3$, extracted (DCM) and washed with 20% HCl_{aq} and water. The organic extract was dried (Na_2SO_4), and concentrated under a reduced pressure. The residue was purified by column chromatography (hexanes/ethyl acetate = 10:1).



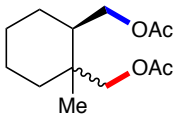
4c

2-Butylbutane-1,4-diyl diacetate (4c) was obtained from compound **3c** according to the general procedure. Product was isolated in 84% yield (average of two runs) as a colorless oil. R_f (hexanes/EtOAc = 4/1): 0.5.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.12 (t, J = 6.8 Hz, 2H), 4.04 (m, 1H), 3.97 (m, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.77 (m, 1H), 1.64-1.70 (m, 2H), 1.30-1.35 (m, 6H), 0.90 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 171.0, 66.9, 62.6, 34.6, 30.8, 30.4, 28.8, 22.8, 20.94, 20.90, 13.9.

HRMS (EI) calcd. for $C_{12}H_{23}O_4$ $[M+H]^+$: 231.15964. Found: 231.15988.



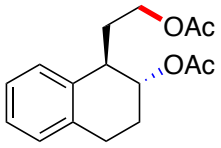
3:1 *cis*/*trans* **4g**

(1-Methylcyclohexane-1,2-diyl)dimethanediyl diacetate (4g) was obtained from compound **3g** according to the general procedure. Product was isolated in 75% yield as a yellow oil; 3:1 mixture of *cis*- and *trans*-products. The stereochemistry of isomers was assigned by hydrolysis of the mixture into corresponding diols and comparison of the obtained NMR with literature data.[41] R_f (hexanes/EtOAc = 4/1): 0.45.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.83-4.29 (m, 4H), 2.02-2.07 (m, 6H), 0.87-1.72 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 72.1, 67.2, 65.8, 65.3, 44.6, 39.9, 35.9, 35.7, 25.4, 25.2, 25.1, 21.7, 21.4, 21.0, 20.9, 16.0.

HRMS (TOF MS ES+) calcd. for $C_{13}H_{23}O_4$ $[M+H]^+$: 243.1596. Found: 243.1602.



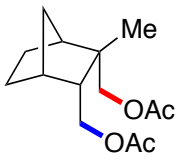
4h

2-((1*R*(*S*),2*R*(*S*))-2-Acetoxy-1,2,3,4-tetrahydronaphthalen-1-yl)ethyl acetate (4h) was obtained from compound **3h** according to the general procedure. Product was isolated in 83% yield (average of two runs) as a pale yellow oil. R_f (hexanes/EtOAc = 4/1): 0.35.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.10-7.19 (m, 4H), 5.17-5.19 (m, 1H), 4.16-4.24 (m, 2H), 3.02-3.05 (m, 1H), 2.88-2.95 (m, 1H), 2.77-2.83 (m, 1H), 2.07 (s, 3H), 2.03-2.05 (m, 1H), 2.02 (s, 3H), 1.93-2.01 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.0, 170.7, 136.9, 135.5, 129.2, 128.8, 126.2, 126.0, 72.1, 62.2, 39.8, 34.5, 24.9, 23.8, 21.3, 21.0.

HRMS (TOF MS ES+) calcd. for $C_{16}H_{20}O_4Na$ $[M+H]^+$: 299.1259. Found: 299.1267.



4r

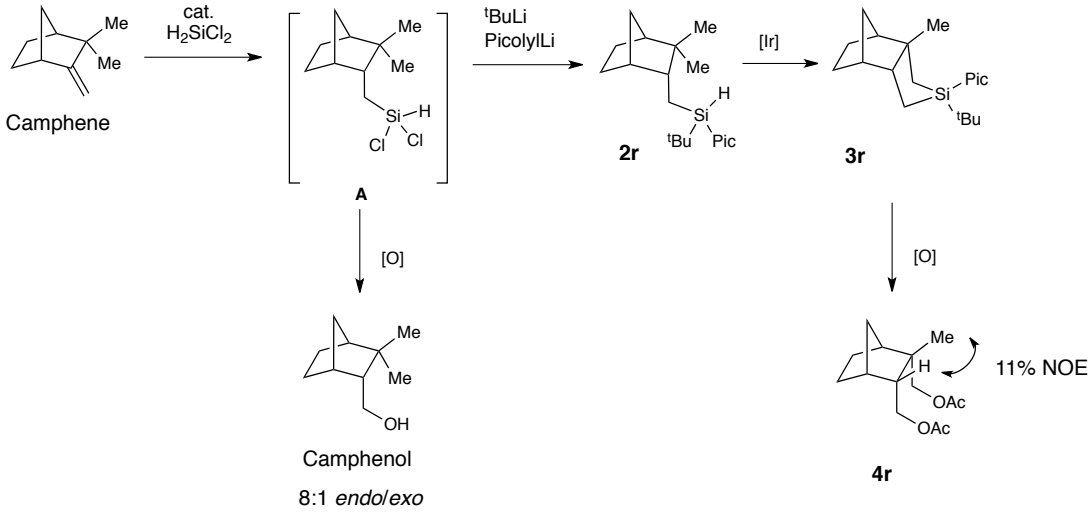
[(1*S*(*R*),2*S*(*R*),3*R*(*S*),4*R*(*S*))-2-methylbicyclo[2.2.1]heptane-2,3-diyl]di(methylene) diacetate (4r) was obtained from compound **3r** according to the general procedure. Product was isolated in 71% yield (average of two runs) as a pale yellow oil. R_f (hexanes/EtOAc = 4/1): 0.45. For assignment of stereochemistry of diol product **4r** we performed additional experiments. After

hydrosilylation of camphene and subsequent Tamao oxidation the camphenol[42] was isolated as 8:1 mixture of *endo*/*exo* isomers. The major *endo*- isomer resulted from the hydrosilylation of alkene from less hindered site of double bond. Based on this and NOE experiment on compound **4r** the stereochemistry of diol derivative was assigned (Supplementary Figure S12).

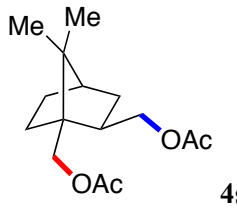
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.13 (d, *J* = 8.1 Hz, 2H), 4.05 (d, *J* = 10.8 Hz, 1H), 3.94 (d, *J* = 11.0 Hz, 1H), 2.27 (br. s, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01(br. s, 1H), 1.84 (td, *J* = 8.0, 3.8 Hz, 1H), 1.26-1.67 (m, 6H), 1.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.2, 170.9, 67.6, 62.1, 49.6, 46.2, 40.2, 40.1, 37.1, 27.0, 24.3, 21.0, 20.9, 20.7.

HRMS (EI+) calcd. for $C_{14}H_{22}O_4$ $[M]^+$: 254.15181. Found: 254.15154.



Supplementary Figure S12. The assignment of stereochemistry of diol **4r**.

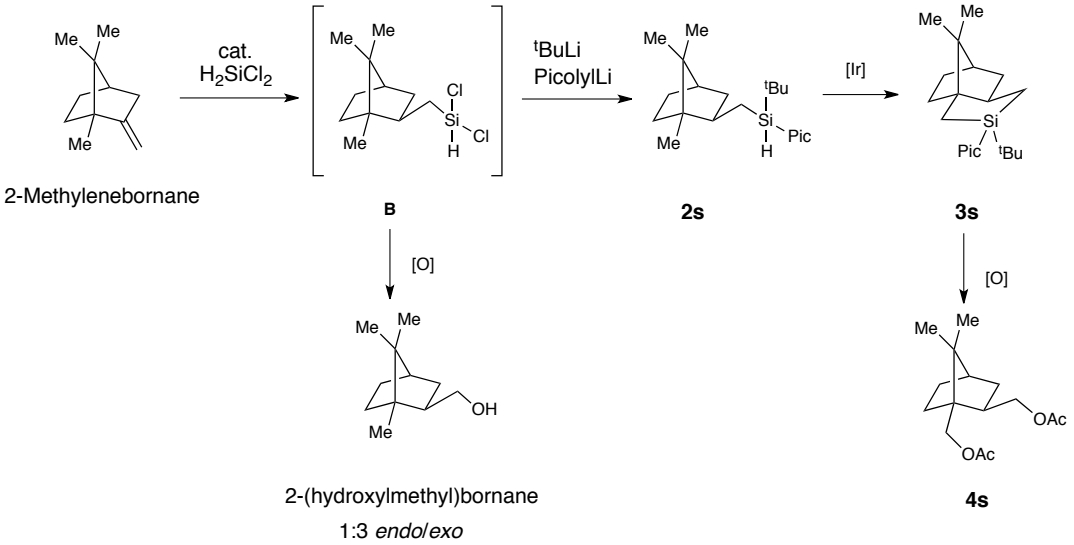


[(1*R*,2*R*,4*R*)-7,7-dimethylbicyclo[2.2.1]heptane-1,2-diyl]di(methylene) diacetate (4s) was obtained from compound **3s** according to the general procedure. Product was isolated in 70% yield (average of two runs) as a yellow oil. R_f (hexanes/EtOAc = 4/1): 0.5. For assignment of stereochemistry of diol product **4s** we performed additional experiments. After hydrosilylation of 2-methylenebornane and subsequent Tamao oxidation the 2-(hydroxymethyl)bornane[42] was isolated as 1:3 mixture of *endo*/*exo* isomers. The major *exo*- isomer resulted from the hydrosilylation of alkene from less hindered site of double bond. Based on this the stereochemistry of diol derivative **4s** was assigned (Supplementary Figure S13).

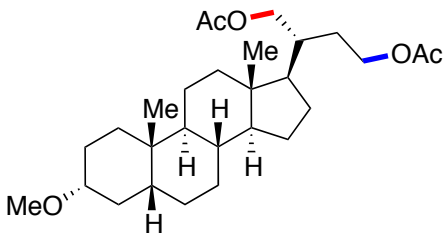
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.23 (dd, *J* = 10.9, 7.4 Hz, 1H), 4.14 (s, 2H), 4.03 (dd, *J* = 10.9, 7.8 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (br. s, 1H), 1.54-1.81 (m, 5H), 1.21-1.37 (m, 2H), 1.00 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.2, 171.1, 67.6, 64.6, 49.6, 47.7, 45.9, 44.5, 35.3, 33.9, 26.9, 21.1, 21.0, 20.96, 20.9.

HRMS (EI+) calcd. for $C_{15}H_{24}O_4$ $[M]^+$: 268.16746. Found: 268.16670.



Supplementary Figure S13. The assignment of stereochemistry of diol **4s**.



4t

(*R*)-2-((3*R*,5*R*,8*R*,9*S*,10*S*,13*S*,14*S*,17*R*)-3-Methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)butane-1,4-diyl diacetate (4t) was obtained from compound **3t** according to the general procedure. Product was isolated in 58% yield as a pale yellow oil. R_f (hexanes/EtOAc = 4/1): 0.55.

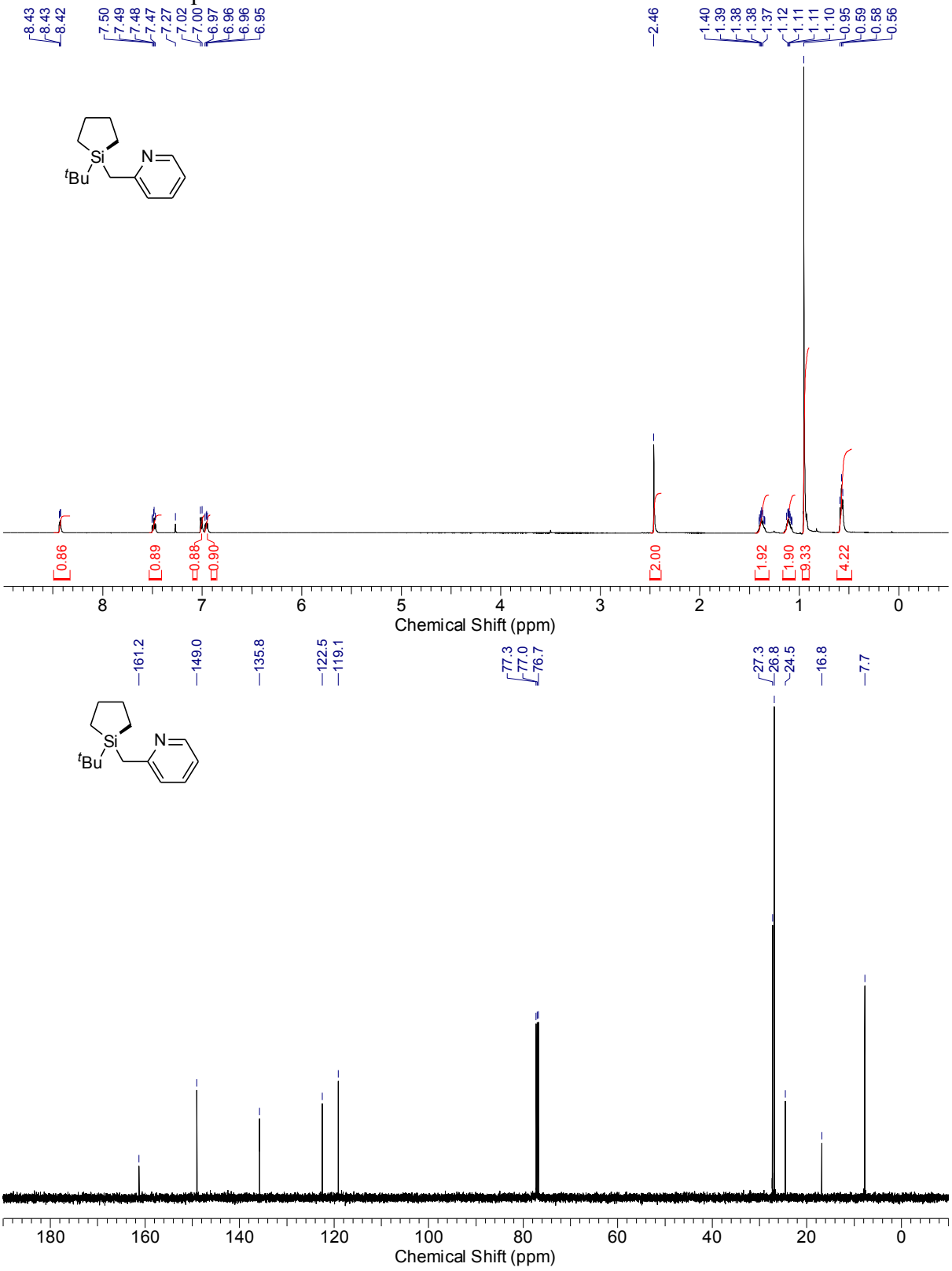
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.12-4.19 (m, 2H), 4.03-4.09 (m, 1H), 3.98 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.34 (s, 3H), 3.13-3.18 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.58-1.87 (m, 11H), 1.03-1.43 (m, 14H), 0.91-0.96 (m, 1H), 0.91 (s, 3H), 0.67 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 171.0, 80.3, 65.2, 62.6, 56.3, 55.5, 50.7, 42.5, 41.9, 40.3, 39.2, 37.0, 35.7, 35.2, 34.8, 32.7, 29.4, 27.8, 27.2, 26.7, 26.3, 24.0, 23.3, 21.0, 20.9, 20.7, 12.1.

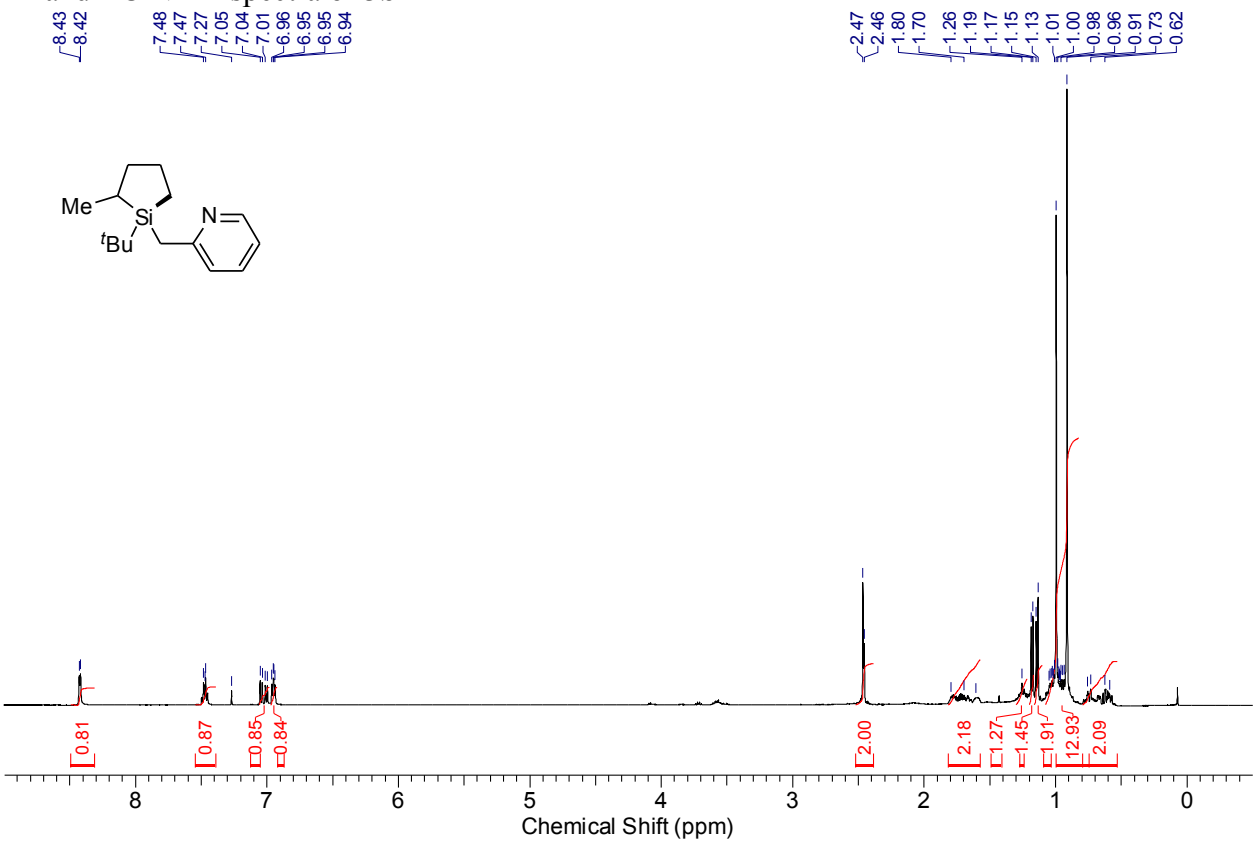
HRMS (TOF MS ES+) calcd. for $C_{28}H_{47}O_5$ $[M+H]^+$: 463.3424. Found: 463.3431.

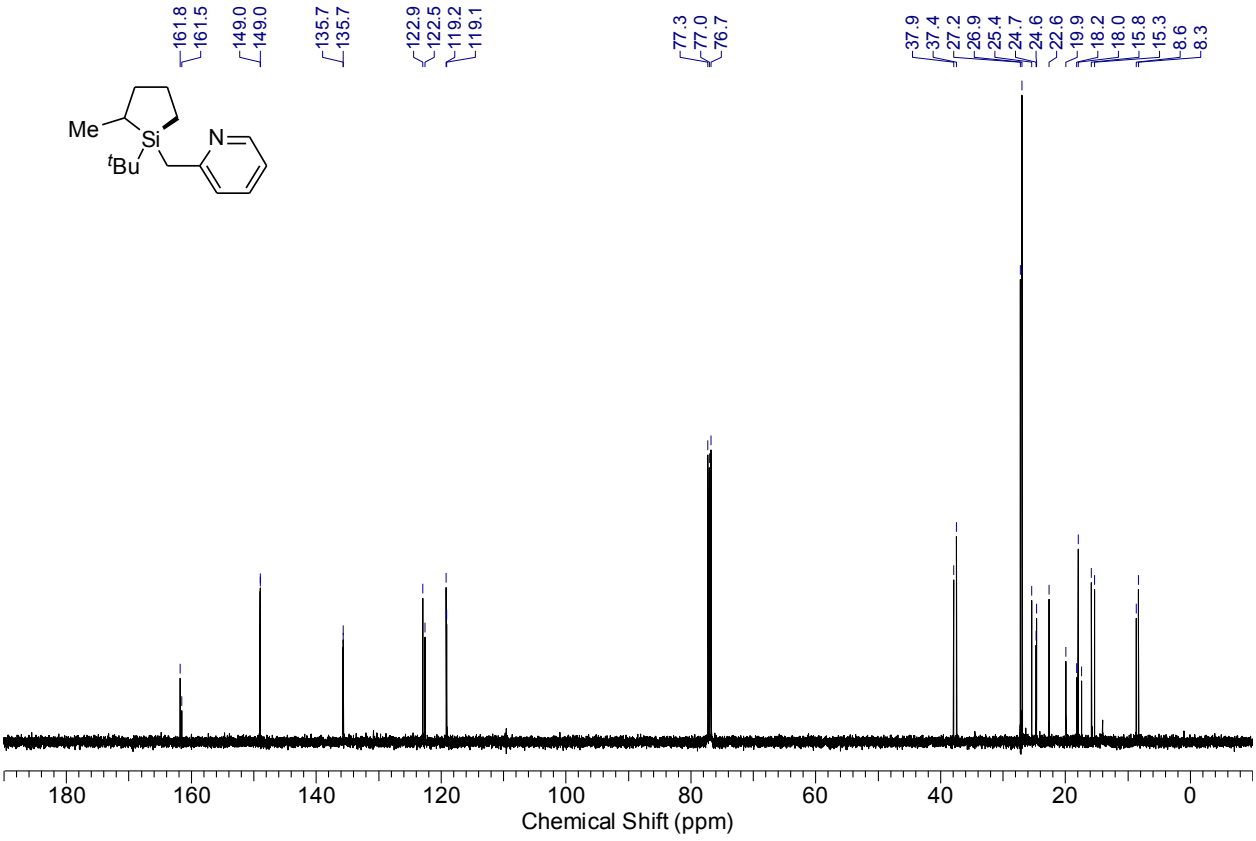
Copies of ^{1}H and ^{13}C NMR Spectra

^{1}H and ^{13}C NMR spectra of **3a**

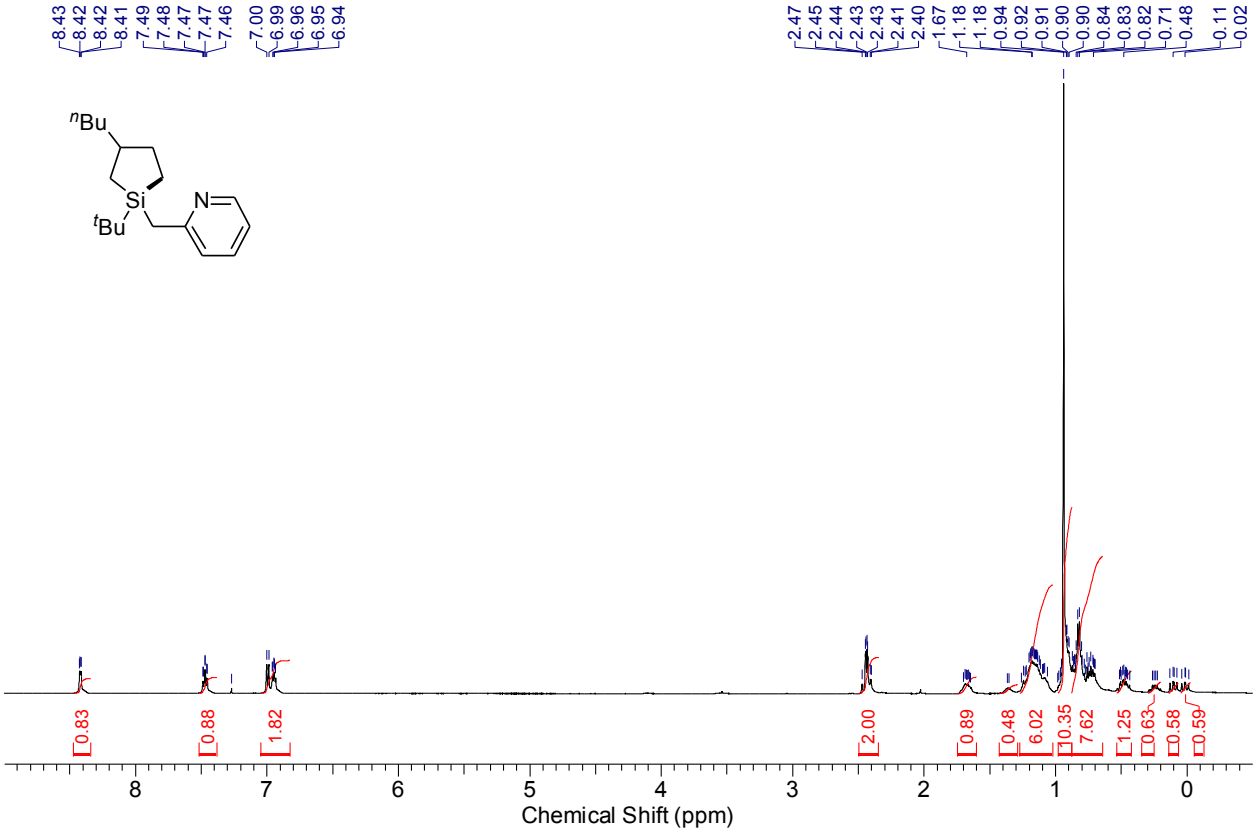


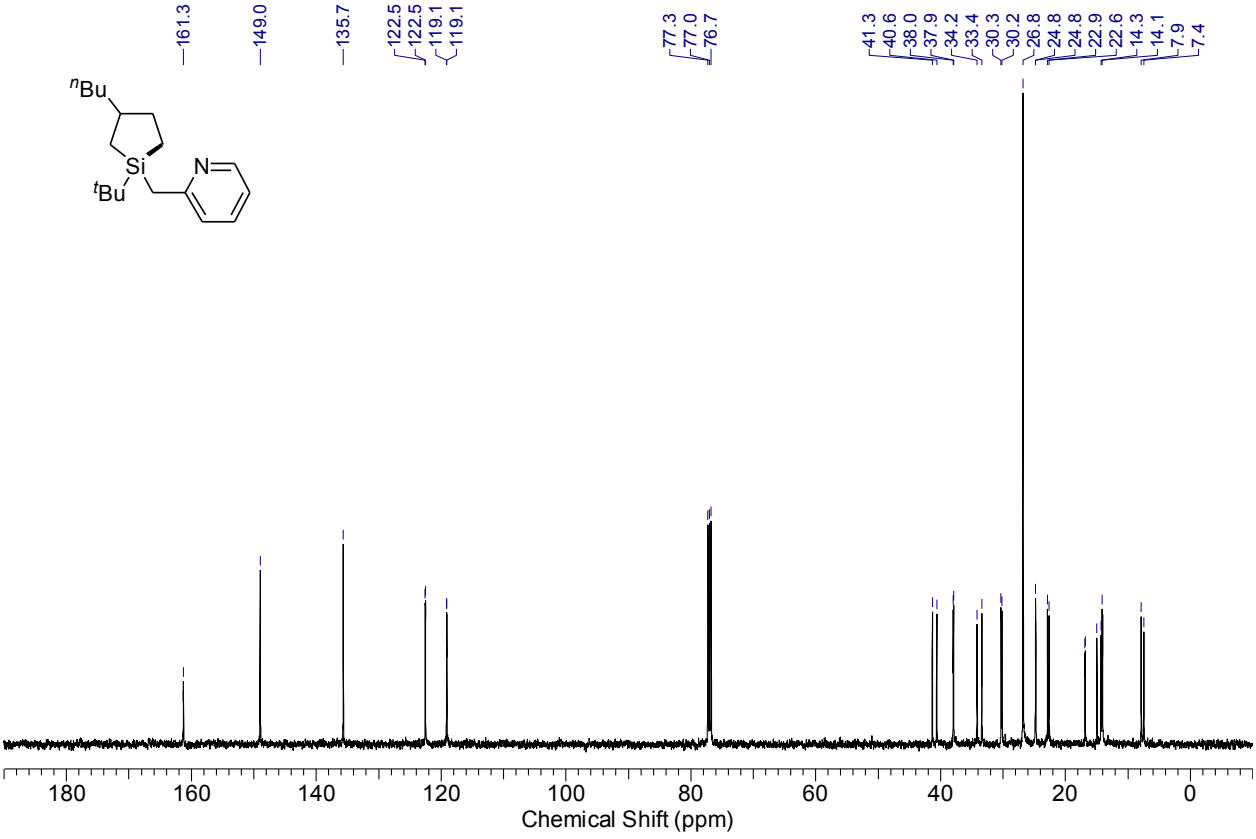
^{1}H and ^{13}C NMR spectra of **3b**



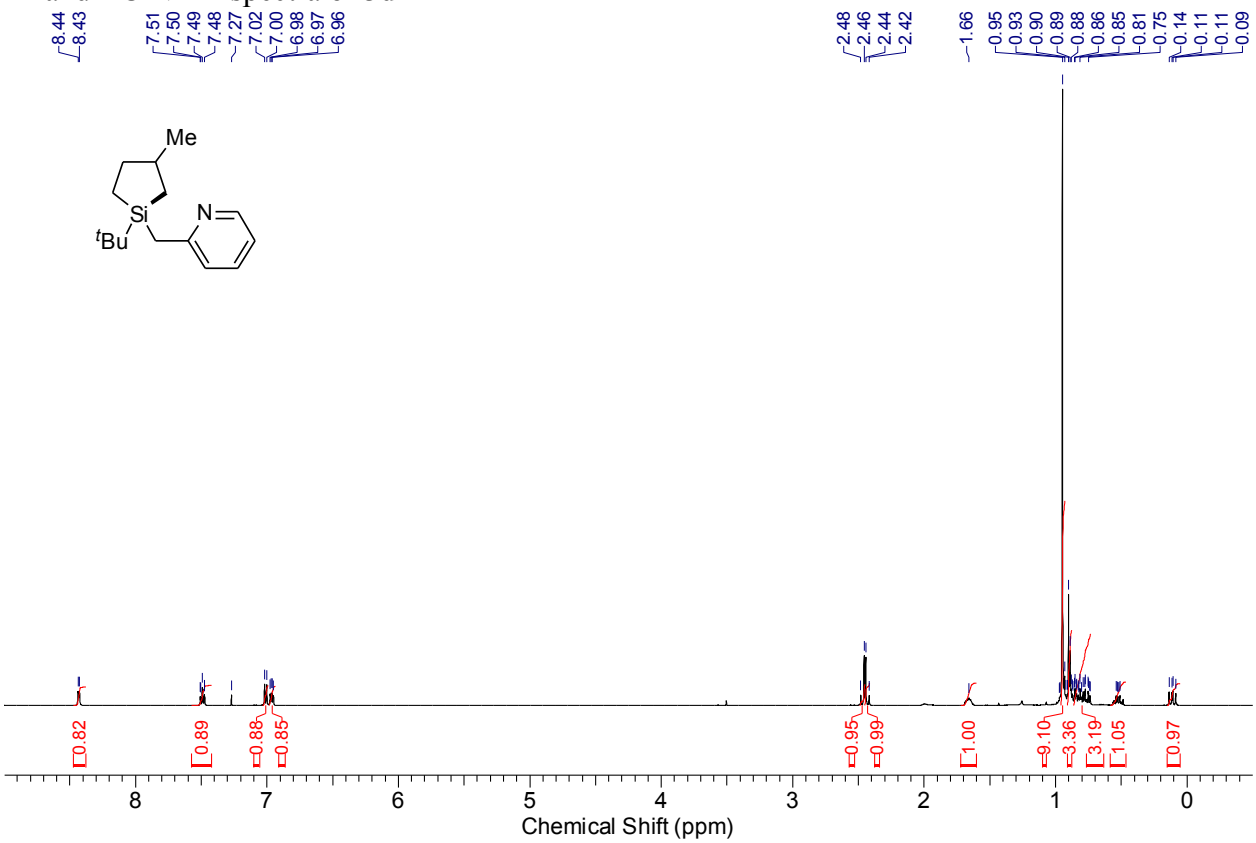


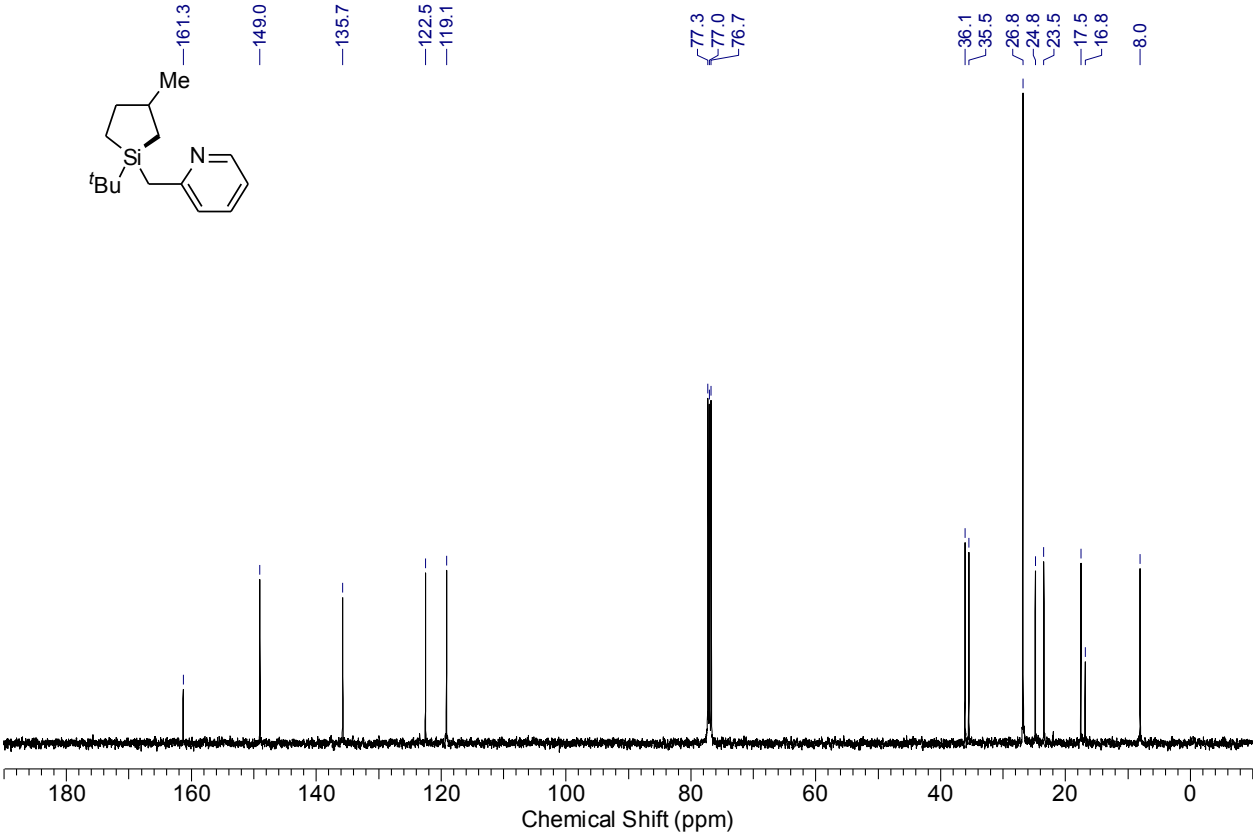
^{1}H and ^{13}C NMR spectra of **3c**



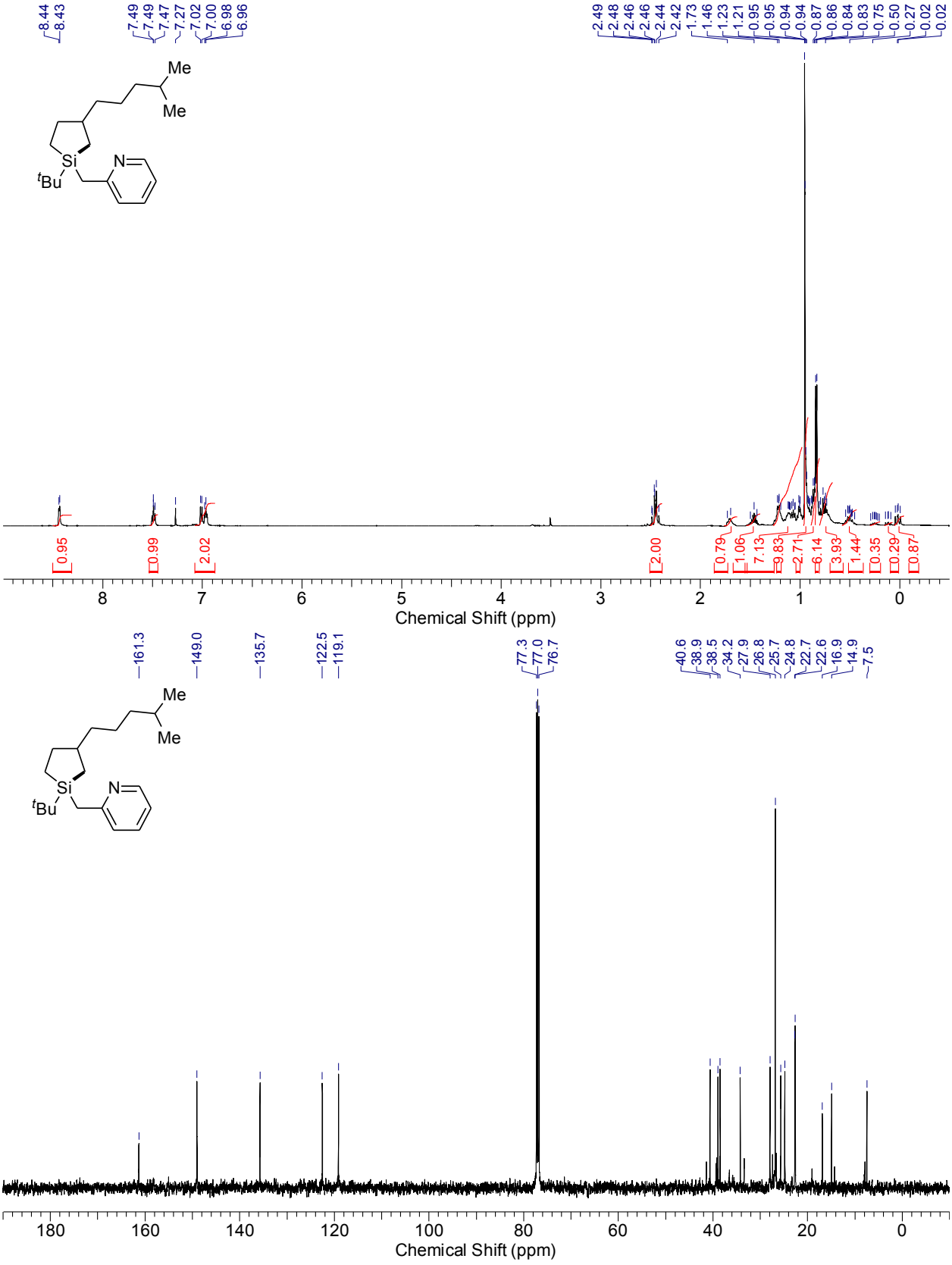


^{1}H and ^{13}C NMR spectra of **3d**

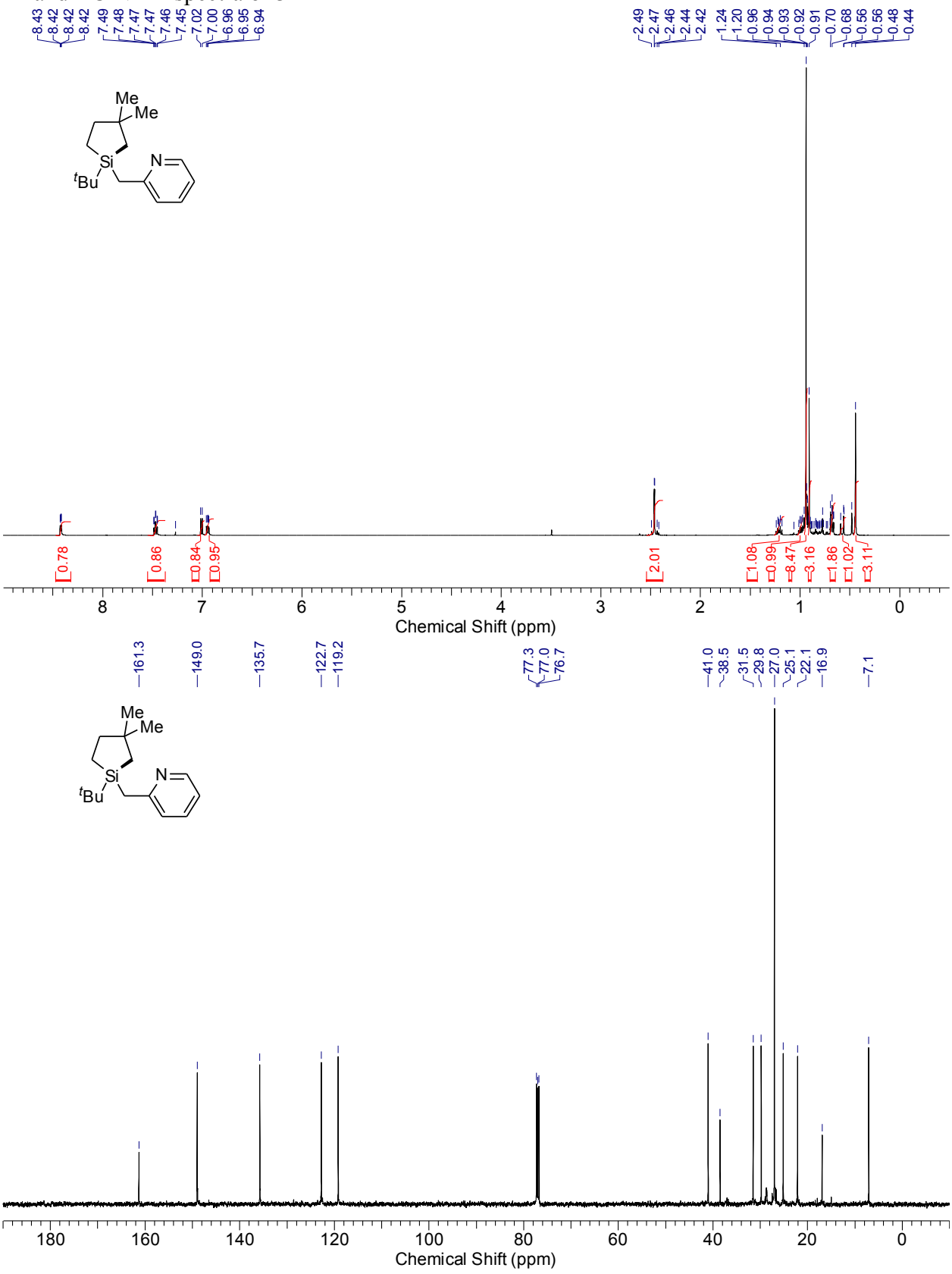




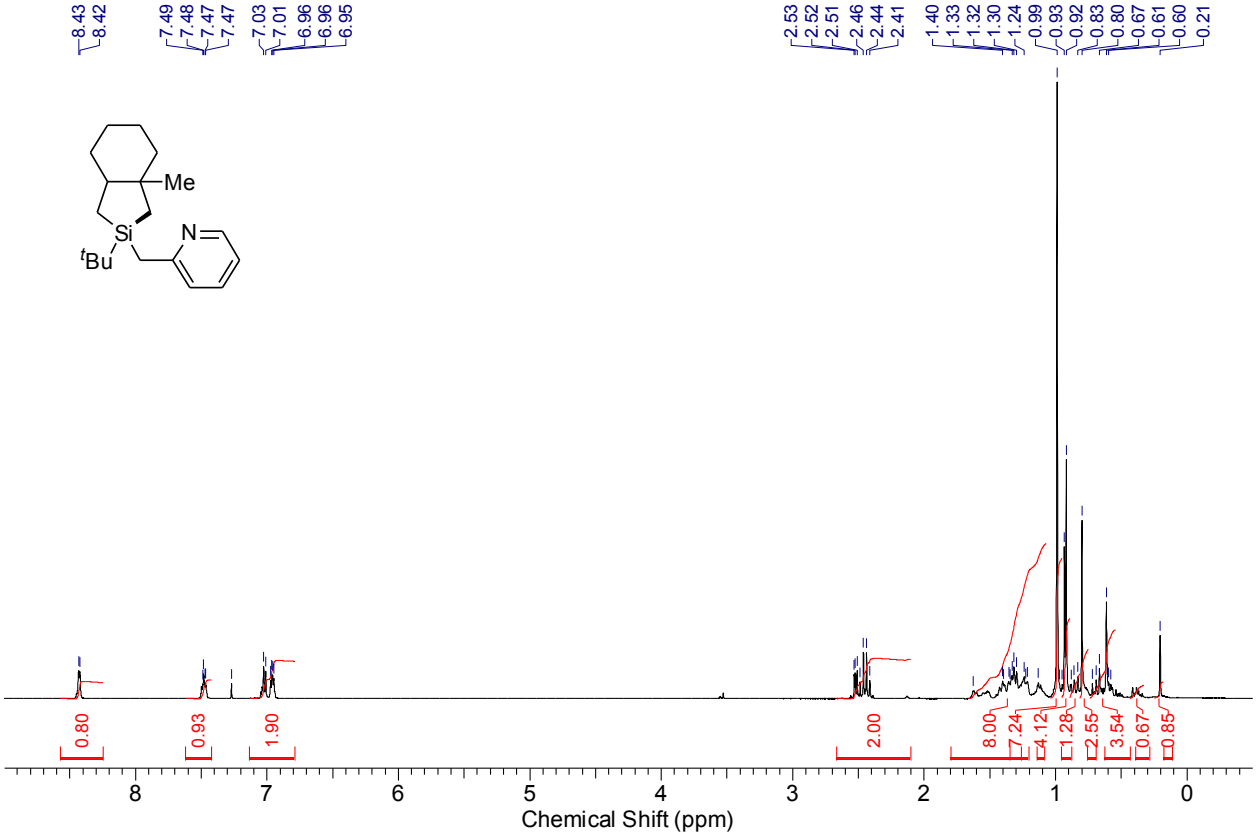
^{1}H and ^{13}C NMR spectra of **3e**

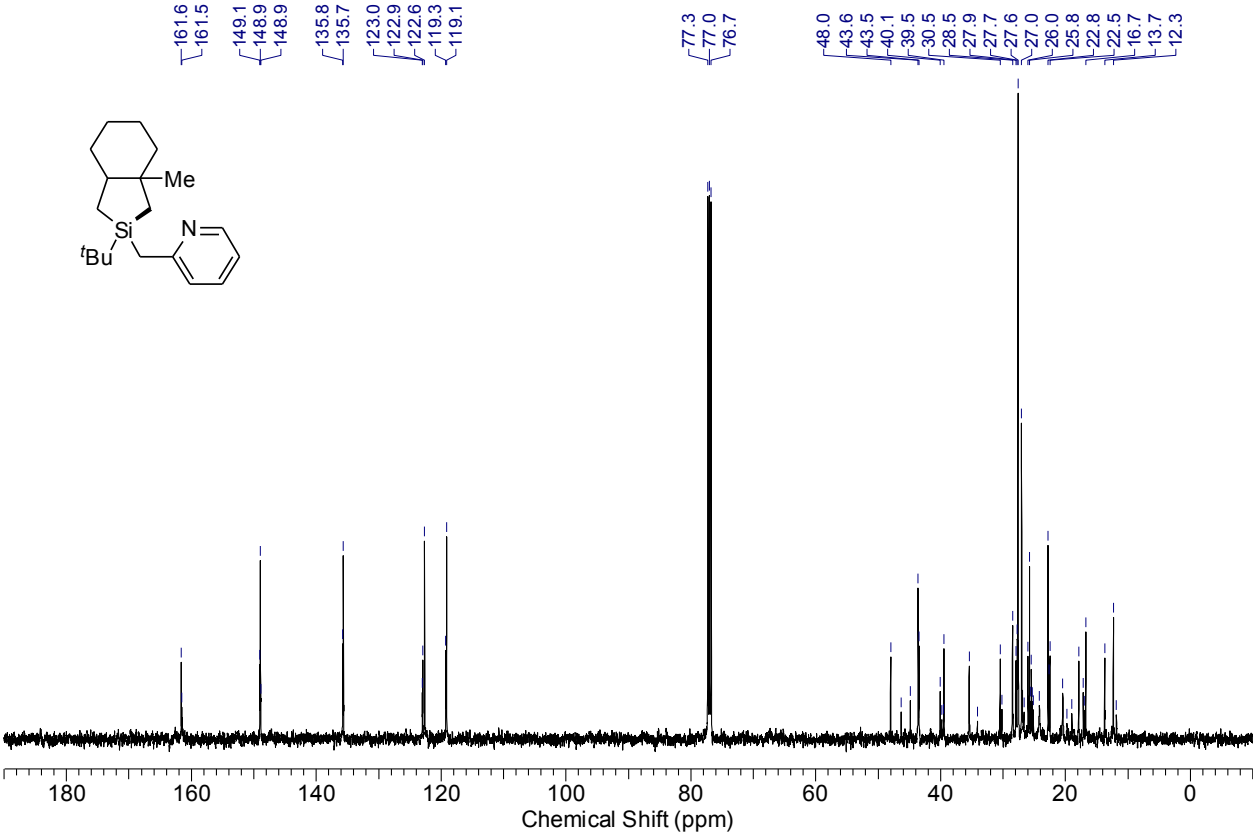


^{1}H and ^{13}C NMR spectra of **3f**

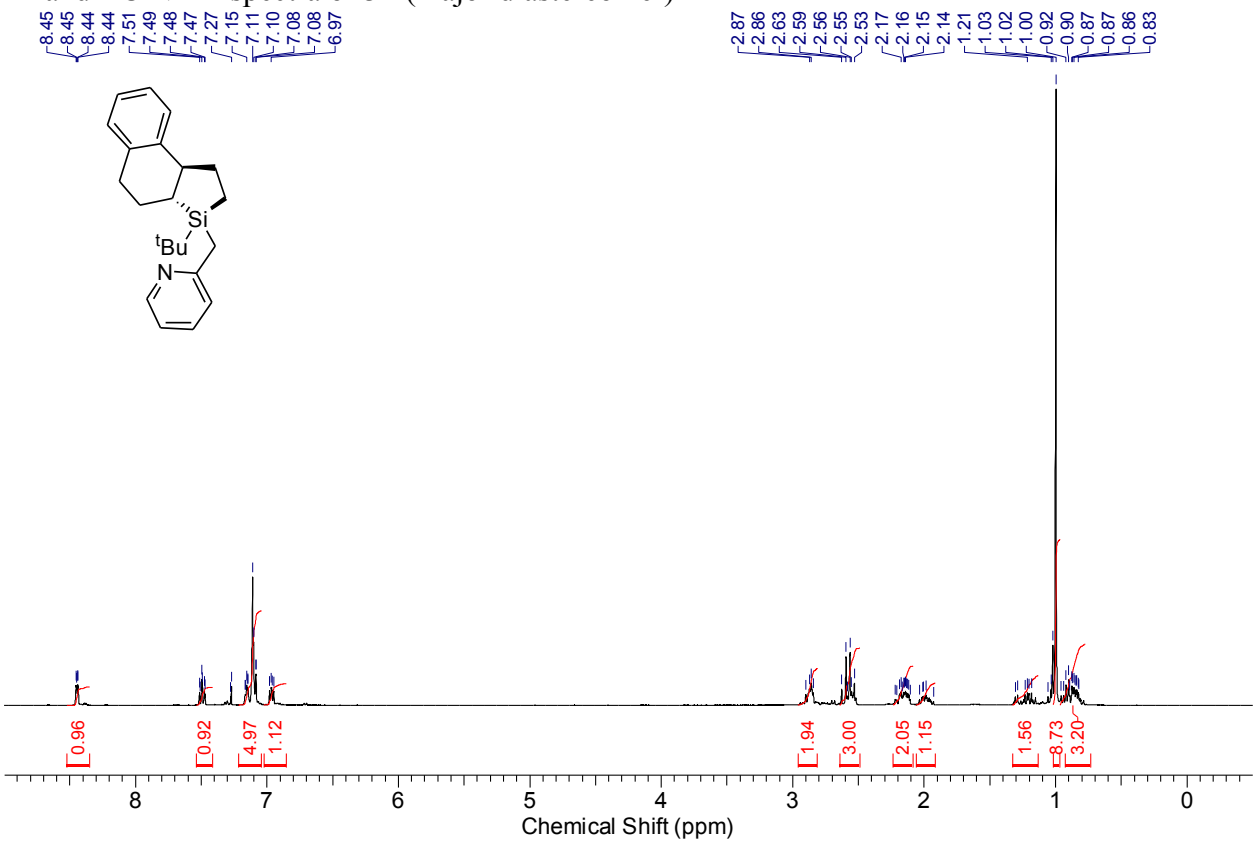


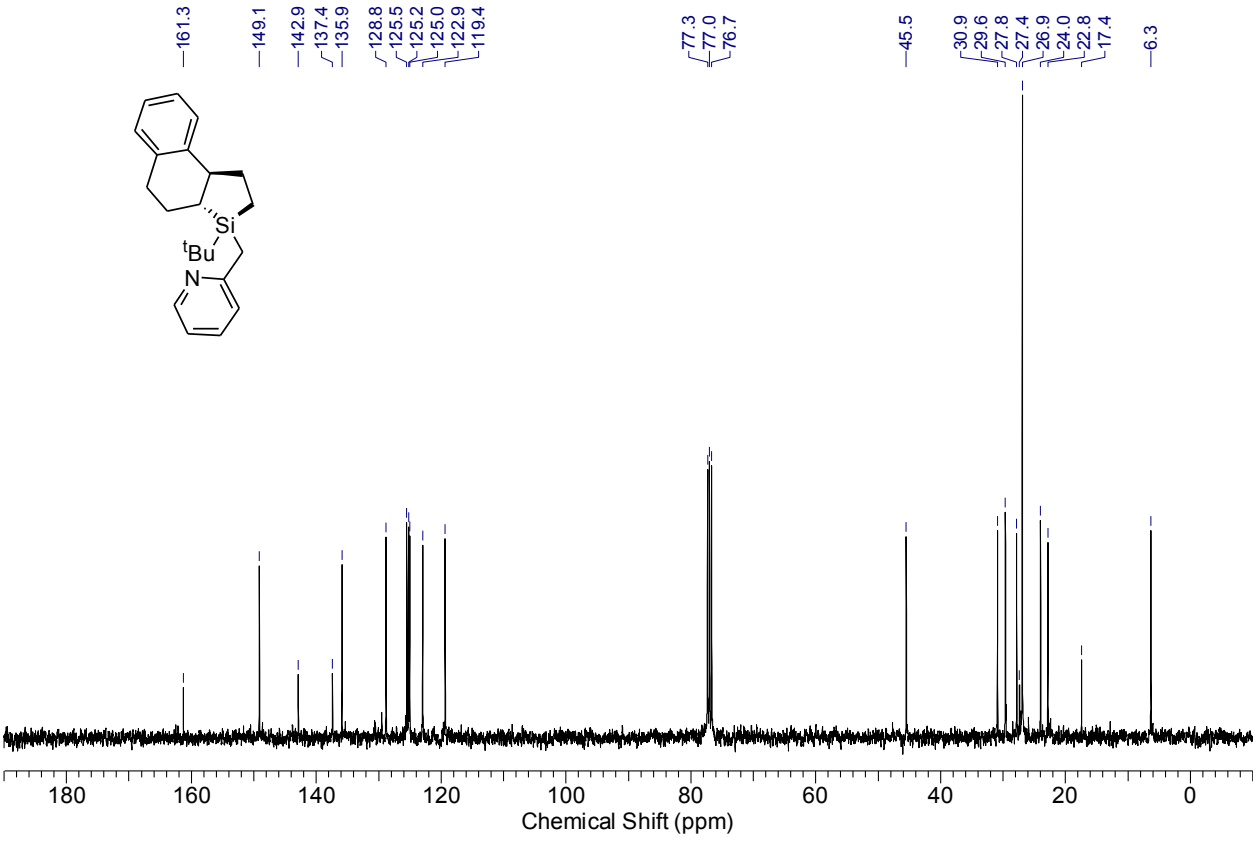
^{1}H and ^{13}C NMR spectra of **3g**



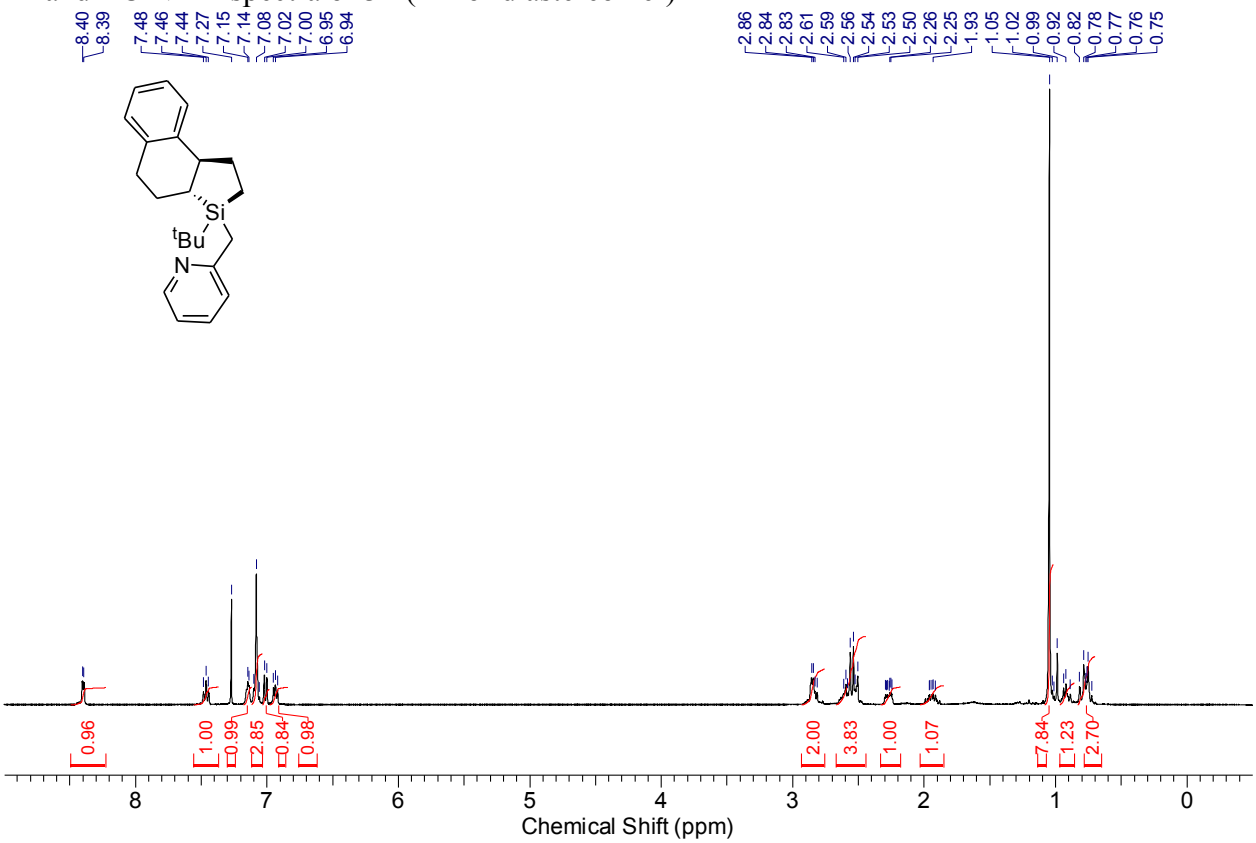


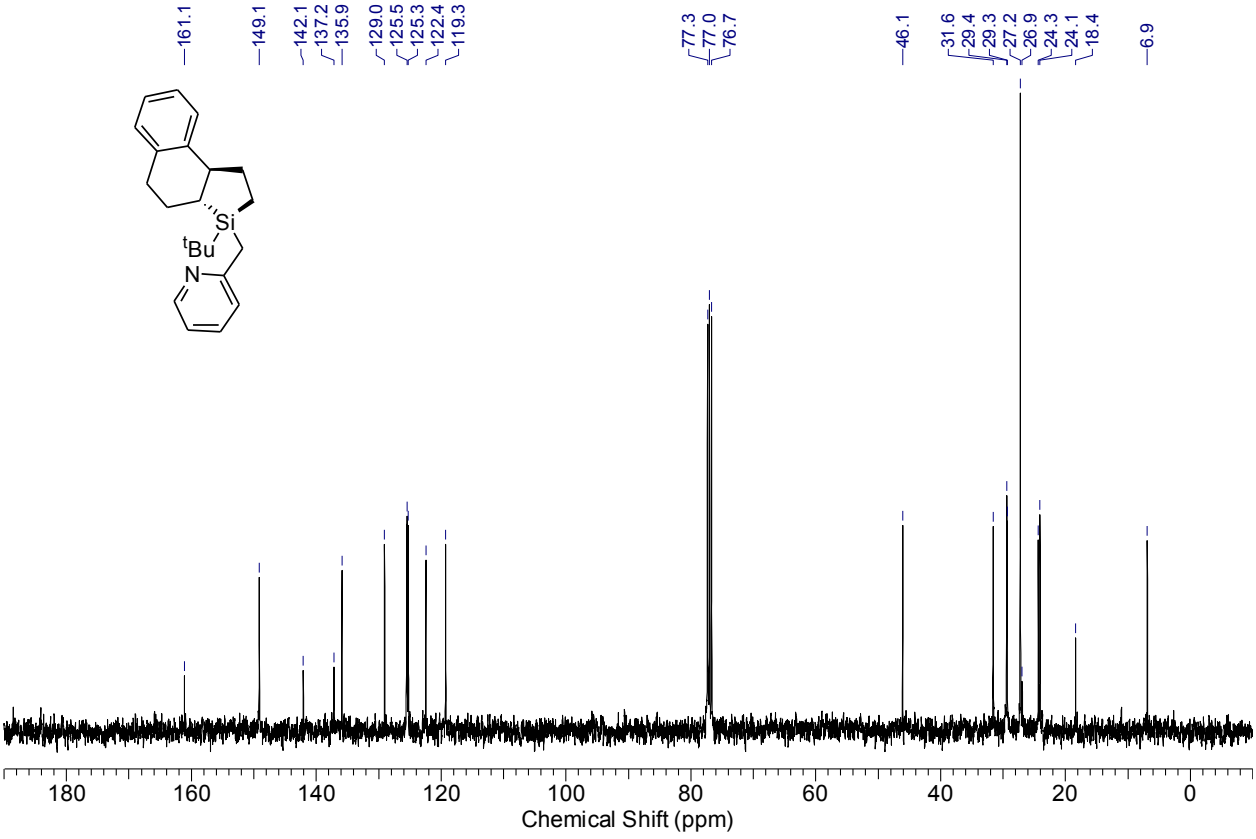
^{1}H and ^{13}C NMR spectra of **3h** (major diastereomer)



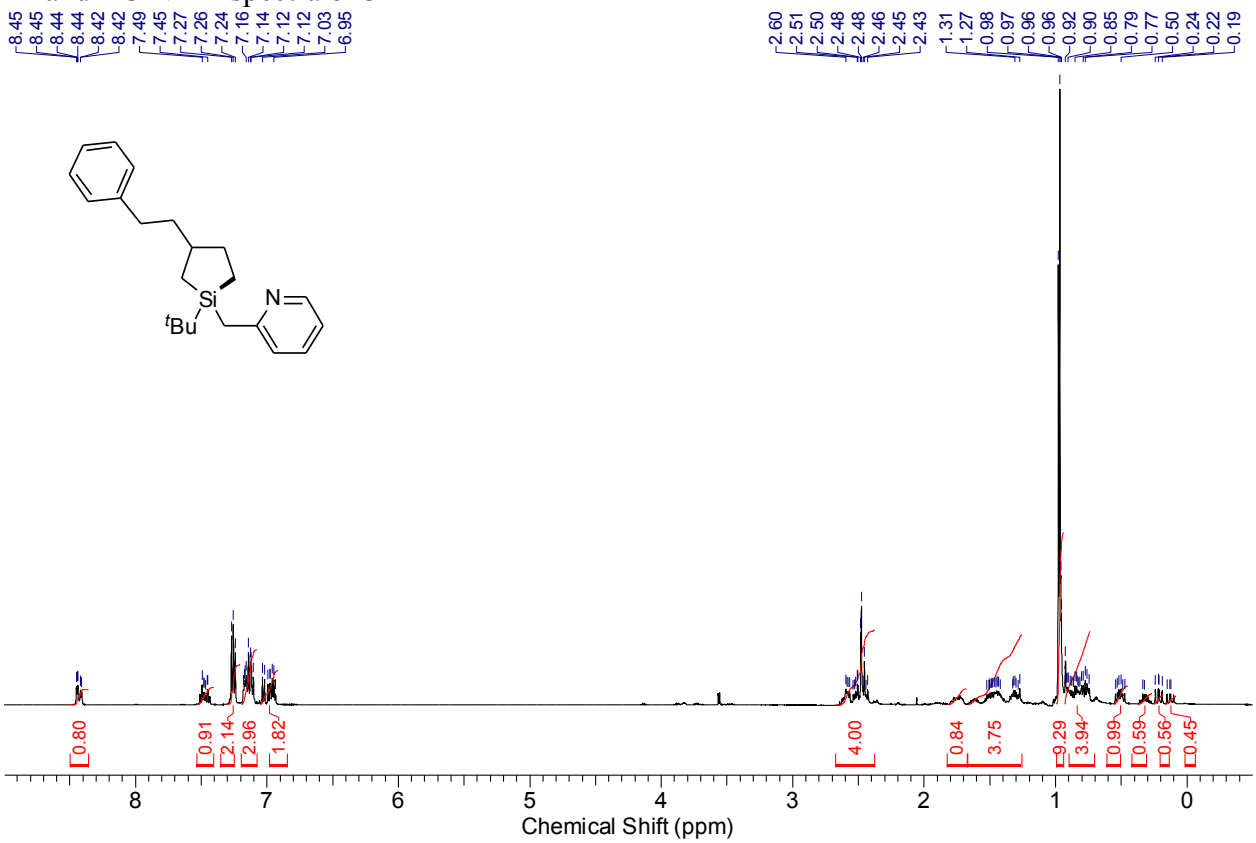


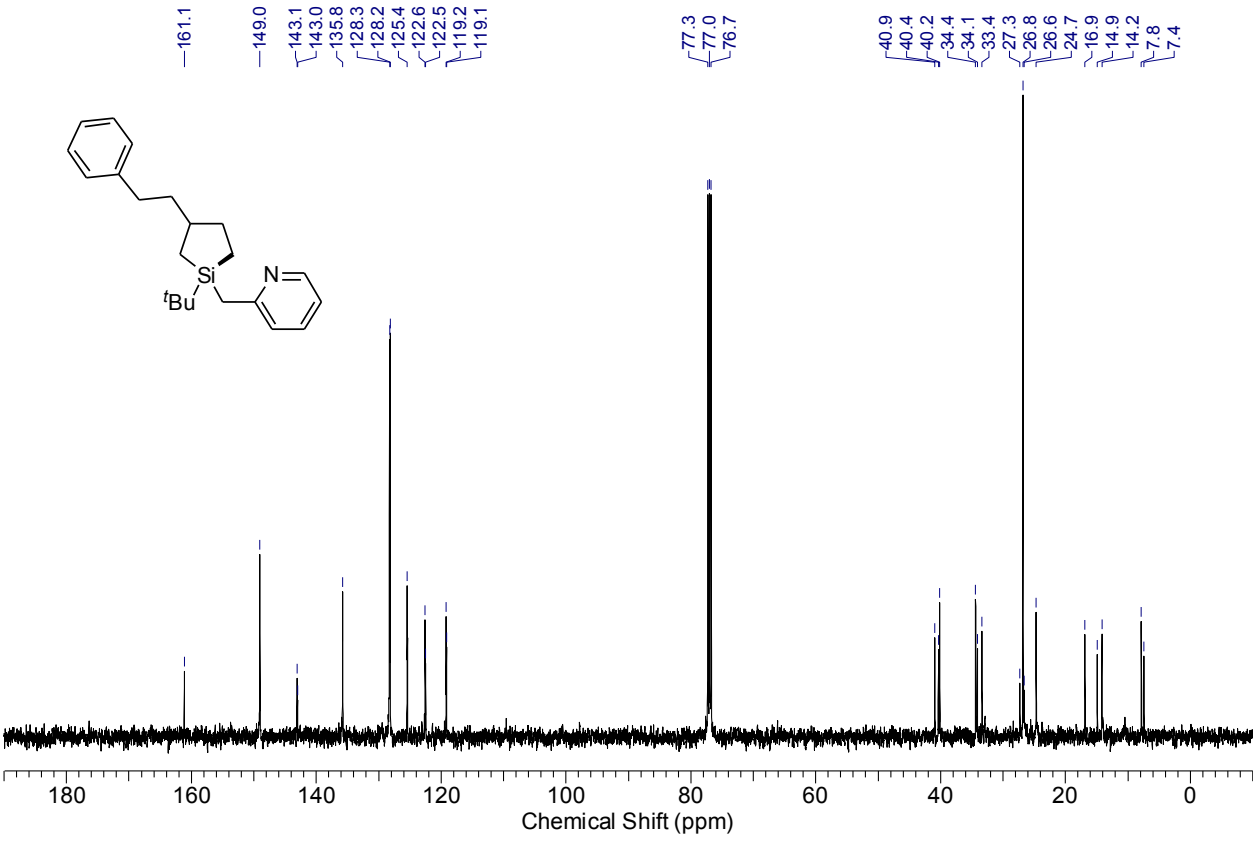
^{1}H and ^{13}C NMR spectra of **3h** (minor diastereomer)



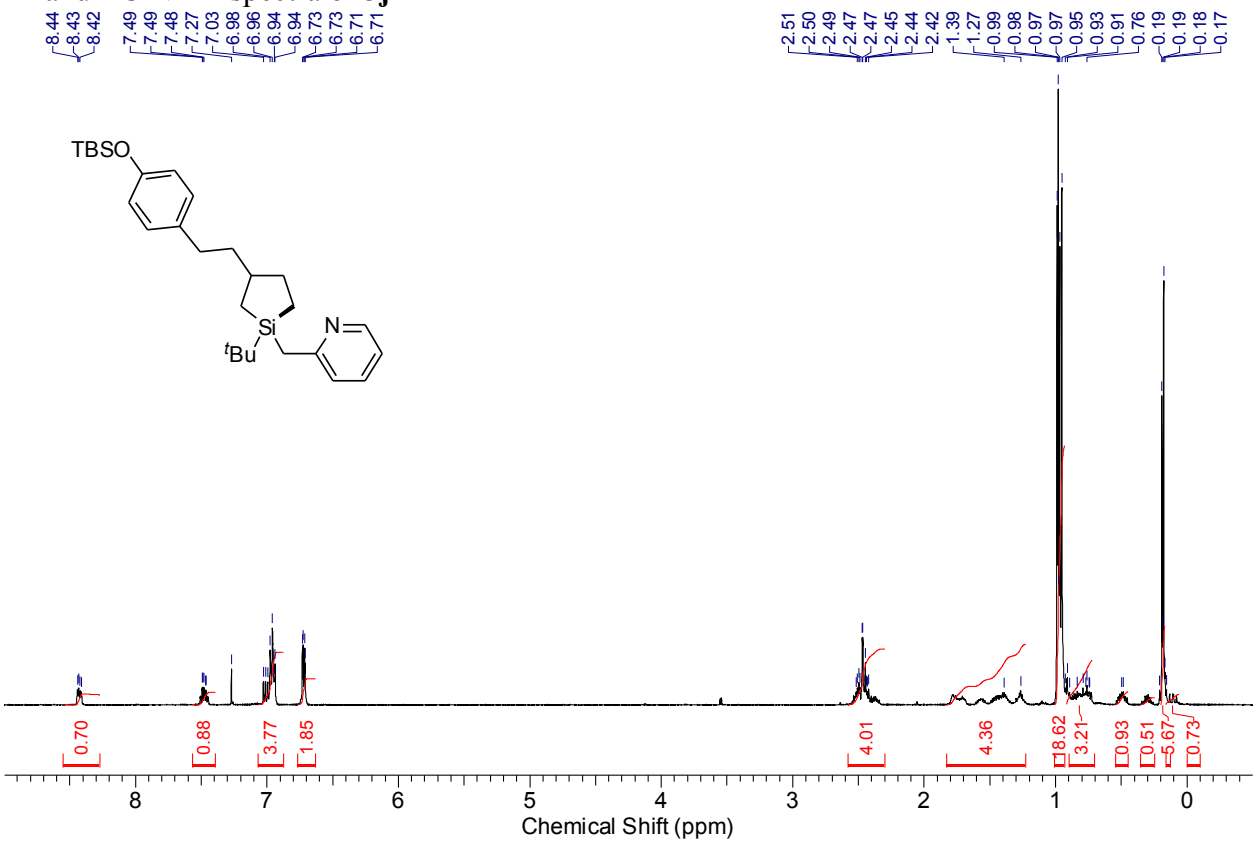


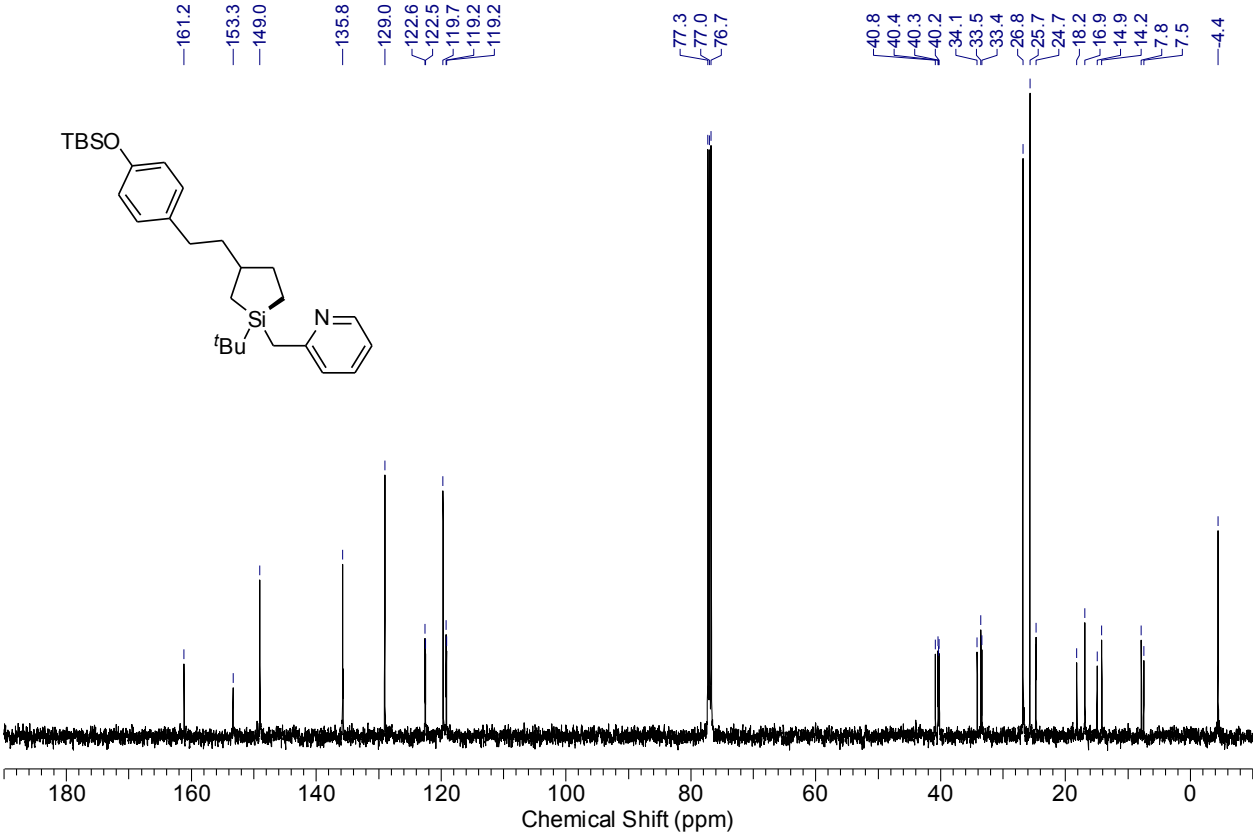
^{1}H and ^{13}C NMR spectra of **3i**



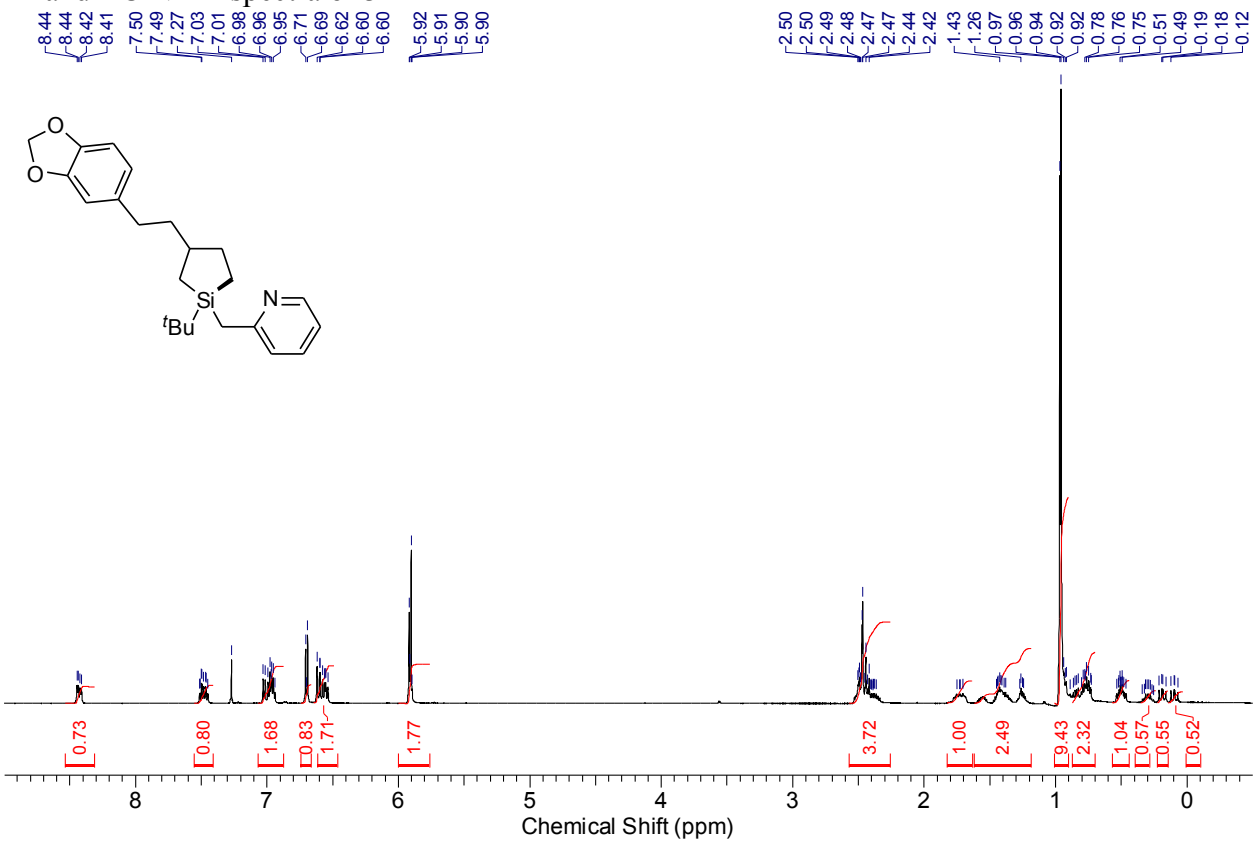


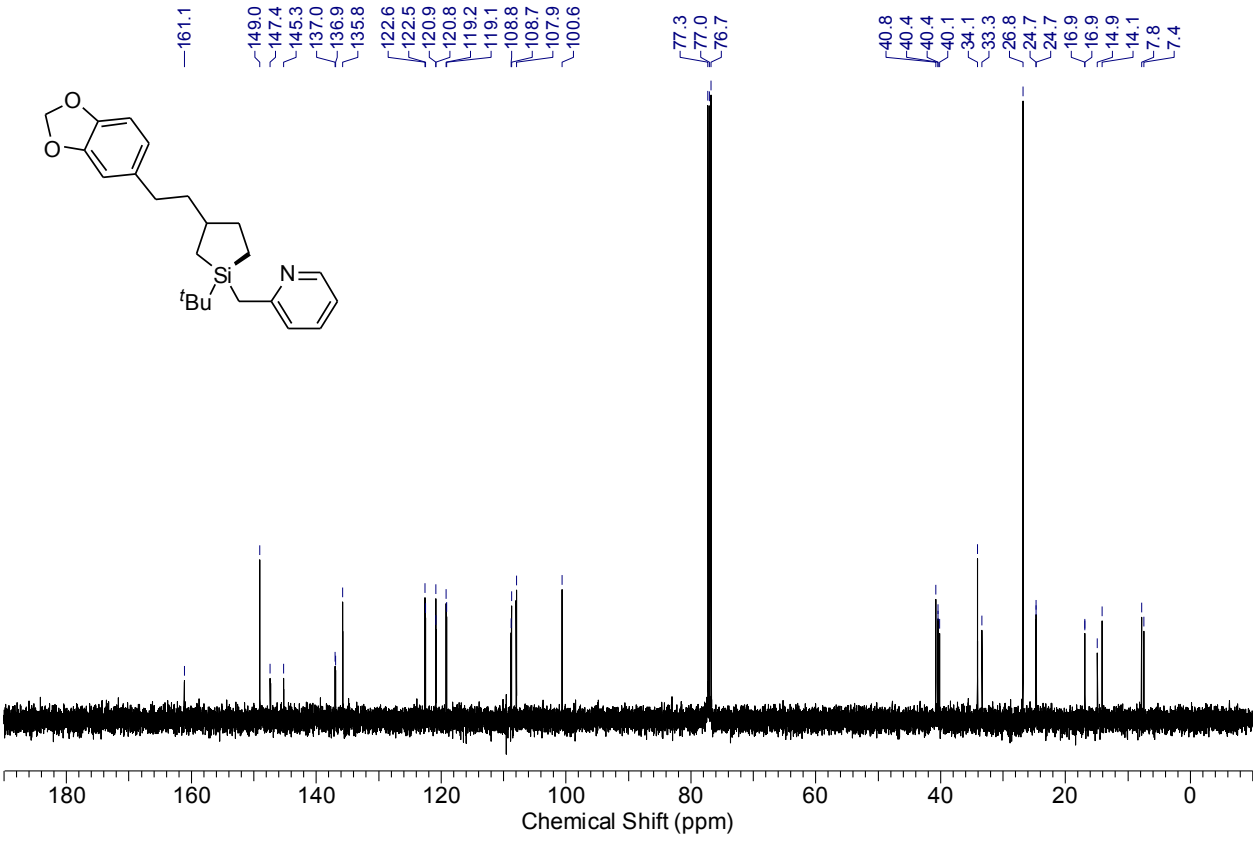
^{1}H and ^{13}C NMR spectra of **3j**



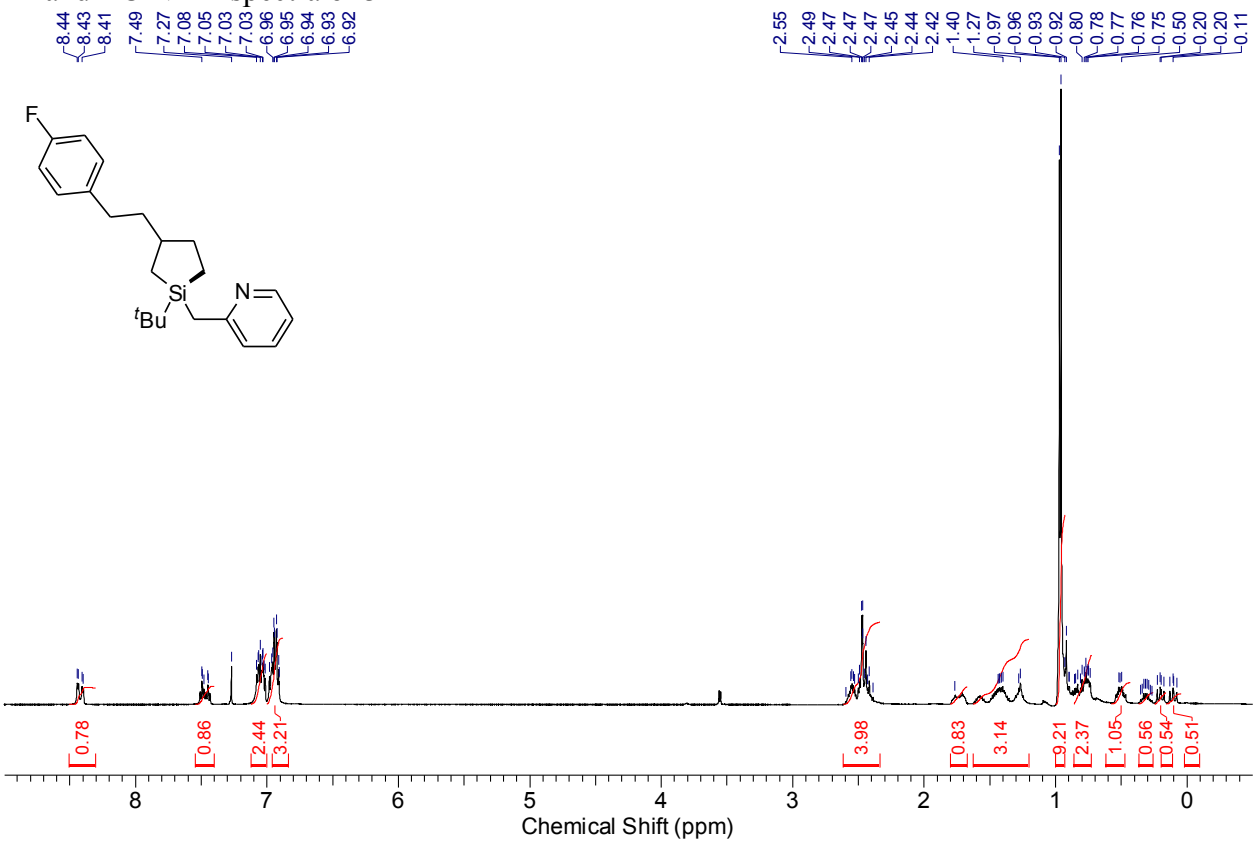


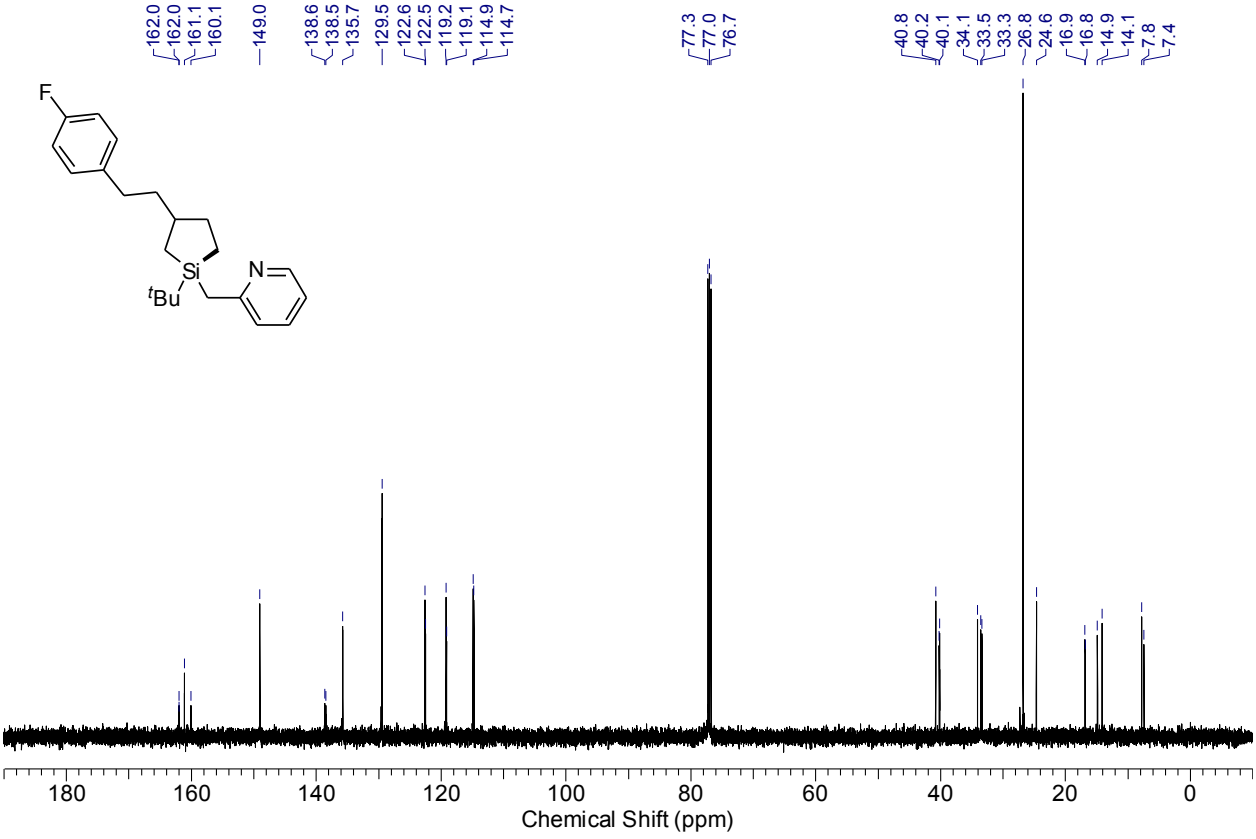
^{1}H and ^{13}C NMR spectra of **3k**



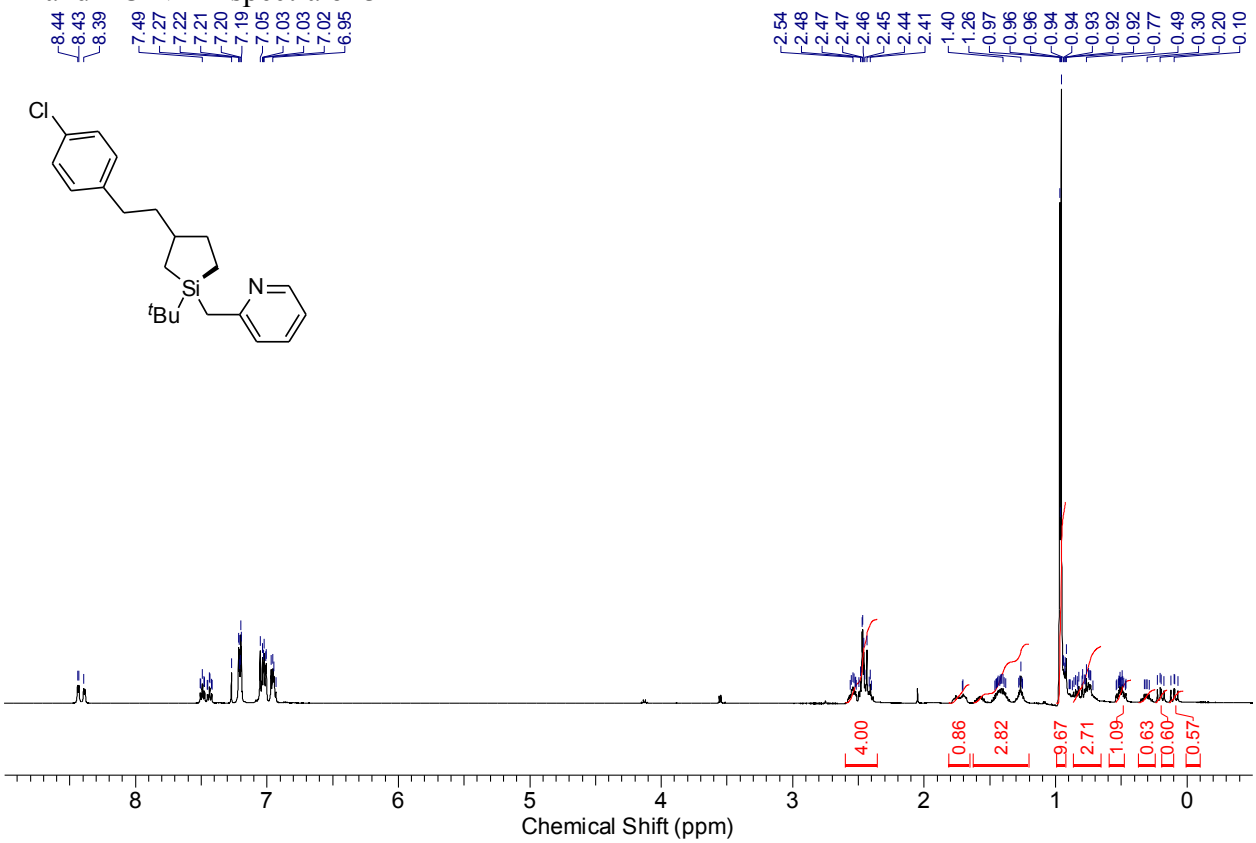


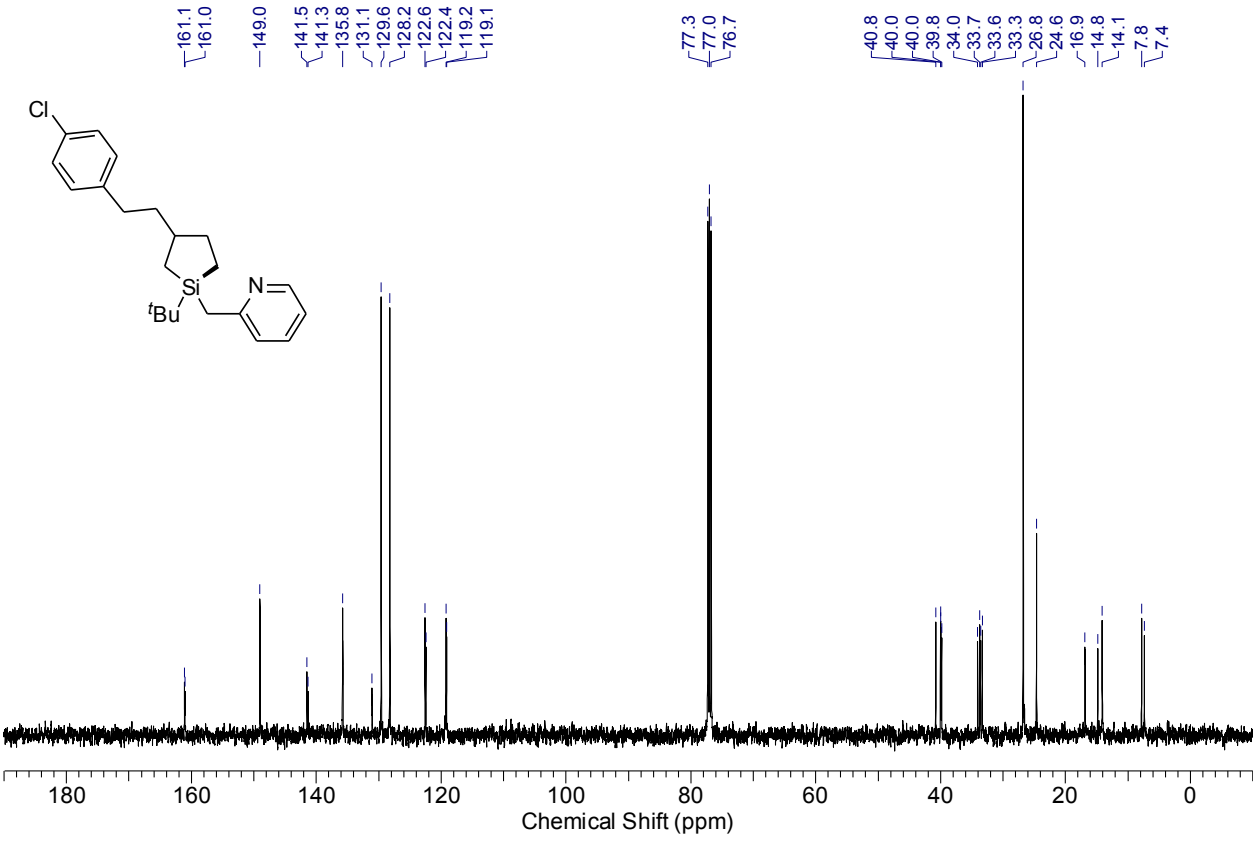
^{1}H and ^{13}C NMR spectra of **3l**



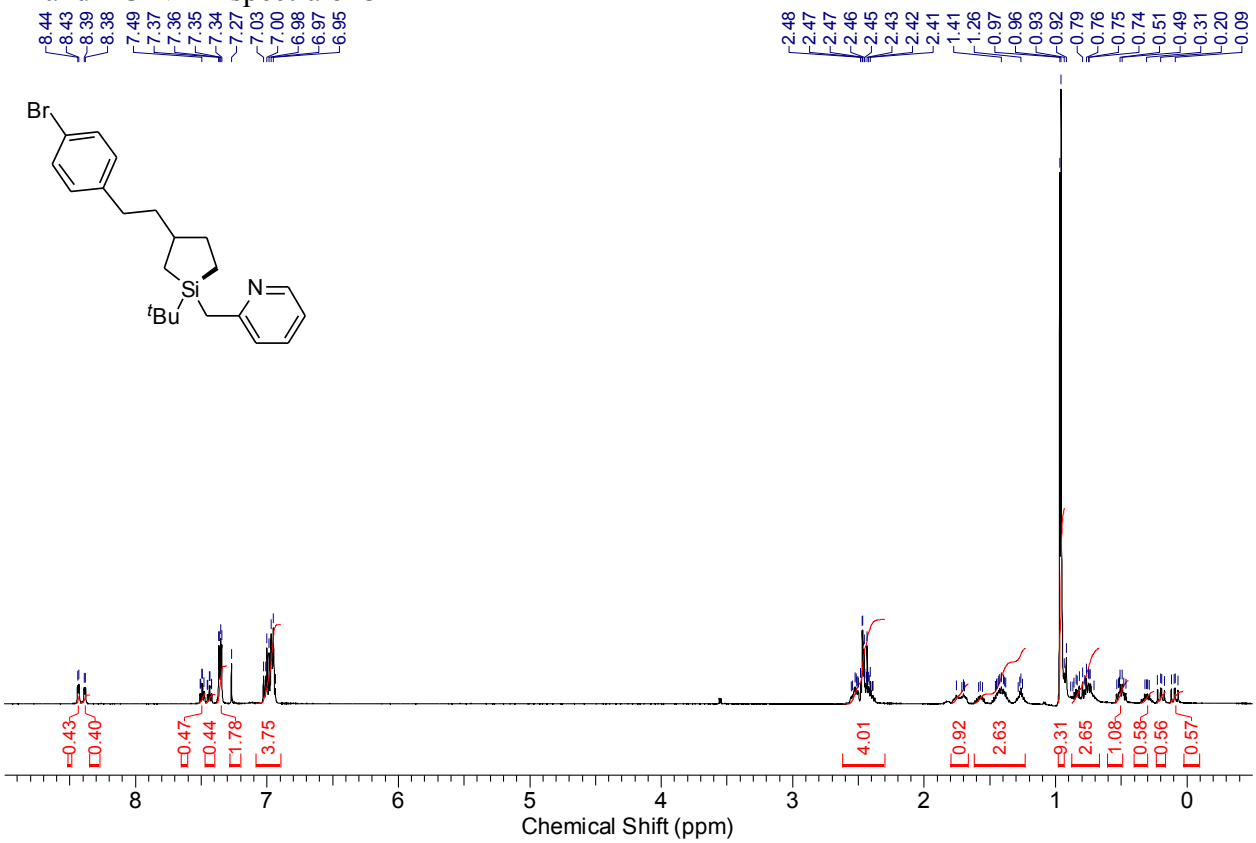


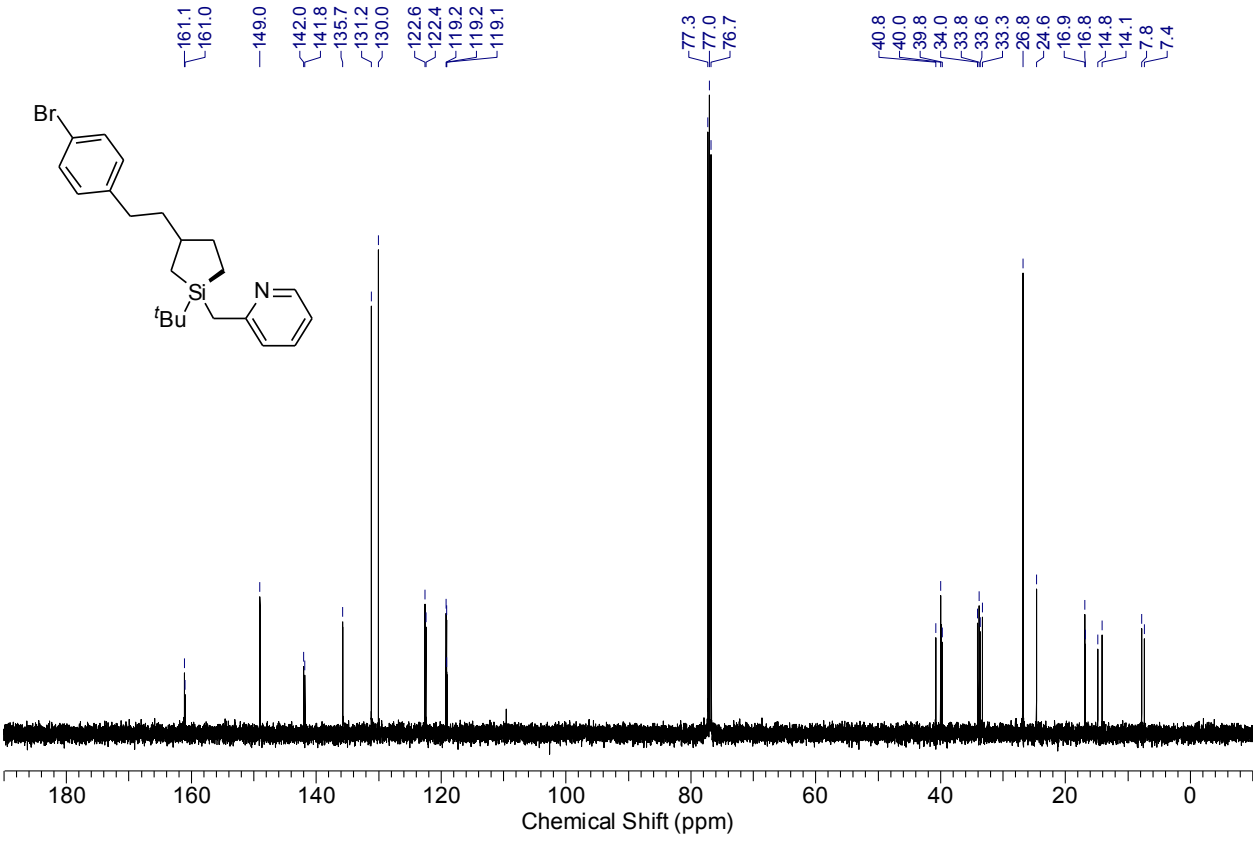
^{1}H and ^{13}C NMR spectra of **3m**



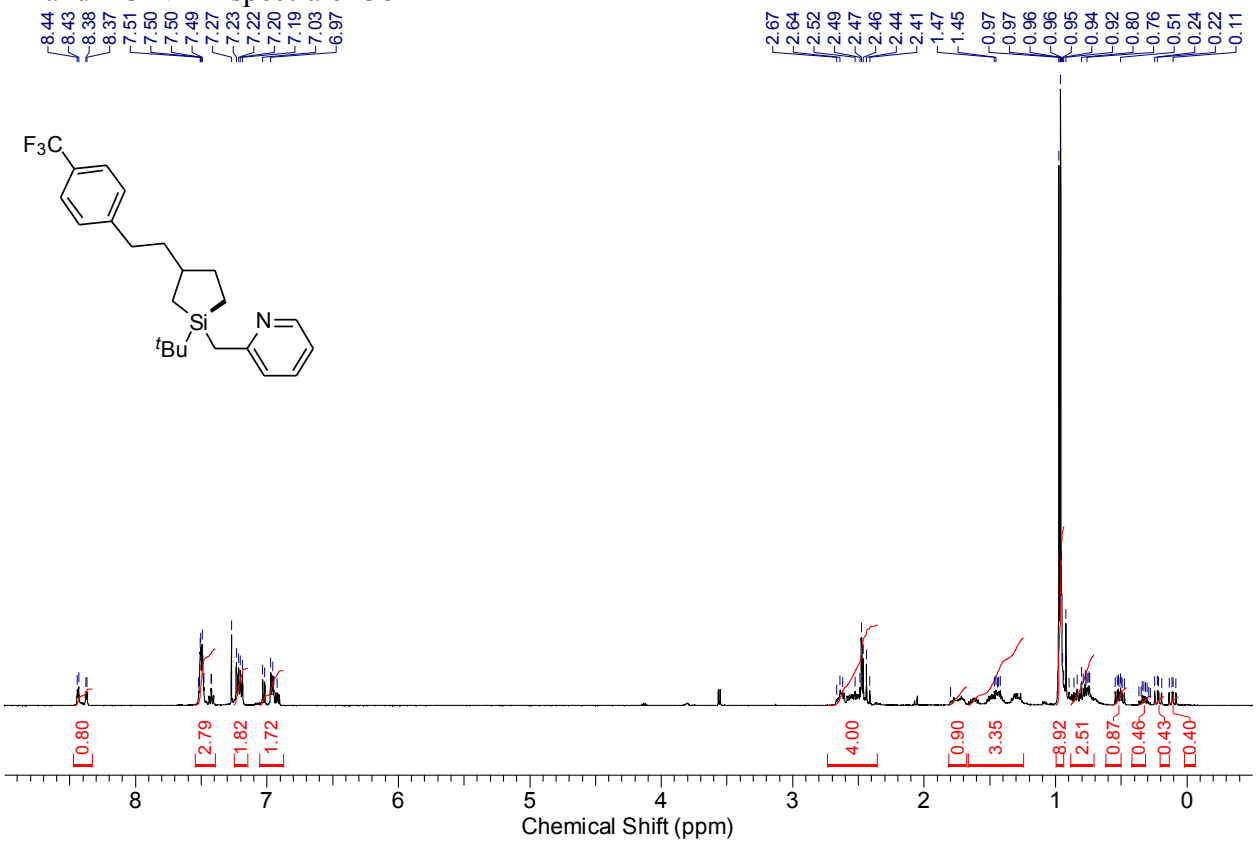


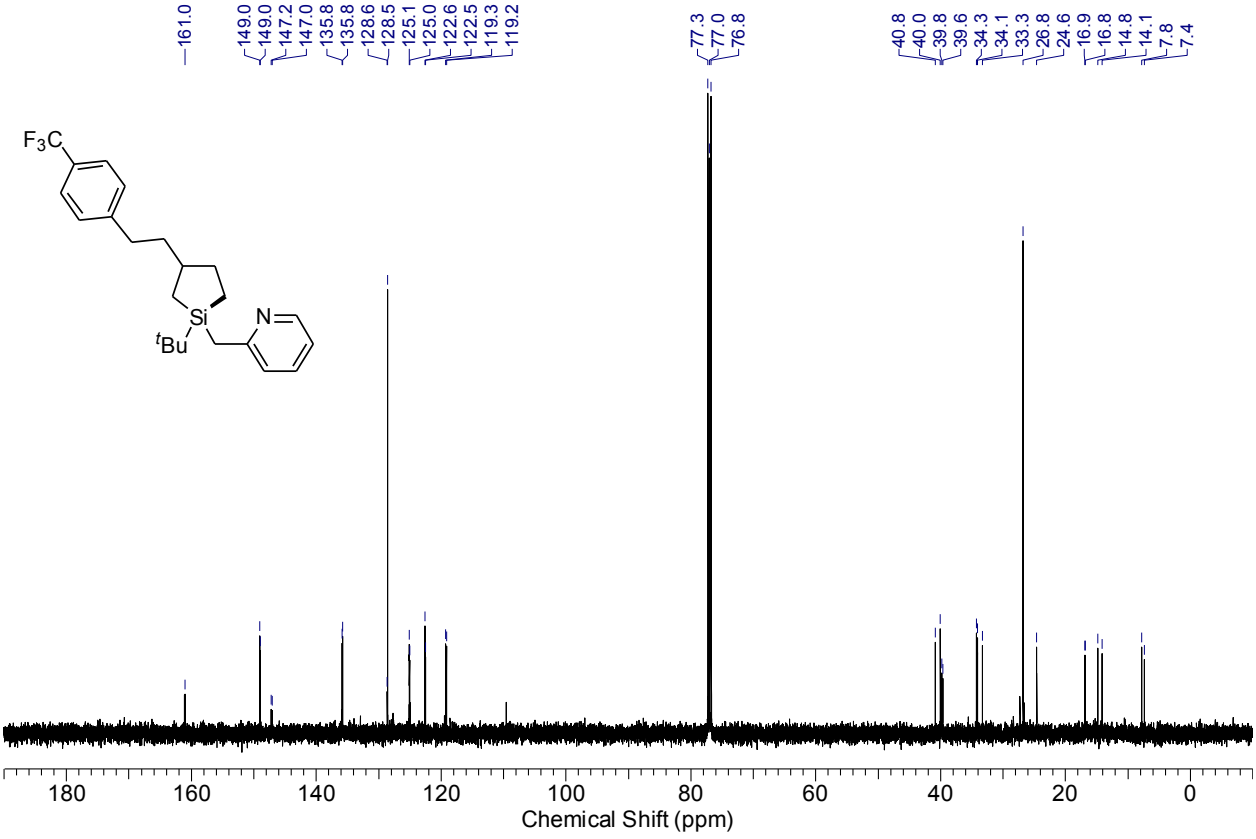
^{1}H and ^{13}C NMR spectra of **3n**



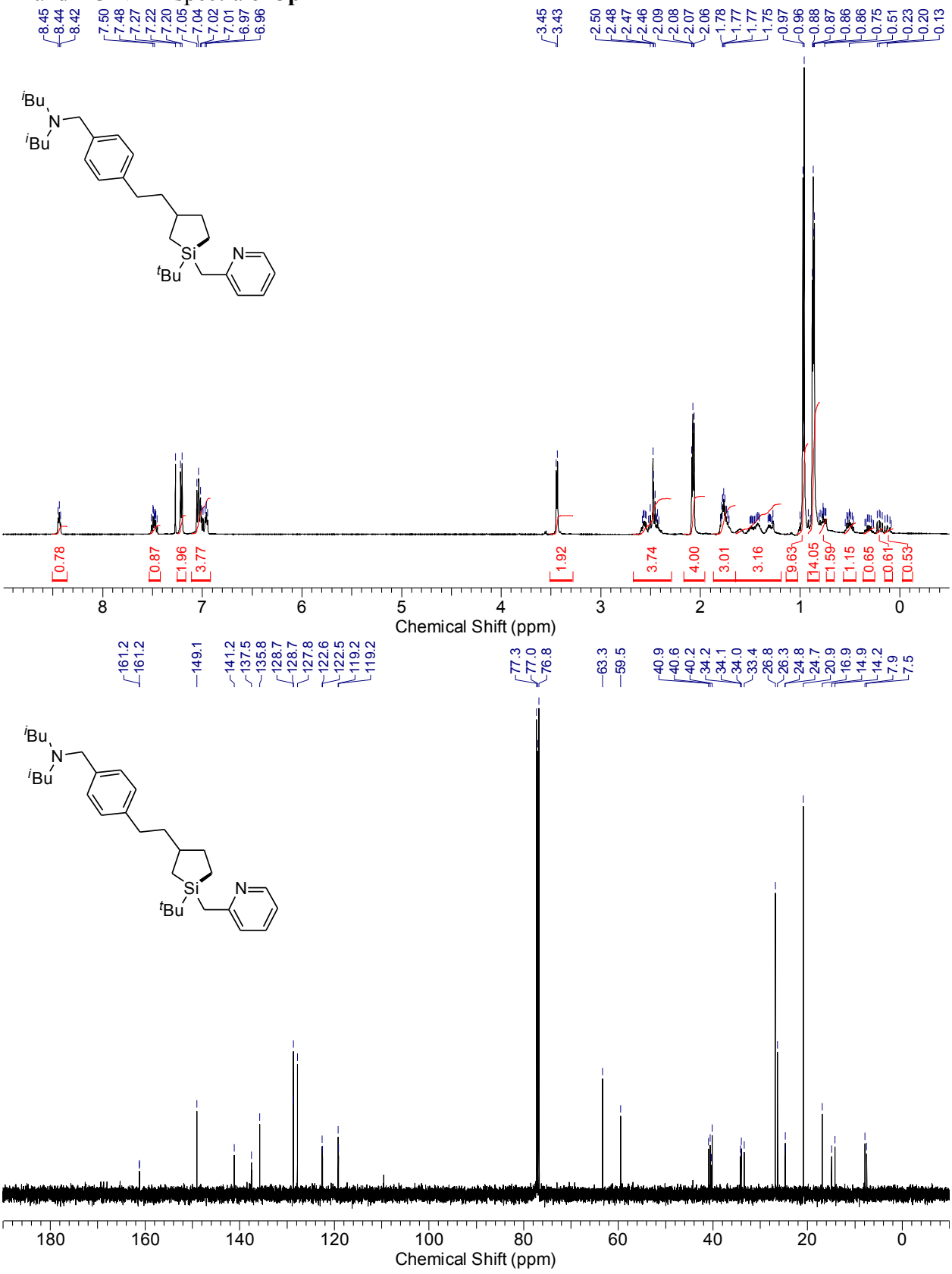


^{1}H and ^{13}C NMR spectra of **3o**

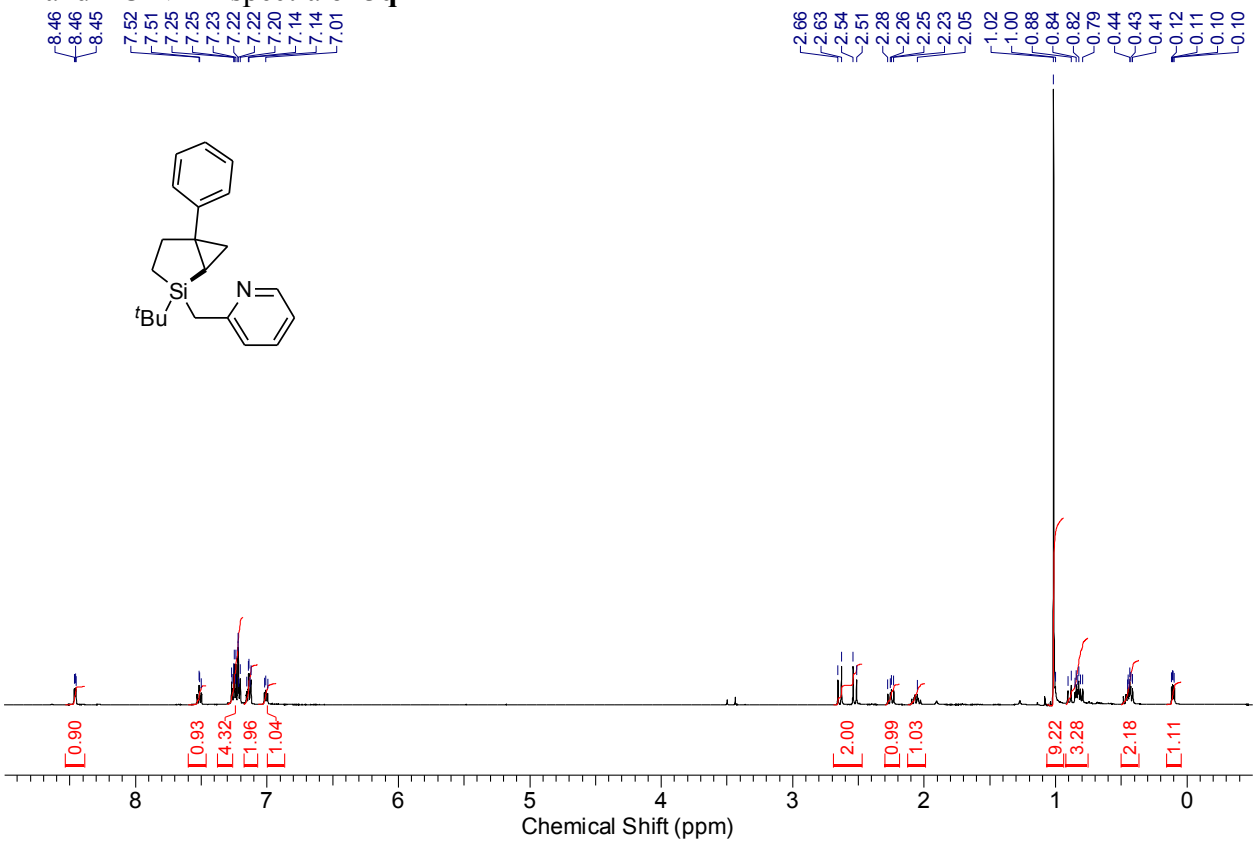


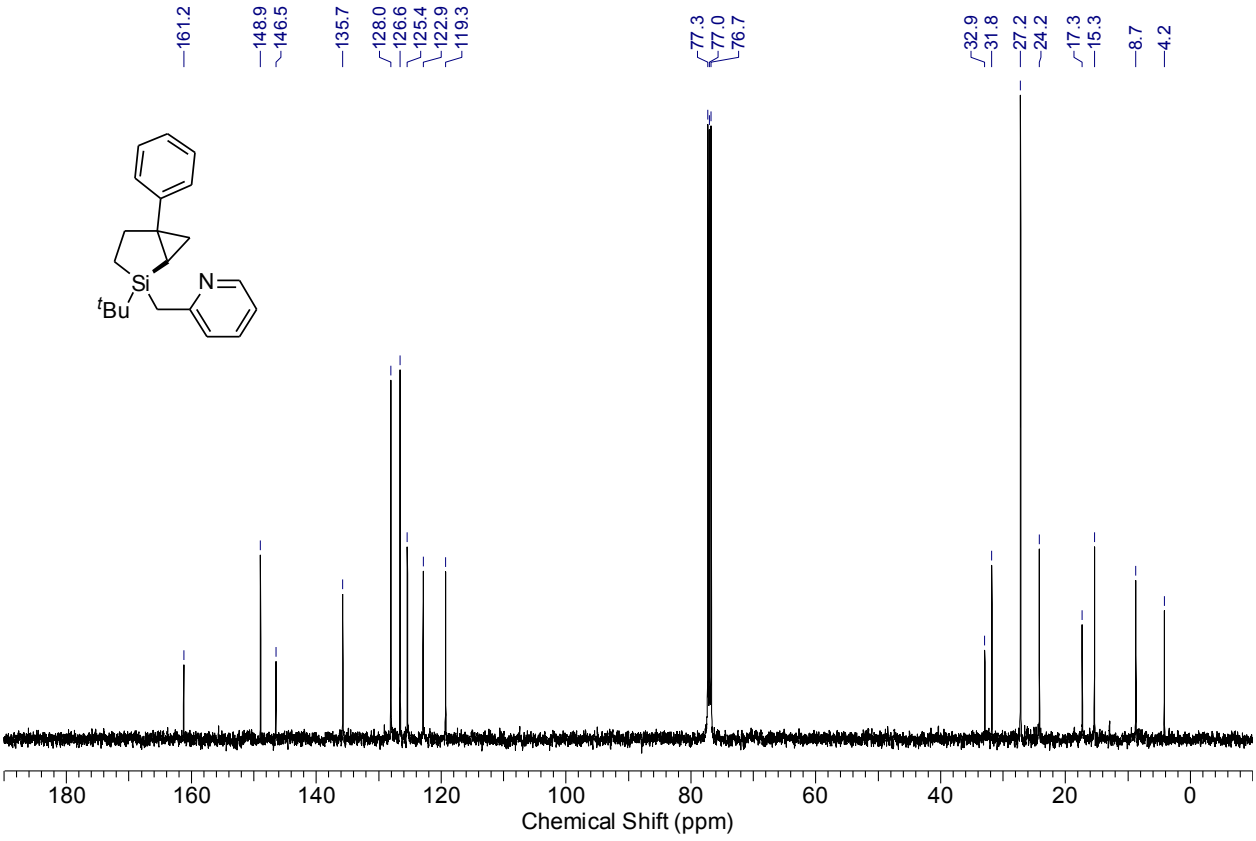


^{1}H and ^{13}C NMR spectra of **3p**

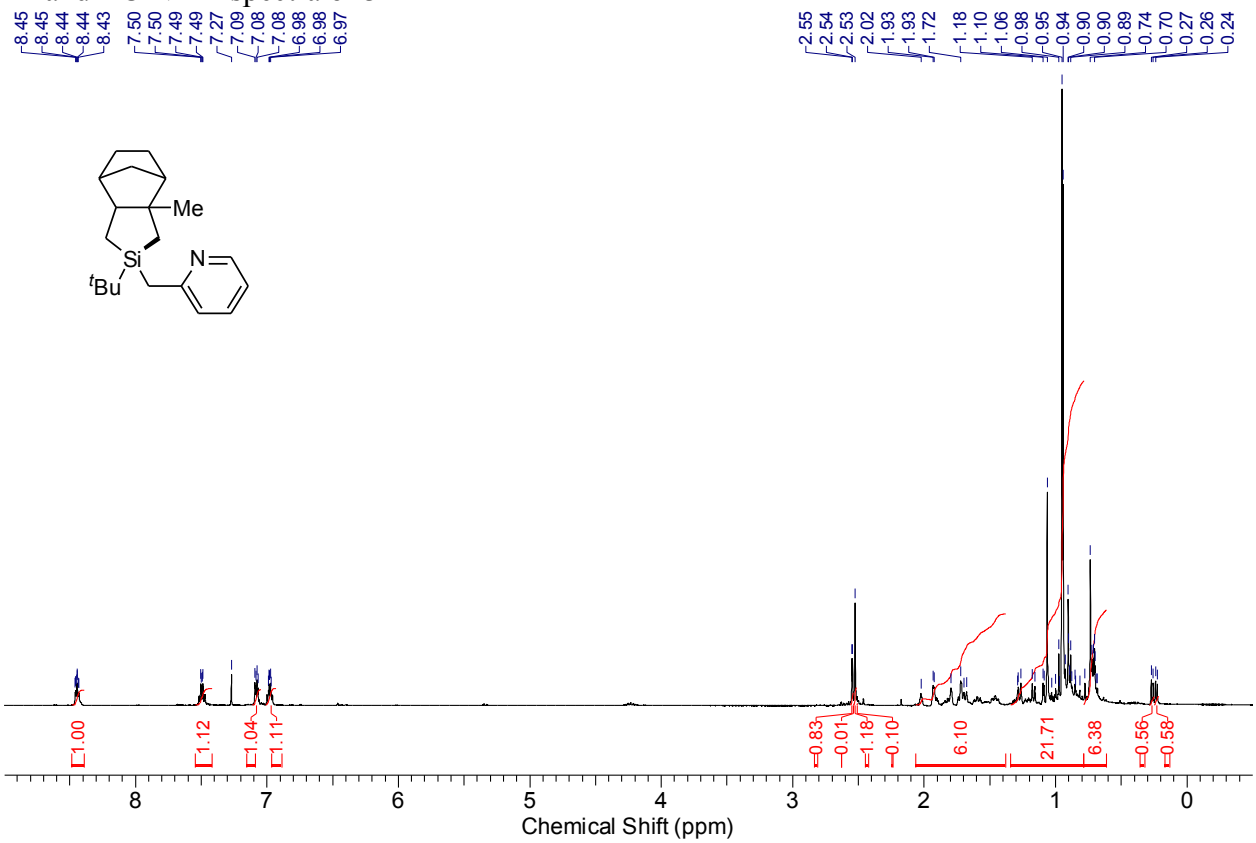


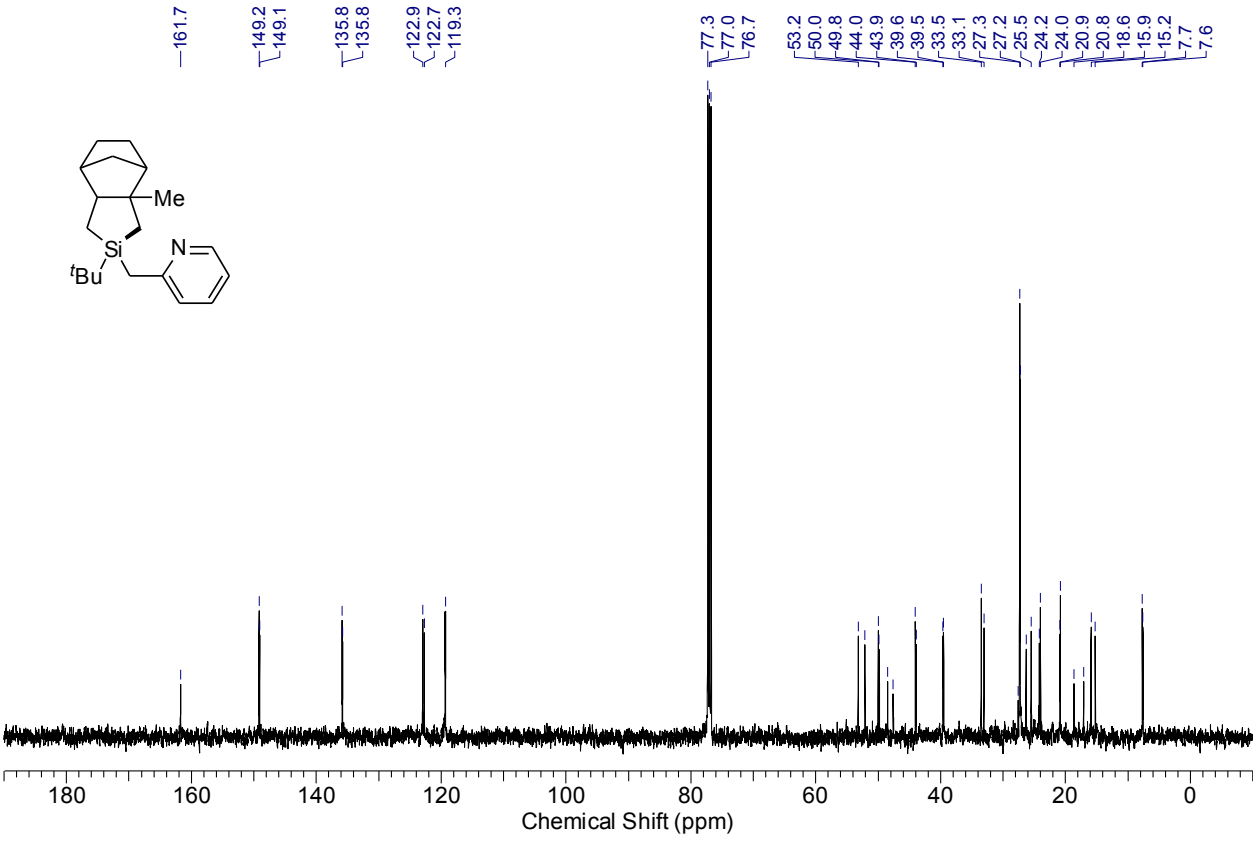
^{1}H and ^{13}C NMR spectra of **3q**



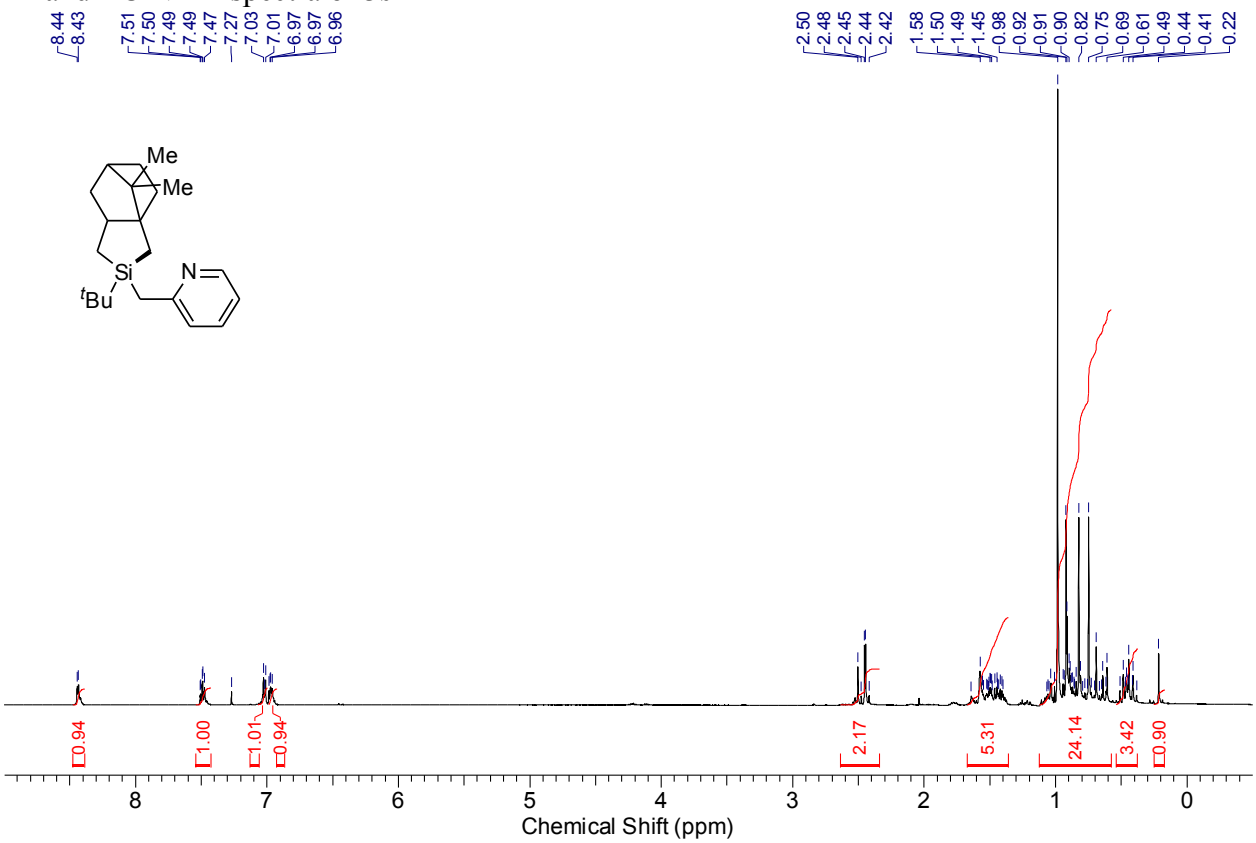


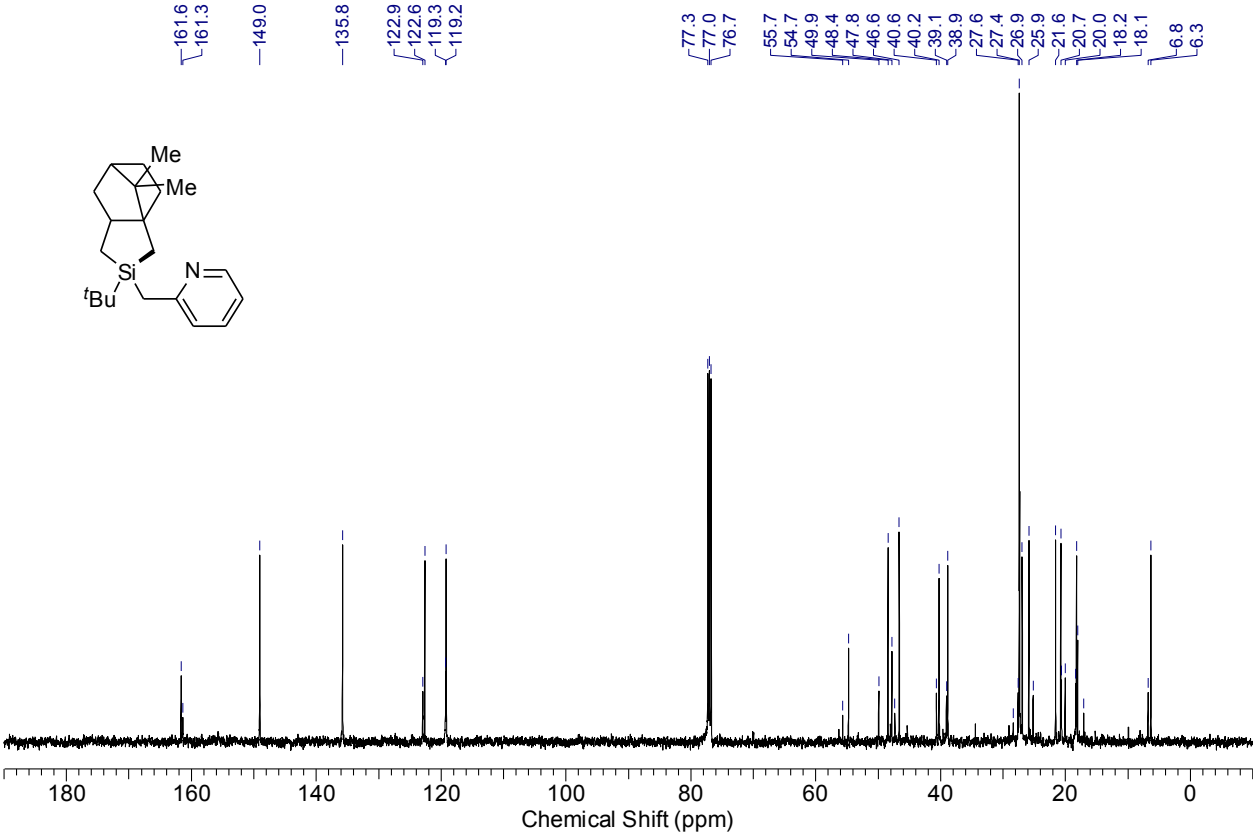
^{1}H and ^{13}C NMR spectra of **3r**



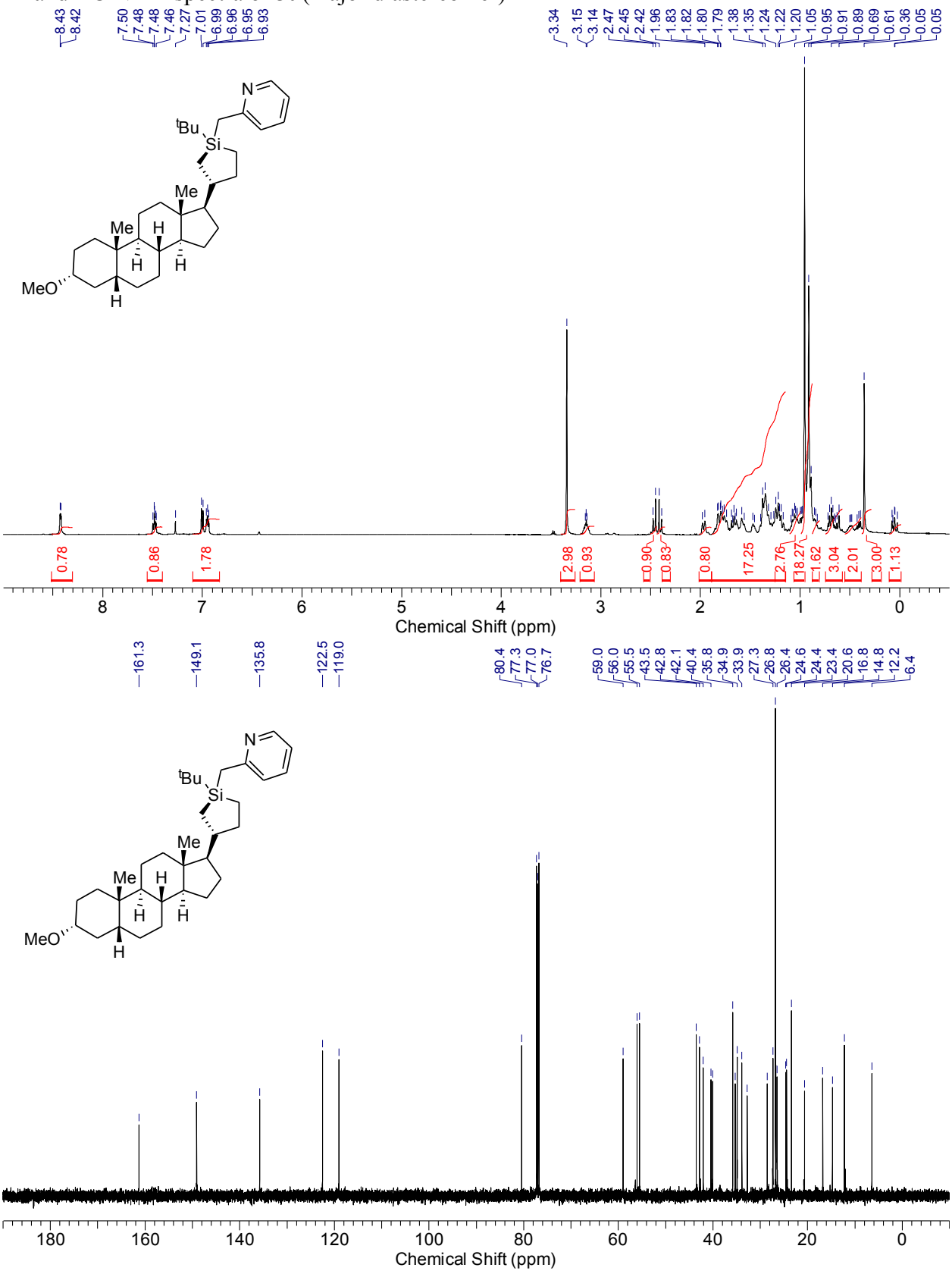


^{1}H and ^{13}C NMR spectra of **3s**

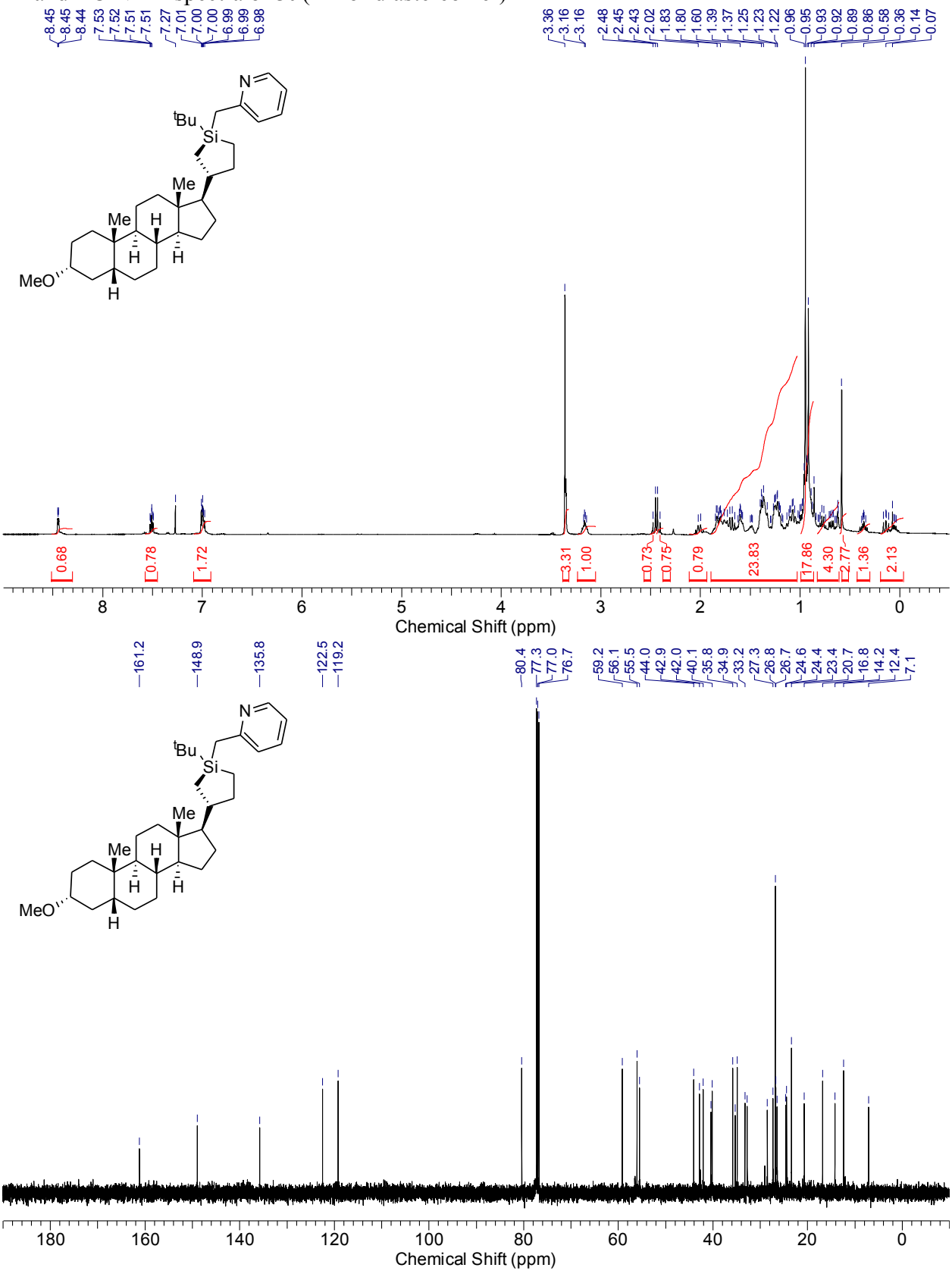




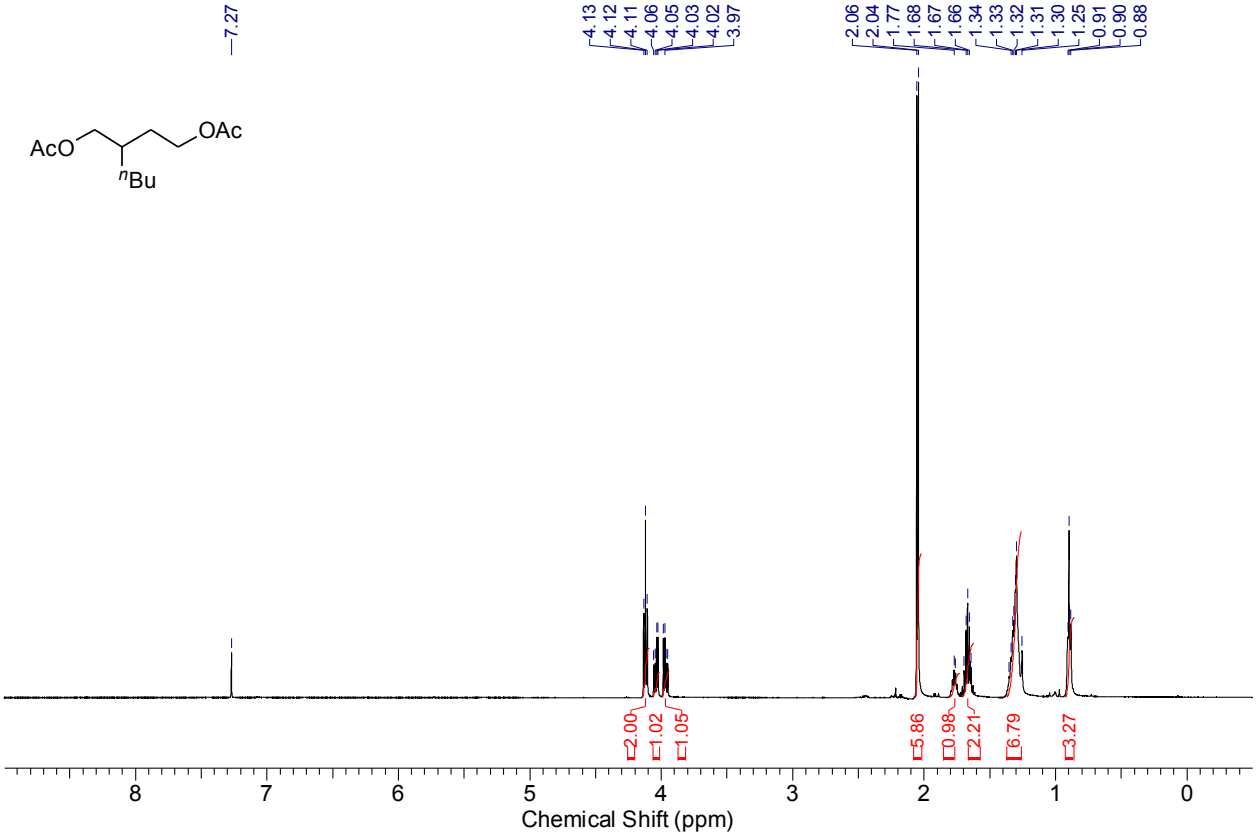
^{1}H and ^{13}C NMR spectra of **3t** (major diastereomer)

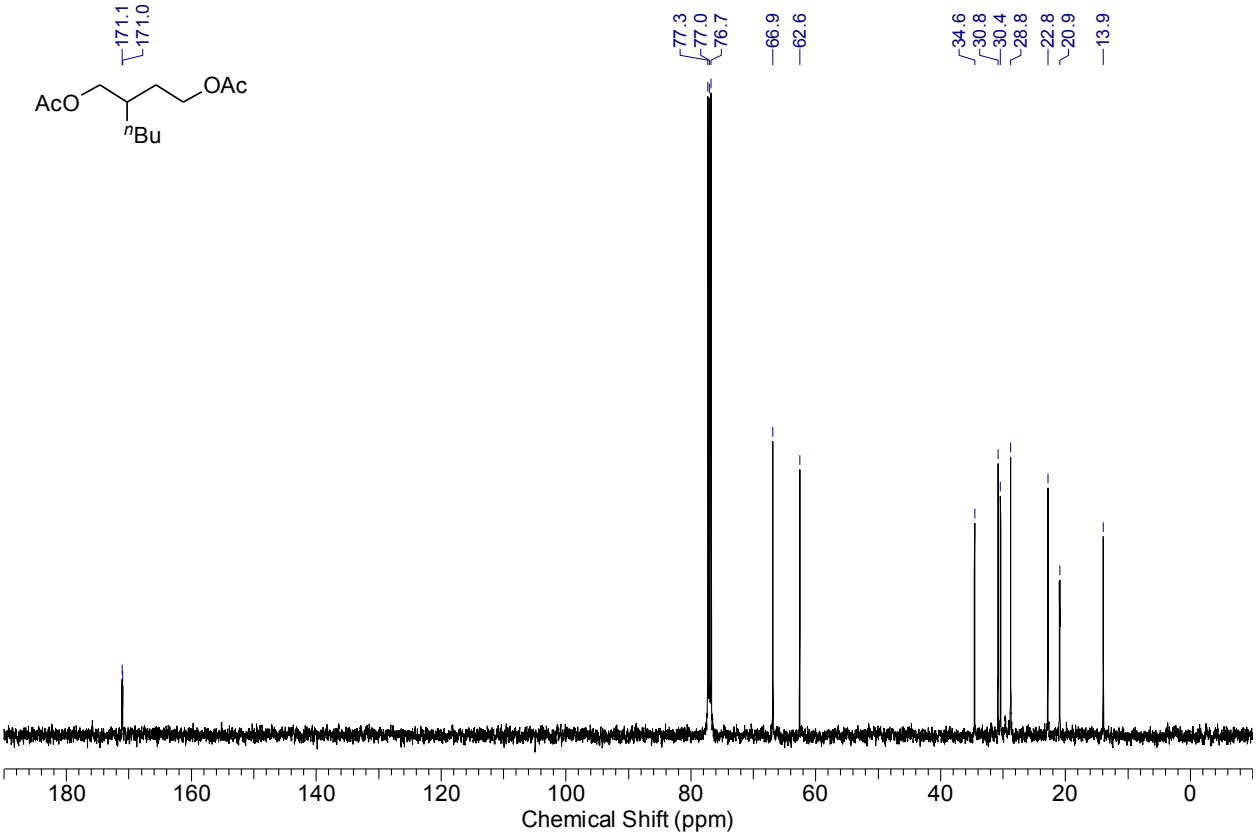


^{1}H and ^{13}C NMR spectra of **3t** (minor diastereomer)

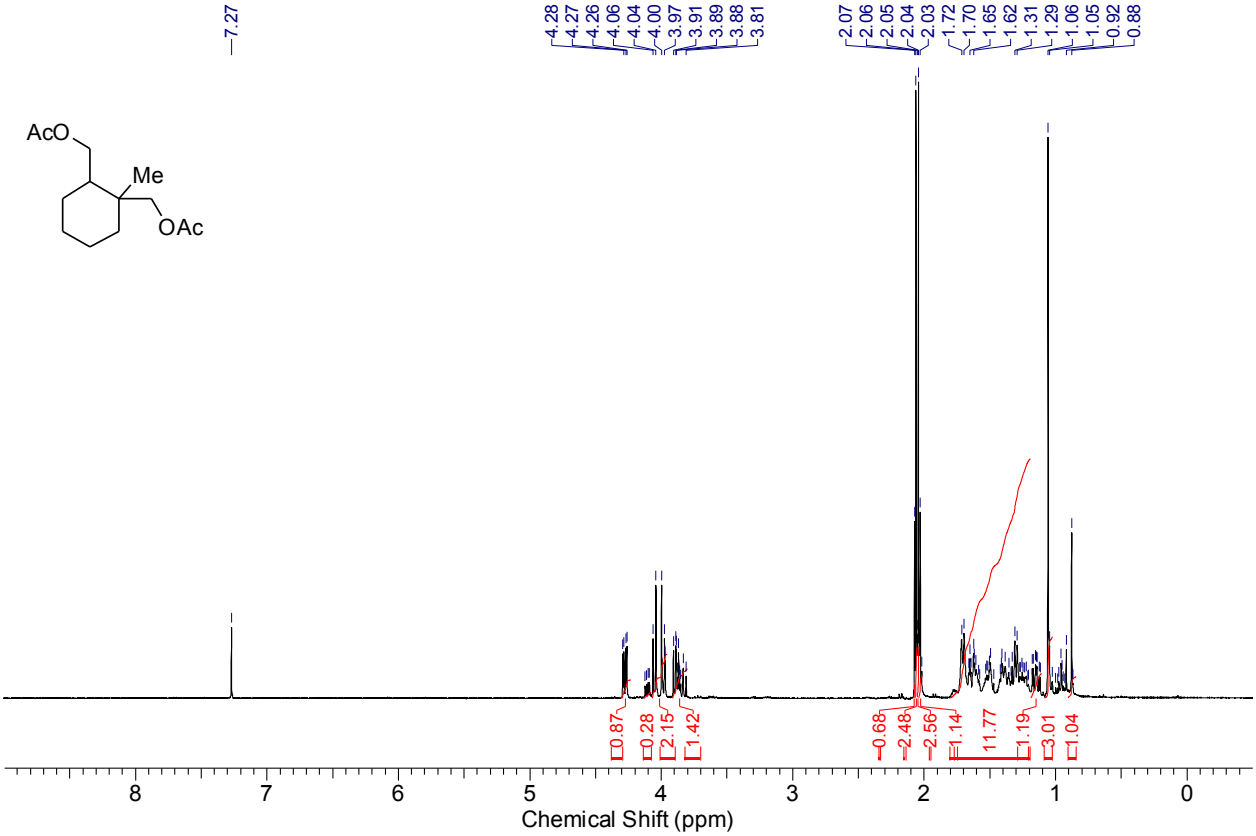


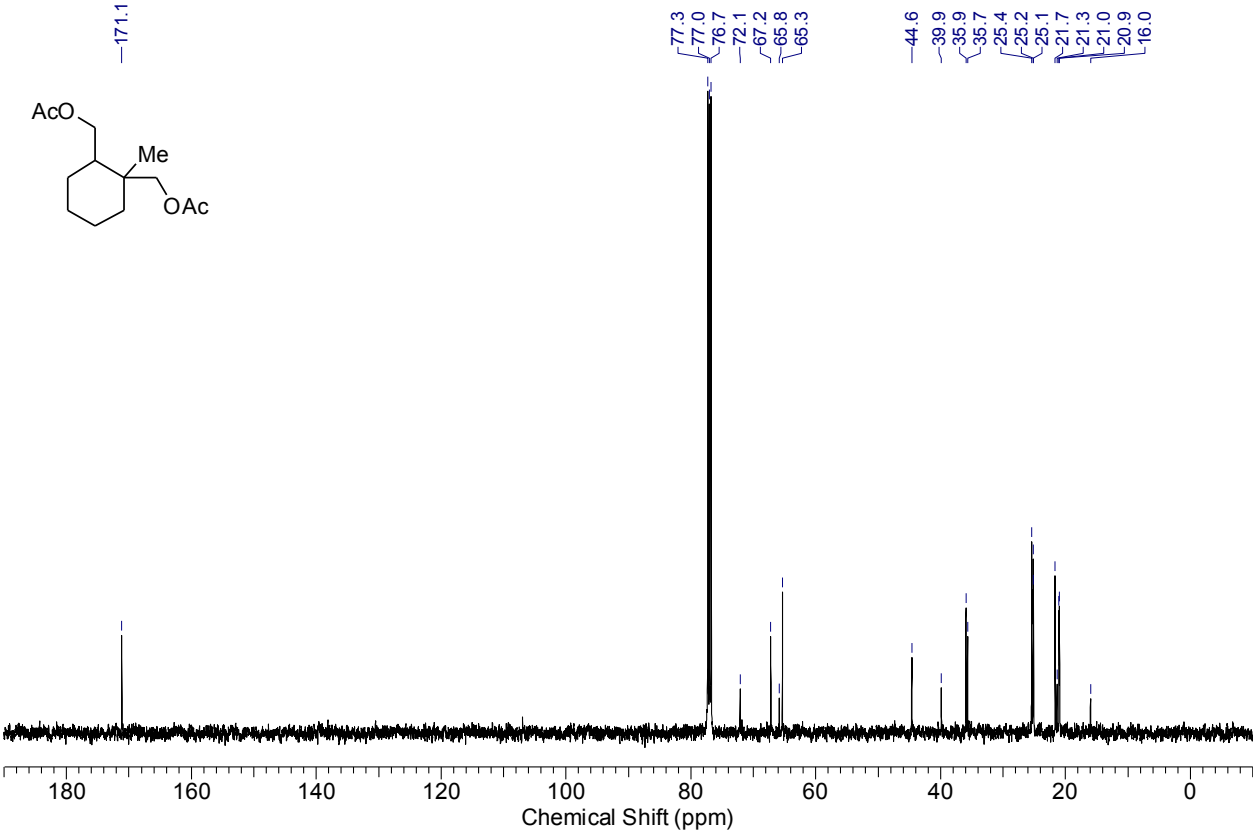
^{1}H and ^{13}C NMR spectra of **4c**



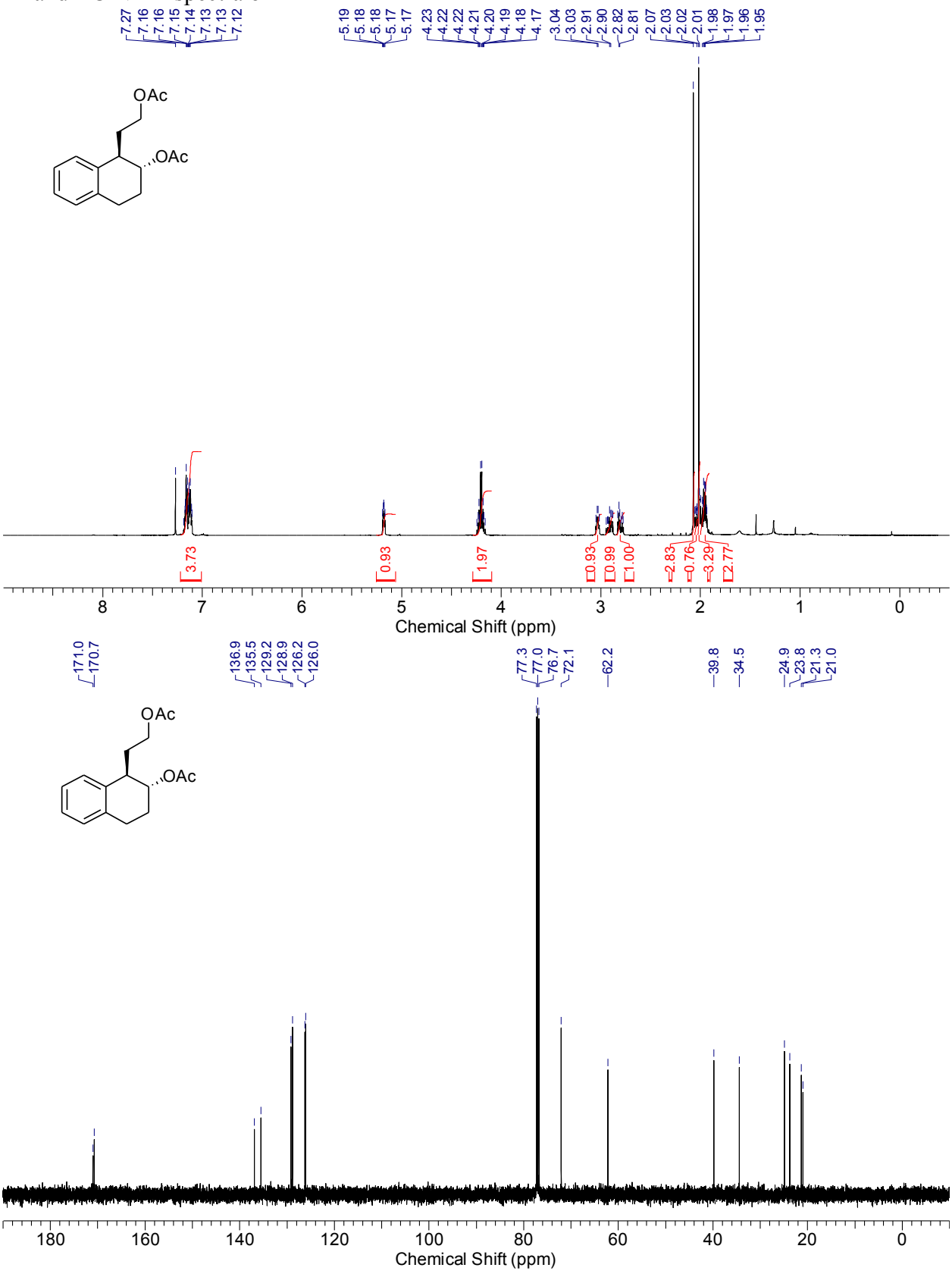


^{1}H and ^{13}C NMR spectra of **4g**

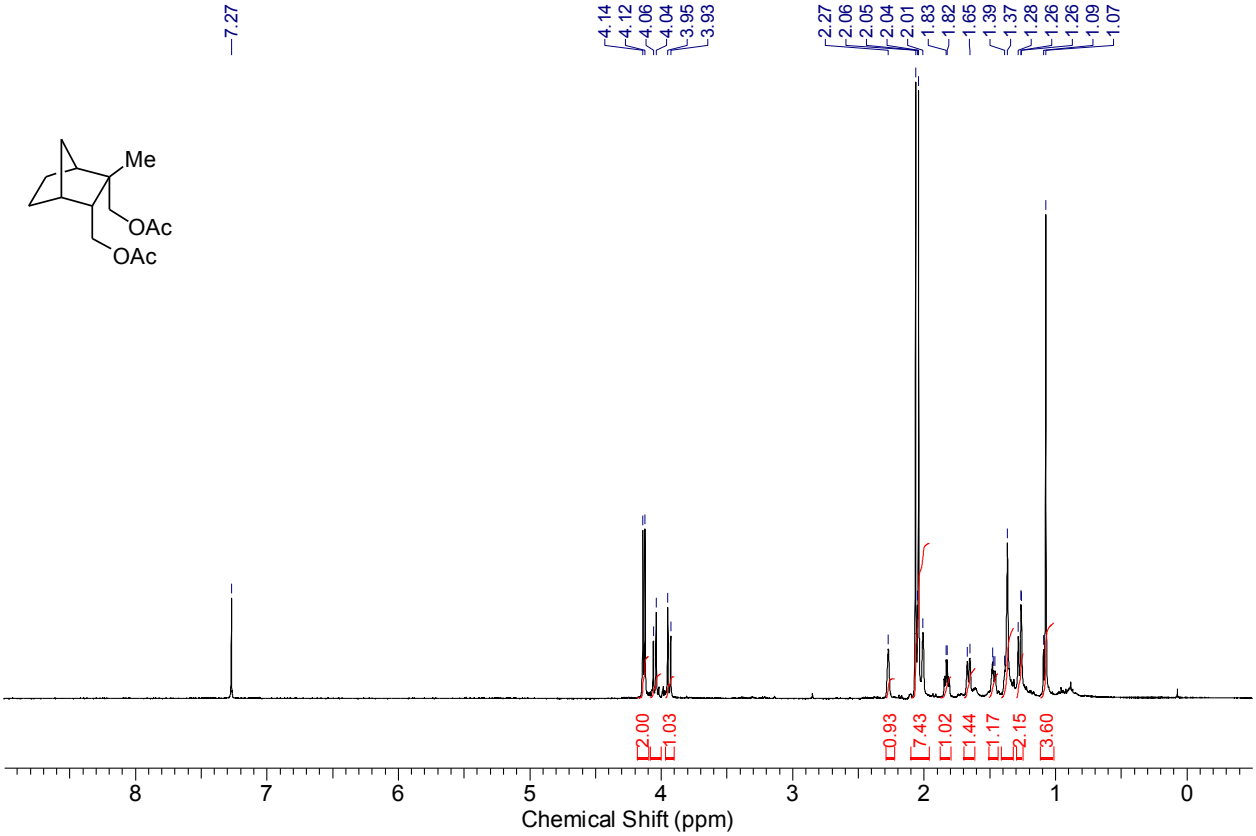


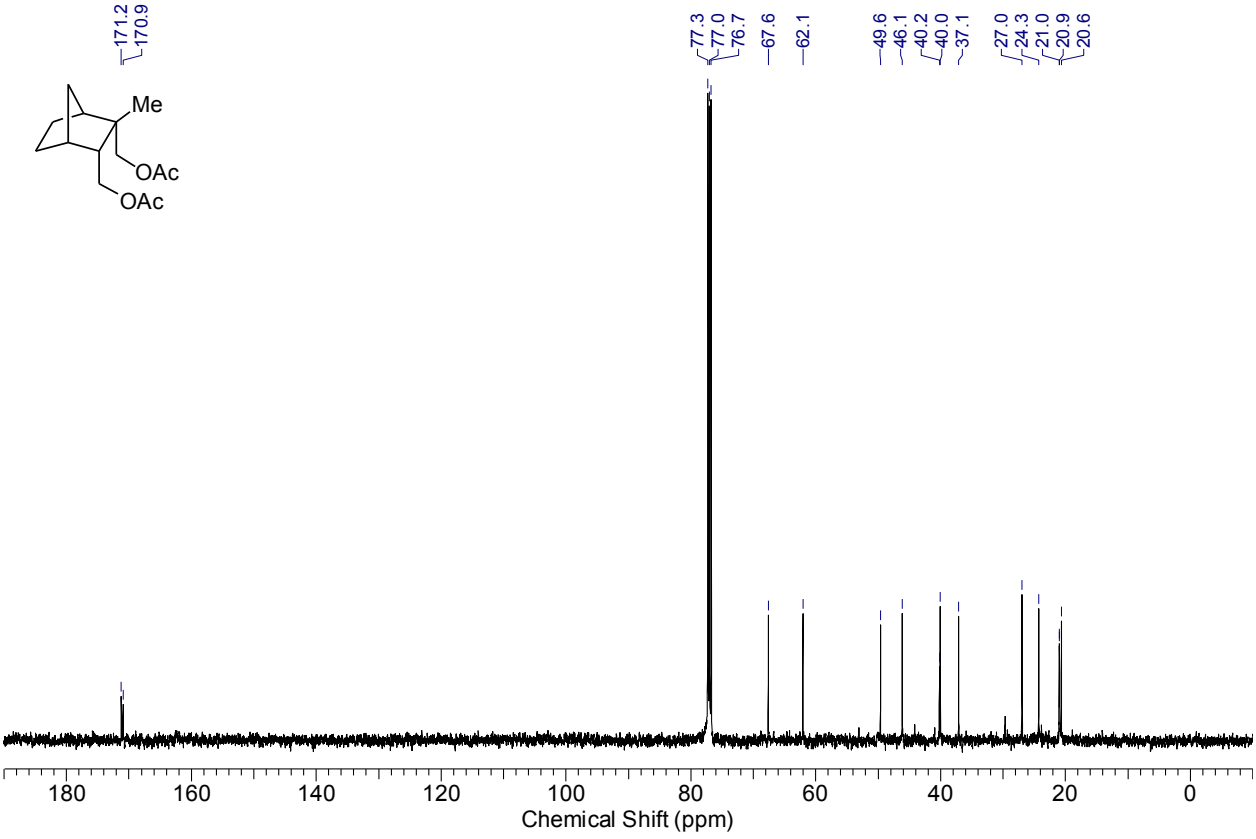


^{1}H and ^{13}C NMR spectra of **4h**

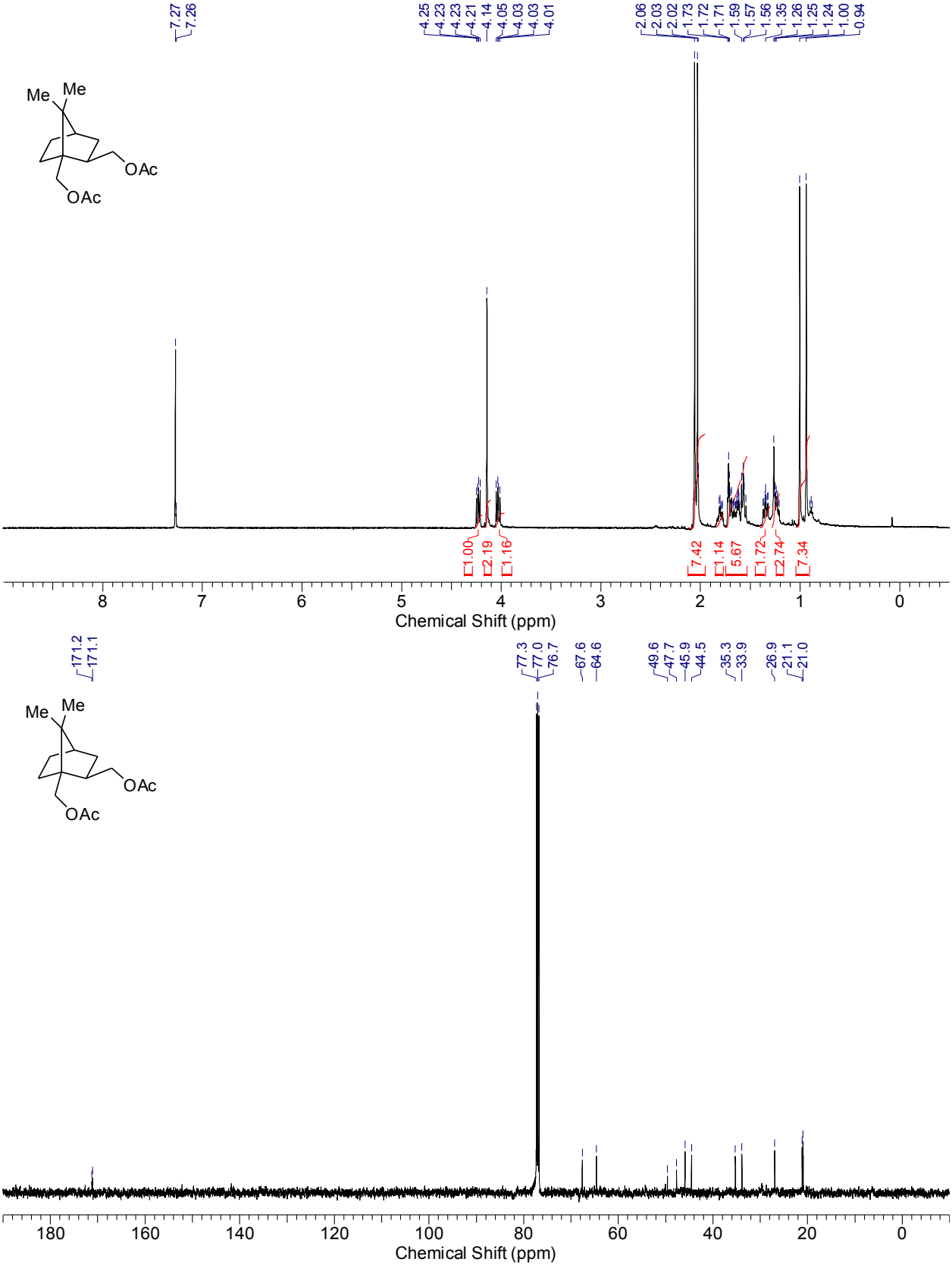


^{1}H and ^{13}C NMR spectra of **4i**

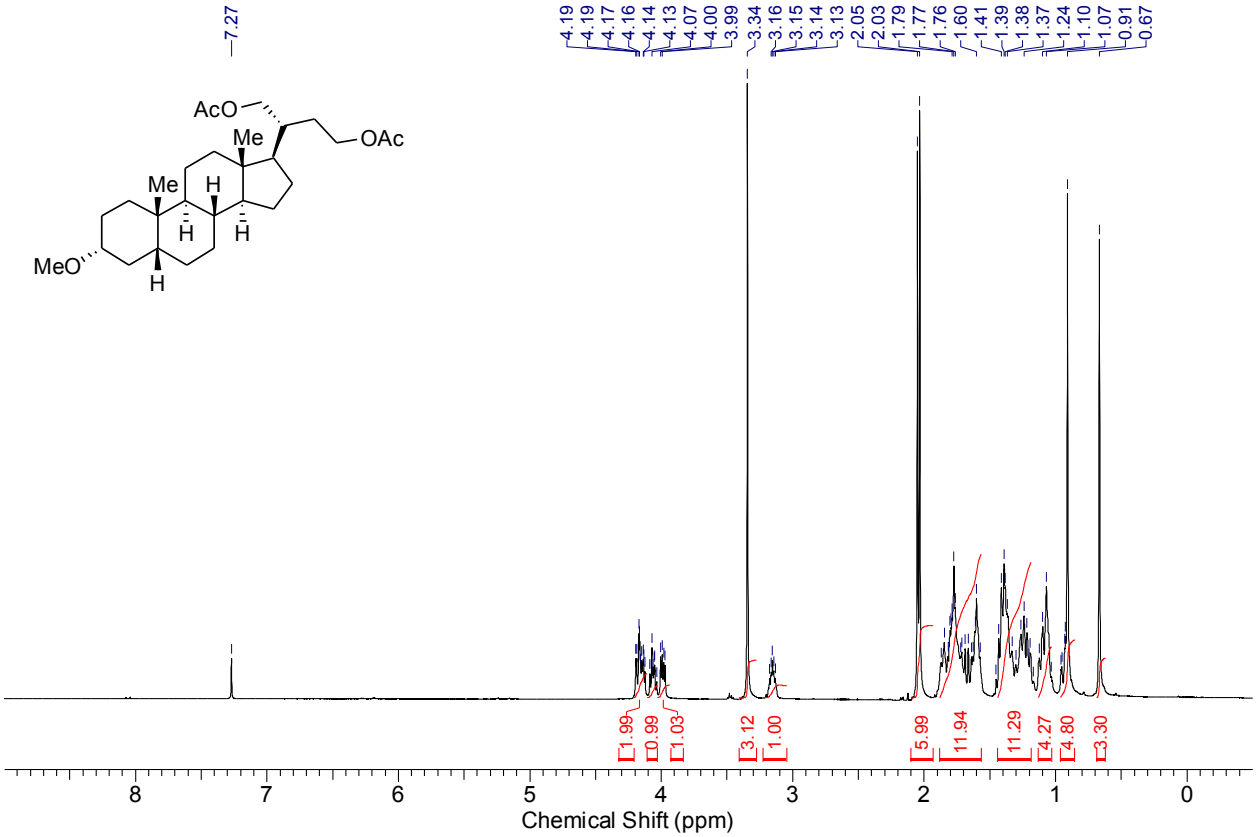


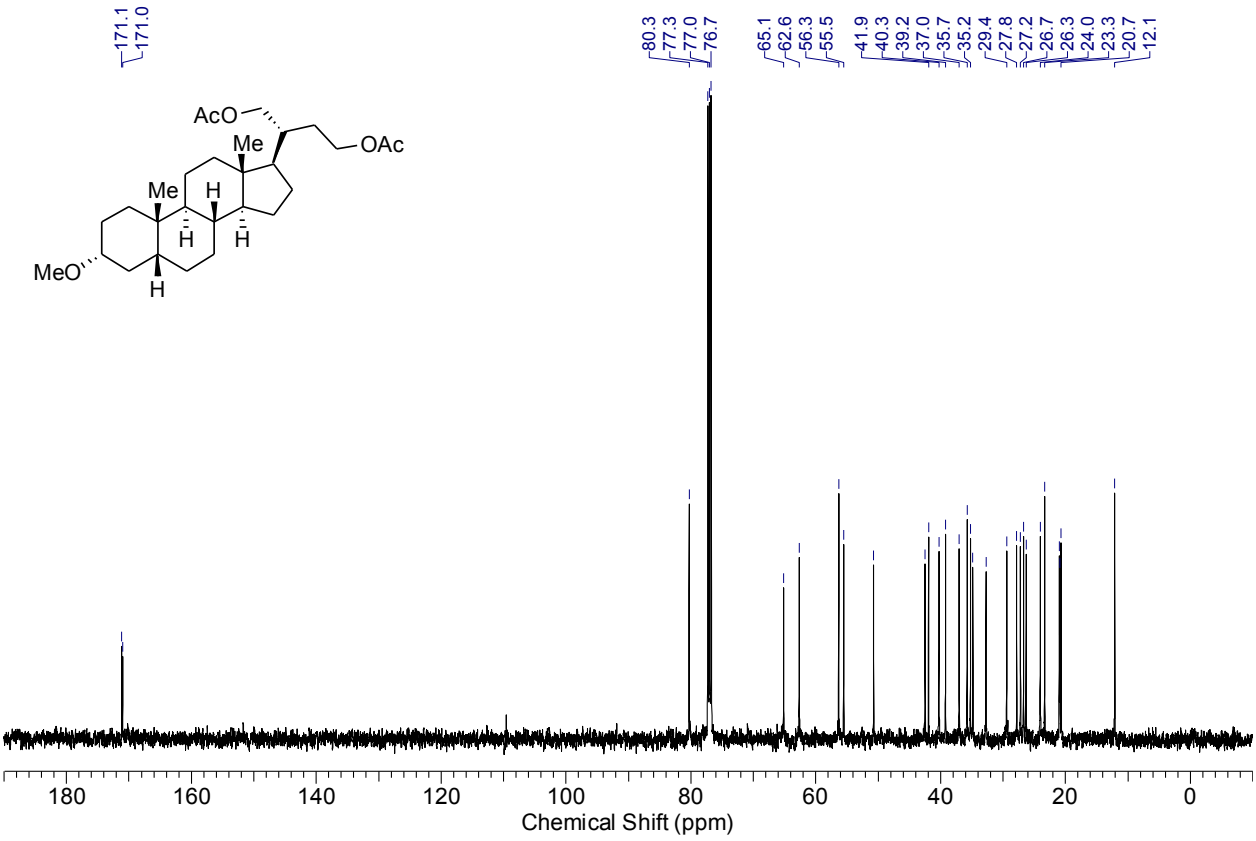


^{1}H and ^{13}C NMR spectra of **4s**



^{1}H and ^{13}C NMR spectra of **4t**





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