Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Palladium-Catalyzed C(sp^3)-Si Cross-Coupling Silylation of Benzyl Halides with Hydrosilanes

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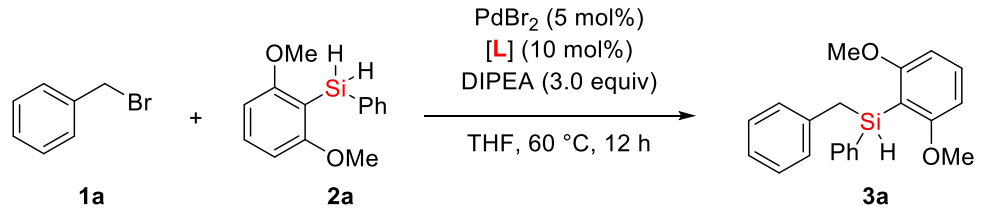
1. General Information

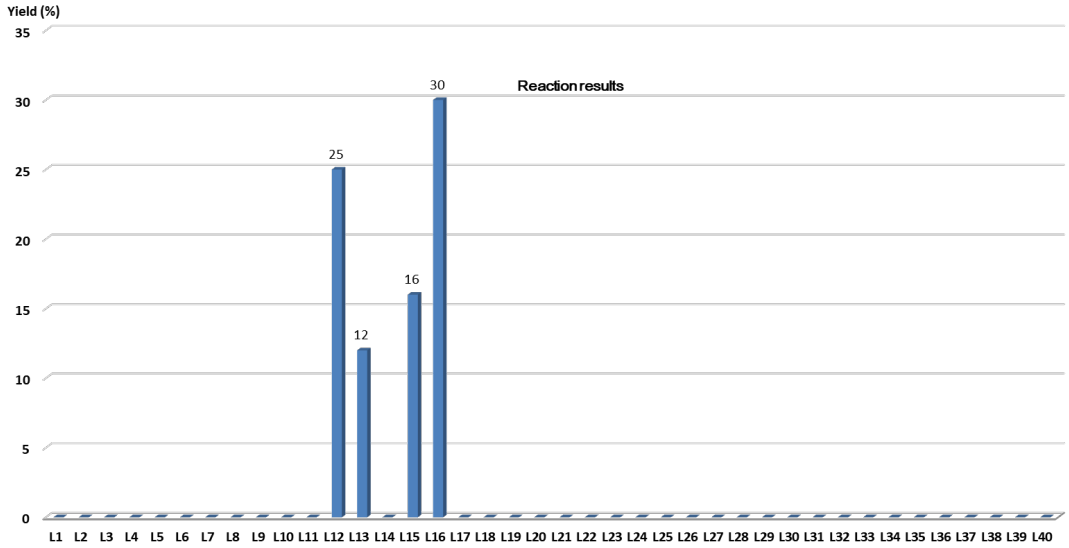
Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. Dichloromethane (DCM), toluene, were freshly distilled from CaH_2, Ether (Et_2O), tetrahydrofuran (THF), 1,4-dioxane and cyclohexane were dried and distilled from metal sodium and benzophenone. Alcohol solvents were dried and distilled from metal magnesium. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh). NMR spectra were recorded on a Bruker 400-, 500- (400 MHz for ^{1} H; 101 MHz for ^{13}C, 500 MHz for ^{19}F). The chemical shifts (δ, ppm) were quoted in parts per million (ppm) referenced to TMS (0.00 ppm for ^{1}H NMR) and $CDCl_3$ (77.16 ppm for ^{13}C NMR) The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublets of doublet, t = triplet, q = quartet, m = multiplets. Coupling constants, J, were reported in Hertz unit (Hz). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer.

2. Evaluation of Reaction Parameters

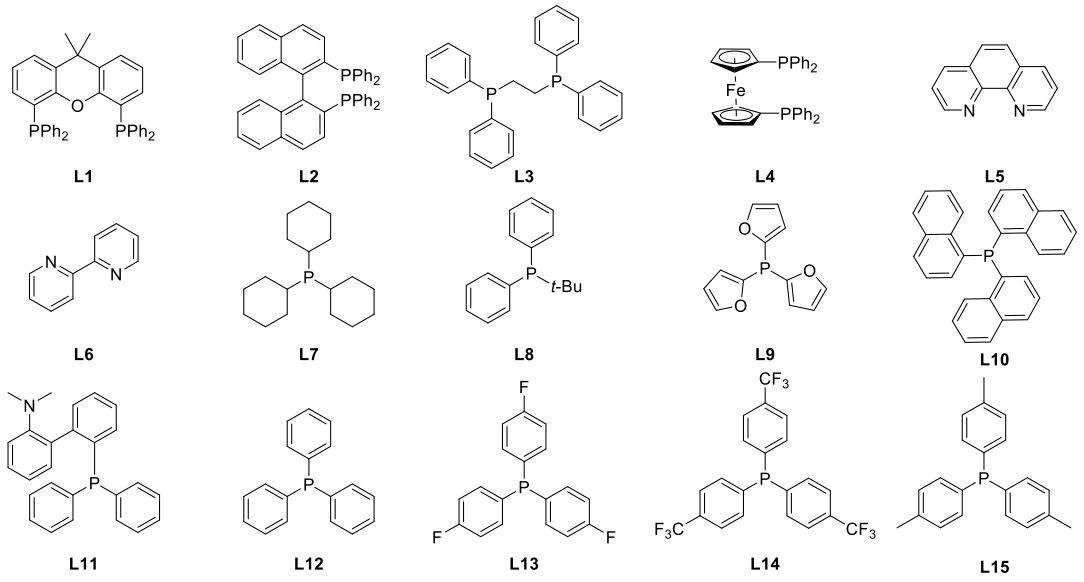
Table S1. Screening of the Phosphine Ligands [a]

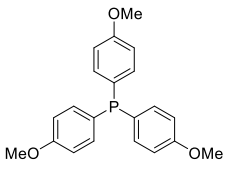


1a 2a 3a



[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (0.3 mmol), $PdBr_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), THF (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.





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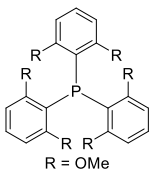

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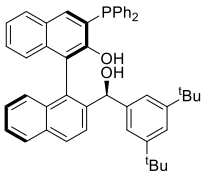

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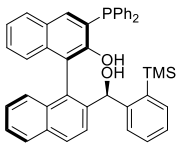

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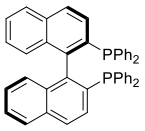

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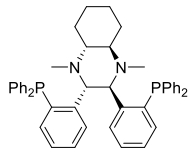

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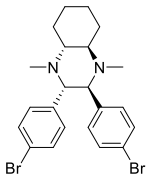

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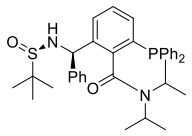

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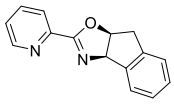

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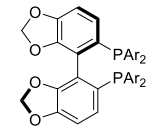

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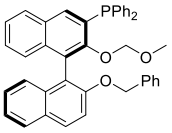

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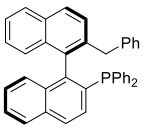

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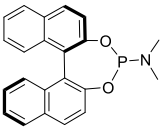

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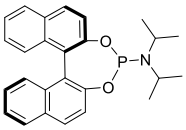

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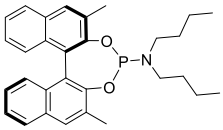

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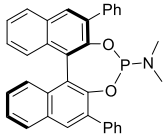

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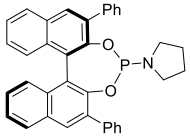

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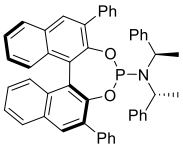

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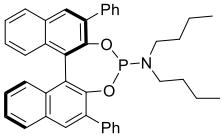

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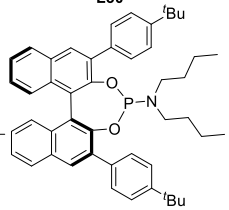

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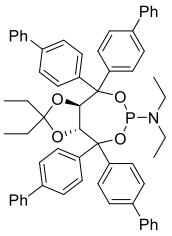

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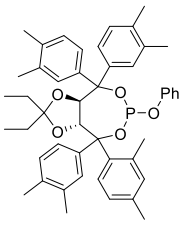

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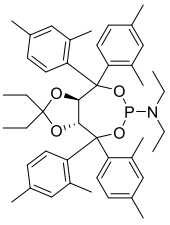

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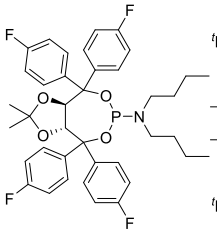

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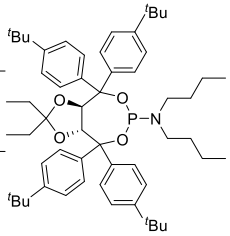
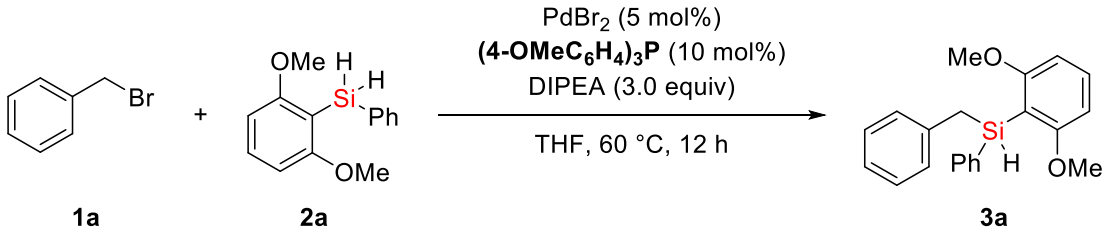


L40

Table S2. Screening of the Additives [a]

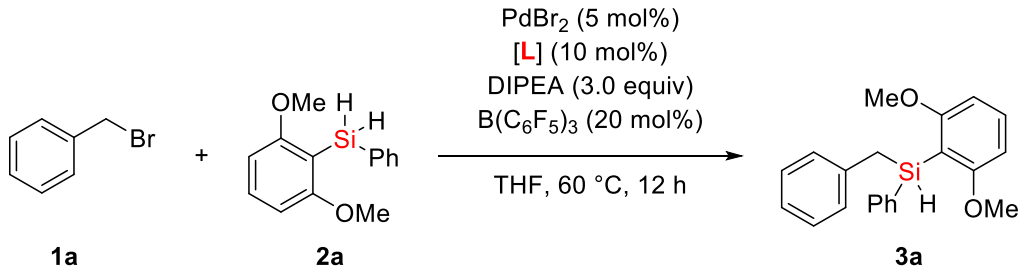


1a **2a** **3a**

Entry	Additive	Yield of (3a) (%)[b]
1	none	39
2	With 20% $B(C_6F_5)_3$	51
3	With 20% $B(C_6F_5)_3$	43[c]
4	With LiBr (2.0 eq.)	36
5	With 20 mol% LiO*t*-Bu	42
6	With 20 mol% $NaBPh_4$	46
7	With 20 mol% 4(3,5-2(CF_3)Ph)BNa	43
8	With 20% $B(C_6F_5)_3$, Without Pd and Ligand	N.R.

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (1 mmol), $PdBr_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), THF (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. [c]with 1.5 equiv **2a**.

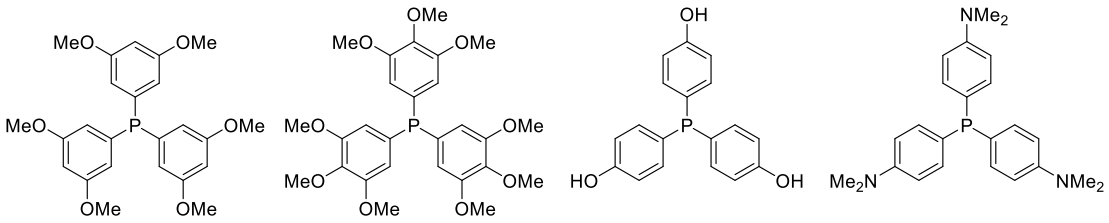
Table S3. Screening of the Triaryl Phosphines [a]



1a **2a** **3a**

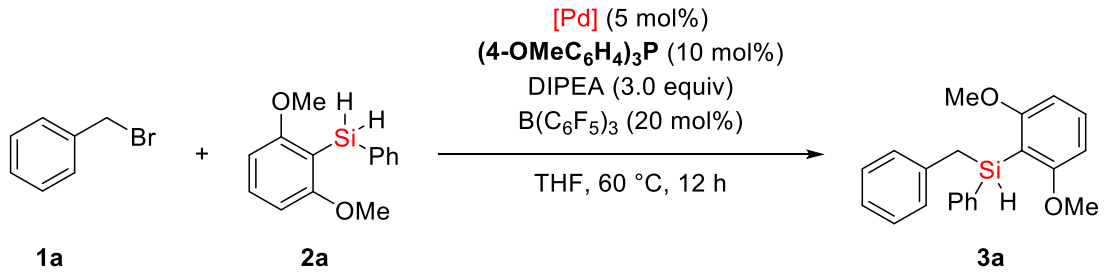
Entry	Ligand	Yield of (3a) (%)[b]
1	**L41**	47
2	**L42**	49
3	**L43**	N.D.
4	**L44**	52

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (1 mmol), $PdBr_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), $B(C_6F_5)_3$ (20 mol%), THF (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.



L41 **L42** **L43** **L44**

Table S4. Screening of the Pd Catalysts [a]

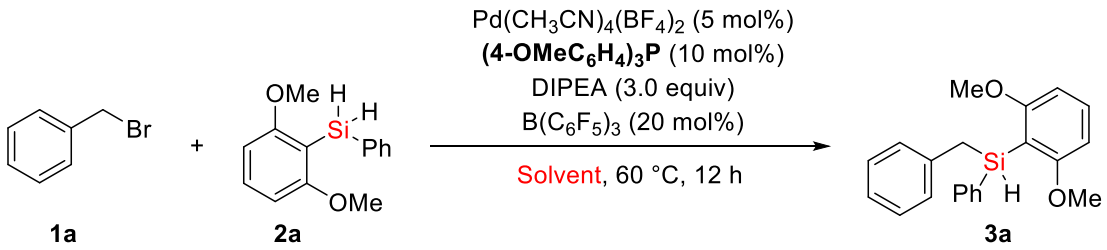


1a **2a** **3a**

Entry	Pd Cat.	Yield of (3a) (%)[b]
1	$PdBr_2$	52
2	$Pd(CH_3CN)_4(BF_4)_2$	55
3	$PdCl_2$	43
4	PdI_2	34
5	$Pd(OAc)_2$	Trace
6	$Pd(TFA)_2$	52
7	$Pd_2(dba)_3$	46
8	$Pd(PPh_3)_4$	55

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (1 mmol), Pd Catalyst (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), $B(C_6F_5)_3$ (20 mol%), THF (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

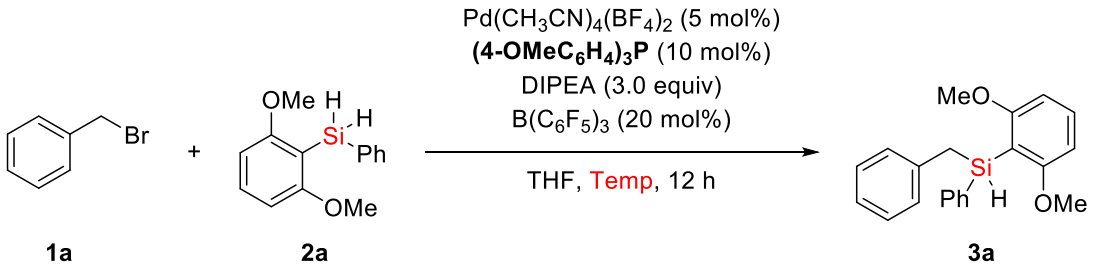
Table S5. Screening of the Solvents [a]



Entry	Solvent	Yield of (3a) (%)[b]
1	THF	55
2	Toluene	45
3	DCM	55
4	CH_3CN	54
5	1,4-Dioxane	53
6	NMP	22
7	Cyhexane	38

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (1 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), $B(C_6F_5)_3$ (20 mol%), Solvent (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S6 . The Effect of the Temperature on the Pd-catalyzed C(sp^3)-Si Cross-Coupling Silylation [a]

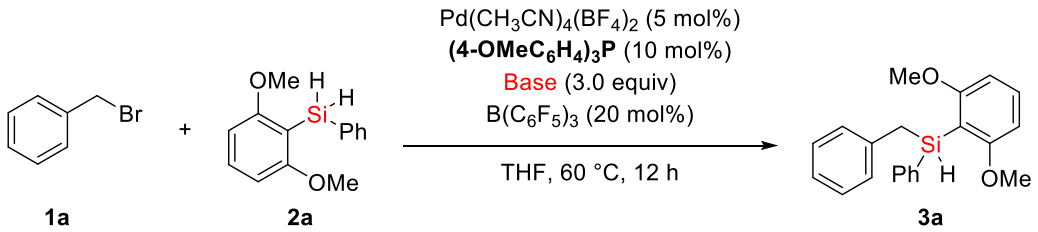


1a **2a** **3a**

Entry	Temp (^{o}C)	Yield of (3a) (%)[b]
1	r.t.	27
2	40	37
3	60	55
4	80	43
5	100	40

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (1 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), $B(C_6F_5)_3$ (20 mol%), THF (2 mL). [b]Determined by ^{1}H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S7. The Effect of the Bases on the Pd-catalyzed C(sp^3)-Si Cross-Coupling Silylation [a]

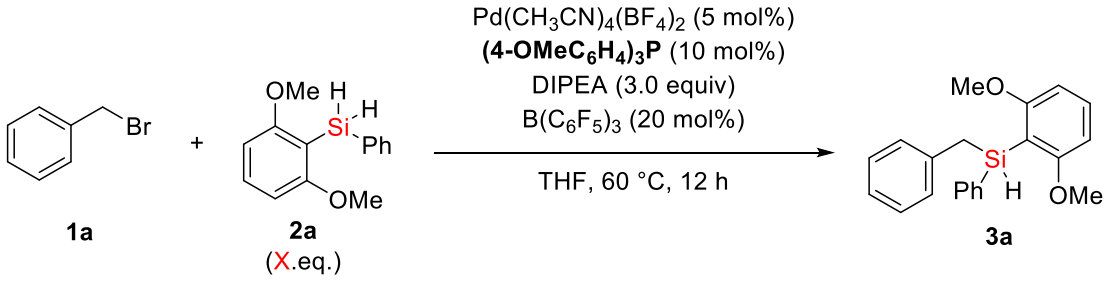


1a **2a** **3a**

Entry	Base	Yield of 3a (%)[b]
1	*N*-Methyl-*N*-phenylaniline	N.D.
2	*N*, *N*-Dimethylaniline	33
3	2,6-di-tert-butylpyridine	N.D.
4	2,6-Lutidine	N.D.
5	Hexamethylphosphorictriamide	N.D.
6	Trioctylamine	N.D.
7	DBU	N.D.
8	DABCO	N.D.
9	Cs_2CO_3	＜5
10	LiO*t*-Bu	＜5
11	K_3PO_4	＜5

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (1 mmol), $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), $B(C_6F_5)_3$ (20 mol%), THF (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

Table S8. The Effect of the Amount of 2a on the Pd-catalyzed C(sp^3)-Si Cross-Coupling Silylation [a]

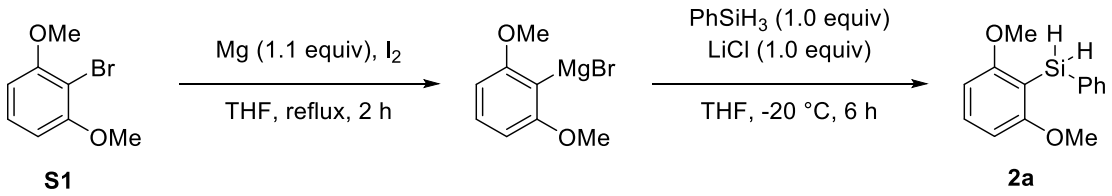


Entry	X eq.	Yield of (3a) (%)[b]
1	2	57
2	3	52
3	4	54
4	5	55

[a]Unless otherwise noted, reactions were conducted under N_2 on 0.2 mmol scale: **1a** (0.2 mmol), **2a** (X equiv), $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%), Ligand (10 mol%), DIPEA (0.6 mmol), $B(C_6F_5)_3$ (20 mol%), THF (2 mL). [b]Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard.

3. Experimental Section

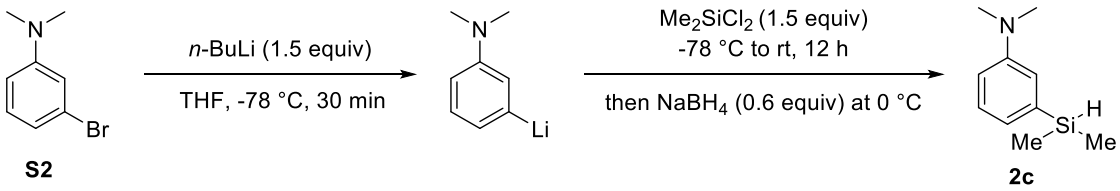
3.1 Procedure for the Synthesis of Dihydrosilanes



1a-1v were purchased from commercial suppliers and used without further purification. Following a literature procedure[1], a flame dried 200 mL, round bottom flask equipped with a water-cooled condenser was charged with magnesium turnings (1.1 equiv), three pieces of iodine partials, THF under nitrogen atmosphere. 2-bromo-1,3-dimethoxybenzene (1.0 equiv) was then slowly added over 15 minutes to the refluxing mixture of THF and magnesium turnings. The mixture was refluxed for an additional 2 hours. The resulting Grignard reagent was cooled to 25 ˚C for the subsequent steps.

A suspension of LiCl (2.0 equiv, 0.5 M in THF) was prepared, and the Grignard reagent (0.97 M in THF) was added to it, followed by the addition of phenylsilane (1 equiv), all at room temperature under an argon atmosphere. The reaction mixture was stirred in an oil bath maintained at -20 °C for 6 hours. The reaction was quenched by the addition of an aqueous solution of NH_4Cl (10 mL) at room temperature. The resulting mixture was filtered through Celite and washed with ethyl acetate (20 mL×3). The organic phase was dried over Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by chromatography on silica gel eluting with PE, affording the title compound (1.5 g, 60% yield) as colorless oil. Other hydrosilanes using the same method or purchased from commercial suppliers.

3.2 Procedure for the Synthesis of 3-(Dimethylsilyl)-*N*, *N*-dimethylaniline

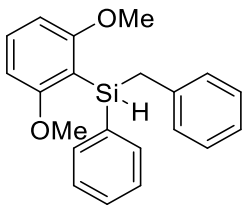


Following a literature procedure[2], 3-bromo-*N*, *N*-dimethylaniline (20.0 mmol, 3.98 g) was dissolved in THF (20 mL), and *n*-BuLi (2.5 M, 9.6 mL, 24 mmol) was added dropwise at -78 ºC under a nitrogen atmosphere. The reaction mixture was stirred at this temperature for 1 hour, and then Me_2SiHCl (25 mmol, 2.35 g) was added dropwise via a syringe. After the addition, the reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was quenched with aqueous saturated NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and filtered, and the filtrate was evaporated under vacuum. The residue was purified by column chromatography (hexane) on silica gel to yield 3-(dimethylsilyl)-*N*, *N*-dimethylaniline (2.15 g, 60% yield) as a colorless oil.

4. Procedure for the Synthesis of Benzylsilanes

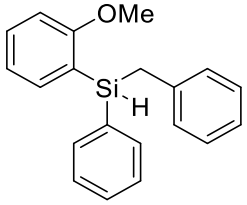
A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with compound **1** (0.2 mmol, if compound **1** was solid), $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%, 4.44mg 0.01 mmol), $(4\text{-}OMeC_6H_4)_3P$ (10 mol%, 7.04 mg 0.02 mmol), $B(C_6F_5)_3$ (20 mol%, 20.48 mg, 0.04 mmol). The tube was evacuated and backfilled with N_2. Then, the solvent THF (2 mL) was added to this mixture under N_2. After that, compound **1** (0.2 mmol, if compound **1** was liquid), hydrosilane (0.4 mmol, 2 equiv), DIPEA (77.54 mg, 3 equiv) were added under N_2. The reaction was stirred at 60 ºC for 12 hours. After completion of the reaction, the mixture was cooled to room temperature. It was then diluted with 10 mL of CH_2Cl_2. The combined organic phases were concentrated, and the resulting residue was purified by column chromatography on silica gel (PE or PE/EA) to provide the desired product.

5. Spectral Data of Products



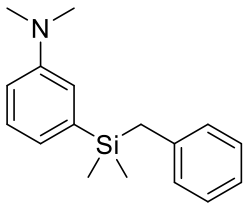
Benzyl(2,6-dimethoxyphenyl)(phenyl)silane (3a)

Colorless oil (34 mg, 50% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.37 (m, 2 H), 7.29-7.15 (m, 4 H), 7.06 (t, J = 8 Hz, 2 H), 7.02-6.91 (m, 3 H), 6.42 (d, J = 8 Hz, 2 H), 4.94 (t, J = 4 Hz, 1 H), 3.63 (s, 6 H), 2.66 (t, J = 4 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.35, 139.47, 134.43, 134.03, 131.46, 127.90, 127.58, 126.99, 126.40, 123.06, 108.27, 102.62, 54.47, 21.89. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{21}H_{22}O_2NaSi$: 357.1281, found: 357.1259.



Benzyl(2-methoxyphenyl)(phenyl)silane (3b)

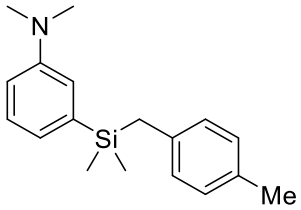
Colorless oil (29 mg, 48% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2 H), 7.31-7.19 (m, 5 H), 7.04 (t, J = 8 Hz, 2 H), 6.97-6.89 (m, 3 H), 6.81 (t, J = 7.2 Hz, 1 H), 6.74 (d, J = 8.4 Hz, 1 H), 4.79 (t, J = 1.8 Hz, 1 H), 3.67 (s, 3 H), 2.72-2.55 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.33, 139.78, 137.34, 135.37, 134.47, 131.93, 129.48, 128.69, 128.27, 127.83, 124.42, 122.32, 120.84, 109.75, 55.24, 22.29. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{20}H_{20}ONaSi$: 327.1176, found: 327.1180.



3-(benzyldimethylsilyl)-*N*, *N*-dimethylaniline (3c)

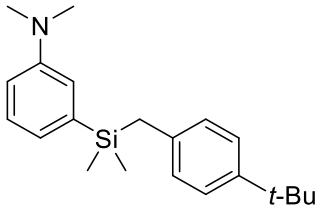
Colorless oil (38 mg, 70% yield for BnBr; 30 mg, 55% yield for BnCl), purified by column

chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 8 Hz, 1 H), 7.09 (t, J = 8 Hz, 2 H), 7.00-6.94 (m, 1H), 6.91-6.86 (m, 2 H), 6.76 (d, J = 4 Hz, 1 H), 6.73-6.65 (m, 2 H), 2.82 (s, 6 H), 2.22 (s, 2 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.96, 140.04, 139.07, 128.60, 128.47, 128.18, 124.10, 122.16, 117.90, 113.73, 40.76, 26.34, -3.22. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{17}H_{24}NSi$: 290.1673, found: 290.1677.



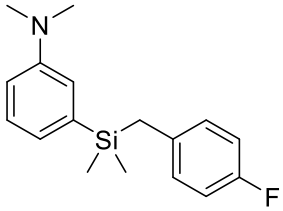
3-(dimethyl(4-methylbenzyl)silyl)-*N*, *N*-dimethylaniline (3d)

Colorless oil (32 mg, 57% yield), purified by chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 8 Hz, 1 H), 6.92 (d, J = 8 Hz, 2 H), 6.82-6.75 (m, 3 H), 6.73-6.63 (m, 2 H), 2.84 (s, 6 H), 2.20 (s, 3 H), 2.18 (s, 2 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.82, 138.14, 135.58, 132.19, 127.75, 127.43, 127.22, 121.06, 116.80, 112.56, 39.62, 24.52, 19.86, -4.34. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{18}H_{26}NSi$: 284.1829, found: 284.1828.



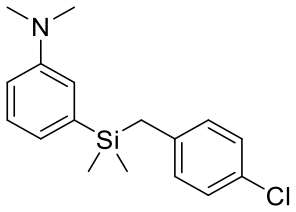
3-((4-(tert-butyl)benzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3e)

Colorless oil (40 mg, 62% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.09 (m, 3 H), 6.87-6.81 (m, 2 H), 6.79 (d, J = 8 Hz, 1 H), 6.71-6.65 (m, 2 H), 2.82 (s, 6 H), 2.19 (s, 2 H), 1.21 (s, 9 H), 0.16 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.78, 145.61, 138.16, 135.58, 127.41, 127.02, 123.91, 121.02, 116.92, 112.55, 39.63, 33.15, 30.42, 24.44, -4.23. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{21}H_{32}NSi$: 326.2299, found: 326.2300.



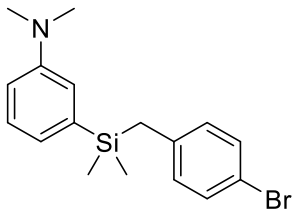
3-((4-fluorobenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3f)

Black oil (37 mg, 64% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.10 (m, 1 H), 6.83-6.72 (m, 5 H), 6.71-6.65 (m, 2 H), 2.84 (s, 6 H), 2.18 (s, 2 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.28 (d, J_{CF} = 242.4 Hz), 148.82, 137.58, 134.37 (d, J_{CF} = 3.03 Hz), 128.34 (d, J_{CF} = 8.08 Hz), 127.49, 120.98, 116.67, 113.72 (d, J_{CF} = 21.21 Hz), 112.61, 39.59, 24.26, -4.47. ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.18. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{17}H_{23}FNSi$: 288.1578, found: 288.1578.



3-((4-chlorobenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3g)

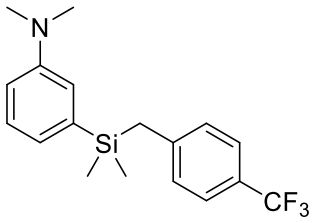
Colorless oil (37 mg, 61% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 8 Hz, 1 H), 7.05 (d, J = 8 Hz, 2 H), 6.78 (d, J = 8 Hz, 2 H), 6.73 (d, J = 8 Hz, 1 H), 6.71-6.64 (m, 2 H), 2.83 (s, 6 H), 2.18 (s, 2 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.97, 138.62, 138.51, 129.74, 129.67, 128.66, 128.21, 122.07, 117.77, 113.79, 40.72, 25.91, -3.31. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}ClNNaSi$: 326.1102, found: 326.1106.



3-((4-bromobenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3h)

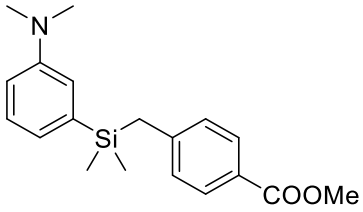
Yellow oil (45 mg, 65% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.12 (m, 3 H), 6.76-6.63 (m, 5 H), 2.84 (s, 6 H), 2.16 (s, 2 H),

0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.80, 138.02, 137.33, 129.99, 128.98, 127.52, 120.97, 116.66, 116.52, 112.68, 39.59, 24.86, -4.47. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{17}H_{23}BrNSi$: 348.0778, found: 348.0777.



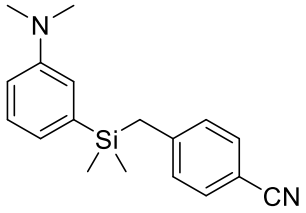
3-(dimethyl(4-(trifluoromethyl)benzyl)silyl)-*N*, *N*-dimethylaniline (3i)

Black oil (31 mg, 46% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 2 H), 7.24-7.09 (m, 1 H), 6.94 (d, J = 8.0 Hz, 2 H), 6.74-6.69 (m, 2 H), 6.62 (d, J = 4 Hz, 1 H), 2.82 (s, 6 H), 2.28 (s, 2 H), 0.17 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.83, 143.57, 136.99, 127.57, 127.35, 125.26 (d, J_{CF} = 32.32 Hz), 123.91 (q, J_{CF} = 4.04 Hz), 123.57 (d, J_{CF} = 271.69 Hz), 120.85, 116.59, 112.72, 39.51, 25.79, -4.50. ^{19}F NMR (471 MHz, Chloroform-d) δ -62.02. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{18}H_{25}F_3NSi$: 333.1546, found: 333.1550.



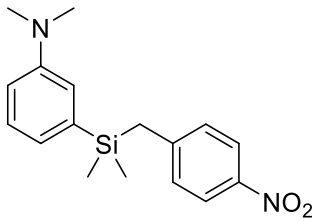
Methyl 4-(((3-(dimethylamino)phenyl)dimethylsilyl)methyl)benzoate (3j)

Colorless oil (33 mg, 50% yield), purified by column chromatography (SiO_2, PE/EA= 50:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8 Hz, 2 H), 7.34-7.20 (m, 1 H), 7.04 (d, J = 8 Hz, 2 H), 6.90-6.71 (m, 3 H), 3.91 (s, 3 H), 2.95 (s, 6 H), 2.41 (s, 2 H), 0.27 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 150.00, 146.45, 138.33, 129.61, 128.70, 128.32, 126.09, 122.05, 117.71, 113.86, 52.01, 40.75, 27.36, -3.30. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{19}H_{27}NO_2Si$: 338.1727, found: 338.1726.



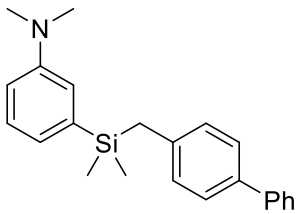
4-(((3-(dimethylamino)phenyl)dimethylsilyl)methyl)benzonitrile (3k)

Yellow oil (28 mg, 47% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 2 H), 7.19-7.14 (m, 1 H), 6.96-6.87 (m, 2 H), 6.74-6.66 (m, 2 H), 6.65-6.59 (m, 1 H), 2.85 (s, 6 H), 2.30 (s, 2 H), 0.17 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.91, 146.62, 137.60, 131.89, 128.87, 128.69, 121.87, 119.52, 117.51, 113.87, 107.61, 40.61, 27.77, -3.40. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{18}H_{24}N_2Si$: 295.1625, found: 295.1628.



3-(dimethyl(4-nitrobenzyl)silyl)-*N*,*N*-dimethylaniline (3l)

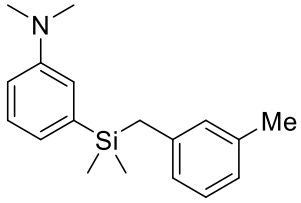
Yellow oil (19 mg, 30% yield), purified by column chromatography (SiO_2, PE/EA= 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99-7.92 (m, 2 H), 7.18 (m, 1 H), 6.98-6.94 (m, 2 H), 6.74-6.69 (m, 2 H), 6.64 (d, J = 4 Hz, 1 H), 2.85 (s, 6 H), 2.36 (s, 2 H), 0.20 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.03, 149.32, 145.10, 137.53, 128.84, 128.76, 123.61, 121.95, 117.55, 114.02, 40.71, 27.92, -3.40. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{17}H_{24}N_2O_2Si$: 315.1523, found: 315.1525.



3-(([1,1'-biphenyl]-4-ylmethyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3m)

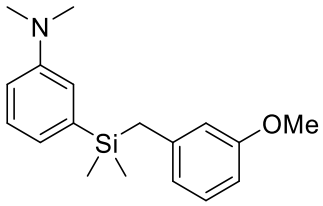
Yellow oil (38.5 mg, 56% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J_1 = 8, J_2 = 4 Hz, 2 H), 7.40-7.29 (m, 4 H), 7.26-7.14 (m, 2 H), 6.97 (d, J = 8 Hz, 2 H), 6.80 (d, J = 8 Hz, 1 H), 6.73-6.67 (m, 2 H), 2.84 (s, 6 H), 2.27 (s, 2 H),

0.20 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.80, 140.16, 138.18, 137.81, 135.81, 127.73, 127.63, 127.47, 125.72, 121.00, 116.77, 112.59, 39.59, 24.93, -4.31. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{23}H_{28}NSi$: 346.1986, found: 346.1987.



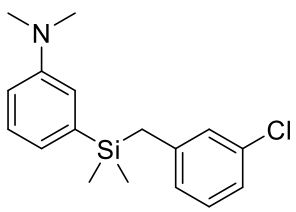
3-(dimethyl(3-methylbenzyl)silyl)-*N*, *N*-dimethylaniline (3n)

Yellow oil (35.5 mg, 63% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 8 Hz, 1 H), 6.99 (t, J = 8 Hz, 1 H), 6.82-6.75 (m, 2 H), 6.74-6.65 (m, 4 H), 2.83 (s, 6 H), 2.18 (s, 5 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.82, 138.76, 138.08, 136.42, 128.20, 127.42, 126.91, 124.37, 123.72, 121.01, 116.76, 112.55, 39.61, 25.02, 20.39, -4.35. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{18}H_{26}NSi$: 284.1829, found: 284.1832.



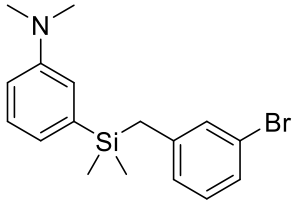
3-((3-methoxybenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3o)

Colorless oil (33.5 mg, 56% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.14 (m, 1 H), 7.02 (t, J = 8 Hz, 1 H), 6.78 (d, J = 8 Hz, 1 H), 6.73-6.65 (m, 2 H), 6.57-6.47 (m, 2 H), 6.43-6.39 (m, 1 H), 3.62 (s, 3 H), 2.84 (s, 6 H), 2.21 (s, 2 H), 0.17 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.51, 150.01, 141.71, 139.09, 129.07, 128.61, 122.20, 121.08, 117.96, 114.00, 113.78, 109.77, 55.10, 40.79, 26.56, -3.17. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{18}H_{26}NOSi$: 300.1778, found: 300.1179.



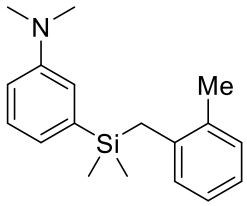
3-((3-chlorobenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3p)

Colorless oil (35 mg, 58% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19-7.13 (m, 1 H), 6.96-6.83 (m, 4 H), 6.81-6.67 (m, 3 H), 2.84 (s, 6 H), 2.23 (s, 2 H), 0.17 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.02, 142.37, 138.47, 133.90, 129.36, 128.70, 128.36, 126.63, 124.30, 122.07, 117.79, 113.90, 40.77, 26.39, -3.28. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{17}H_{23}ClNSi$: 304.1283, found: 304.1284.



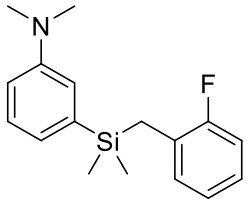
3-((3-bromobenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3q)

Colorless oil (42 mg, 61% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 8 Hz, 1 H), 7.11 (d, J = 8.0 Hz, 1 H), 7.02 (s, 1 H), 6.95 (t, J = 8 Hz, 1 H), 6.76 (dd, J_1 = 20, J_2 =8 Hz, 2 H), 6.69 (m, 2 H), 2.84 (s, 6 H), 2.18 (s, 2 H), 0.17 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.83, 141.53, 137.26, 130.09, 128.51, 127.54, 126.04, 125.90, 121.12, 120.93, 116.63, 112.76, 39.63, 25.20, -4.47. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{23}H_{28}NSi$: 348.0778, found: 348.0779.



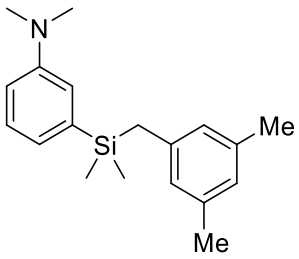
3-(dimethyl(2-methylbenzyl)silyl)-*N*, *N*-dimethylaniline (3r)

Colorless oil (35.5 mg, 63% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.18-7.14 (m, 1 H), 7.00-6.95 (m, 2 H), 6.93-6.86 (m, 2 H), 6.77 (d, J = 8 Hz, 1 H), 6.71-6.68 (m, 2 H), 2.83 (s, 6 H), 2.23 (s, 2 H), 2.02 (s, 3 H), 0.18 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.84, 138.22, 137.37, 133.93, 129.02, 127.88, 124.51, 123.13, 120.96, 121.01, 116.69, 112.65, 39.64, 22.04, 19.23, -4.01. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{18}H_{26}NSi$: 284.1829, found: 284.1837.



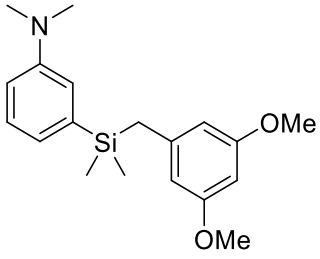
3-((2-fluorobenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3s)

Colorless oil (34.5 mg, 60% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.11 (m, 1 H), 6.98-6.92 (m, 1 H), 6.89-6.83 (m, 3 H), 6.78 (d, J = 4 Hz, 1 H), 6.74 (d, J = 8 Hz, 1 H), 6.71-6.65 (m, 1 H), 2.84 (s, 6 H), 2.23 (s, 2 H), 0.17 (s, 6 H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.29 (d, J = 243.41 Hz), 148.84 , 137.73 , 129.56 (d, J_{CF} = 5.05 Hz), 127.49 , 126.09 (d, J_{CF} = 17.17 Hz), 124.52 (d, J_{CF} = 7.07 Hz), 122.59 (d, J_{CF} = 4.04 Hz), 120.92 , 116.59 , 113.93 (d, J_{CF}= 22.22 Hz), 112.64 , 39.61 , 17.66 (d, J_{CF} = 3.03 Hz), -4.40. ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.98. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{17}H_{22}FNNaSi$: 310.1398, found: 310.1397.



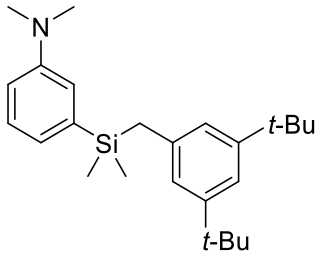
3-((3,5-dimethylbenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3t)

Colorless oil (31.5 mg, 53% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 8 Hz, 1 H), 6.78 (d, J = 8 Hz, 1 H), 6.74 (d, J = 2 Hz, 1 H), 6.69 (m, 1 H), 6.63 (s, 1 H), 6.53 (s, 2 H), 2.85 (s, 6 H), 2.15 (m, 8 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.00, 139.83, 139.43, 137.49, 128.57, 126.44, 125.82, 122.23, 117.98, 113.74, 40.81, 26.01, 21.42, -3.16. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{19}H_{28}NSi$: 298.1986, found: 298.1988.



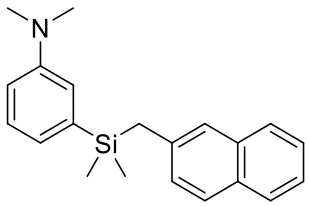
3-((3,5-dimethoxybenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3u)

Colorless oil (36 mg, 55% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17-7.09 (t, J = 8 Hz, 1 H), 6.75 (d, J = 8 Hz, 1 H), 6.71-6.63 (m, 2 H), 6.09 (t, J = 2 Hz, 1 H), 6.01 (d, J = 4 Hz, 2 H), 3.58 (s, 6 H), 2.80 (s, 6 H), 2.14 (s, 2 H), 0.15 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.54, 150.00, 142.45, 139.04, 128.59, 122.19, 117.96, 113.76, 106.52, 96.53, 55.20, 40.77, 26.95, -3.17. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{19}H_{28}NO_2Si$:330.1884 , found: 330.1882.



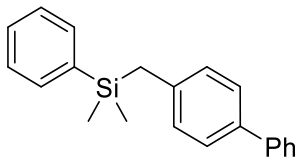
3-((3,5-di-tert-butylbenzyl)dimethylsilyl)-*N*, *N*-dimethylaniline (3v)

Colorless oil (41 mg, 54% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (m, 1 H), 7.02 (t, J = 4 Hz, 1 H), 6.75 (d, J = 8 Hz, 1 H), 6.70-6.63 (m, 4 H), 2.81 (s, 6 H), 2.20 (s, 2 H), 1.17 (s, 18 H), 0.16 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.04, 148.75, 138.02, 137.44, 127.35, 121.70, 121.10, 116.72, 112.47, 39.61, 33.54, 30.42, 25.58, -4.45. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{25}H_{40}NSi$: 382.2925, found: 382.2925.



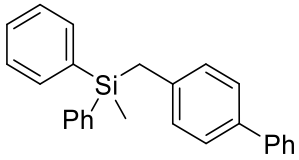
3-(dimethyl(naphthalen-2-ylmethyl)silyl)-*N*, *N*-dimethylaniline (3w)

Colorless oil (35.5 mg, 56% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8 Hz, 1 H), 7.61-7.55 (m, 2 H), 7.34-7.23 (m, 3 H), 7.19-7.13 (m, 1 H), 7.06-6.99 (m, 1 H), 6.80-6.76 (m, 1 H), 6.73-6.64 (m, 2 H), 2.78 (s, 6 H), 2.38 (s, 2 H), 0.17 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.84, 137.86, 136.68, 132.72, 130.00, 127.48, 127.05, 126.49, 126.39, 125.97, 124.64, 124.54, 123.31, 120.98, 116.71, 112.60, 39.55, 25.52, -4.29. HRMS (ESI+) m/z: $[M+H]^+$ calculated for $C_{21}H_{26}NSi$: 320.1829, found: 320.1826.



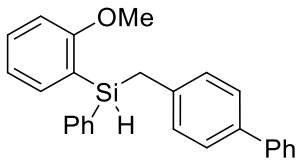
([1,1'-biphenyl]-4-ylmethyl)dimethyl(phenyl)silane (3x)

Colorless oil (46 mg, 76% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8 Hz, 2 H), 7.42-7.37 (m, 2 H), 7.36-7.20 (m, 8 H), 6.91 (d, J = 8 Hz, 2 H), 2.26 (s, 2 H), 0.19 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.80, 140.15, 138.18, 137.82, 135.79, 127.72, 127.62, 127.46, 125.73, 125.72, 125.70, 120.99, 116.77, 112.59, 39.62, 24.93, -4.31. HRMS (ESI+) m/z: [M+Na]+ calculated for $C_{21}H_{22}NaSi$: 325.1383, found: 325.1396.



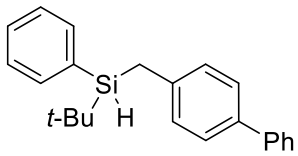
([1,1'-biphenyl]-4-ylmethyl)(methyl)diphenylsilane (3y)

Colorless oil (32 mg, 44% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8 Hz, 2 H), 7.40 (d, J = 8 Hz, 4 H), 7.33-7.18 (m, 11 H), 6.85 (d, J = 8 Hz, 2 H), 2.57 (s, 2 H), 0.42 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.00, 137.04, 136.02, 135.23, 133.65, 128.31, 128.01, 127.62, 126.76, 125.75, 125.71, 125.66, 23.12, -5.81. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}NaSi$: 385.1539, found: 385.1542.



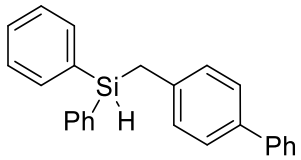
([1,1'-biphenyl]-4-ylmethyl)(2-methoxyphenyl)(phenyl)silane (3z)

Colorless oil (51.5 mg, 68% yield), purified by column chromatography (SiO_2, PE/EA= 100:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.39 (m, 4 H), 7.32-7.14 (m, 11 H), 6.99 (d, J = 8 Hz, 2 H), 6.81 (t, J = 8 Hz, 1 H), 6.73 (d, J = 8 Hz, 1 H), 4.82 (s, 1 H), 3.65 (s, 3 H), 2.67 (qd, J_1 = 16, J_2 = 4 Hz, 2 H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.14, 140.09, 137.87, 136.19, 136.05, 134.22, 133.18, 130.81, 128.37, 127.90, 127.59, 126.69, 125.78, 125.72, 121.01, 119.67, 108.54, 54.05, 20.80. HRMS (ESI+) m/z: $[M+K]^+$ calculated for $C_{27}H_{26}OKSi$: 433.1385, found: 433.1387.



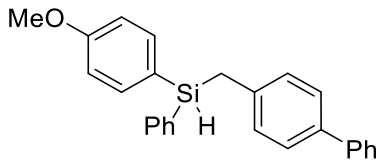
([1,1'-biphenyl]-4-ylmethyl)(tert-butyl)(phenyl)silane (3aa)

Colorless oil (42mg, 63% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.37 (m, 4 H), 7.35-7.21 (m, 7 H), 7.17 (t, J = 8 Hz, 1 H), 7.01 (d, J = 8 Hz, 2 H), 4.10 (t, J = 4 Hz, 1 H), 2.42 (d, J = 4 Hz, 2 H), 0.89 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.18, 138.99, 137.27, 135.58, 133.74, 129.57, 129.11, 128.77, 127.82, 127.06, 126.91, 27.36, 19.06, 17.68. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{23}H_{26}NaSi$: 353.1701, found: 353.1710.



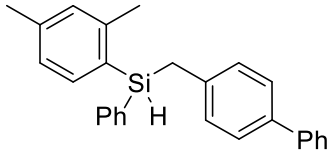
([1,1'-biphenyl]-4-ylmethyl)diphenylsilane (3ab)

Colorless oil (37 mg, 53% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.36 (m, 6 H), 7.34-7.16 (m, 10 H), 7.13-7.04 (m, 1 H), 6.98 (d, J = 8 Hz, 2 H), 4.89 (t, J = 4 Hz, 1 H), 2.63 (d, J = 4 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.98, 136.75, 136.37, 134.24, 133.31, 132.44, 128.96, 128.74, 128.05, 127.63, 126.94, 126.72, 126.55, 125.91, 125.81, 125.76, 20.96. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{25}H_{22}NaSi$: 373.1378, found: 373.1368.



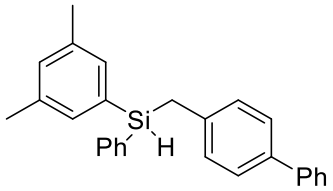
([1,1'-biphenyl]-4-ylmethyl)(4-methoxyphenyl)(phenyl)silane (3ac)

Colorless oil (42 mg, 55% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2 H), 7.43-7.37 (m, 2 H), 7.35-7.19 (m, 10 H), 6.97 (d, J = 8 Hz, 2 H), 6.80 (d, J = 8 Hz, 2 H), 4.86 (t, J = 4 Hz, 1 H), 3.70 (s, 3 H), 2.60 (s, 2 H),. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.94, 140.00, 136.93, 136.29, 135.77, 134.18, 132.93, 128.64, 128.05, 127.63, 126.90, 125.88, 125.80, 125.75, 123.00, 112.75, 53.96, 21.23. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{26}H_{24}NaOSi$: 403.1494, found: 403.1489.



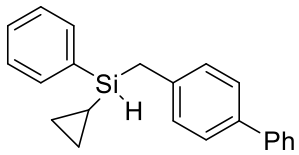
([1,1'-biphenyl]-4-ylmethyl)(2,4-dimethylphenyl)(phenyl)silane (3ad)

Colorless oil (51 mg, 67% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2 H), 7.39-7.13 (m, 11 H), 7.04-6.96 (m, 2 H), 6.95 - 6.84 (m, 2 H), 4.95 (t, J = 4 Hz, 1 H), 2.63 (s, 2 H), 2.22 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 140.01, 139.05, 137.23, 136.30, 135.02, 134.10, 133.02, 129.70, 128.49, 128.01, 127.68, 127.61, 126.86, 125.90, 125.75, 124.89, 21.52, 20.77, 20.35. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{27}H_{26}NaSi$: 401.1701, found: 401.1712.



([1,1'-biphenyl]-4-ylmethyl)(3,5-dimethylphenyl)(phenyl)silane (3ae)

Colorless oil (52 mg, 69% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.39 (m, 4 H), 7.32-7.26 (m, 5 H), 7.25-7.15 (m, 3 H), 7.05-7.01 (m, 2 H), 6.99-6.92 (m, 3 H), 4.84 (t, J = 4 Hz, 1 H), 2.60 (d, J = 4 Hz, 2 H), 2.18 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.22, 138.15, 137.50, 137.41, 135.41, 133.90, 133.23, 133.07, 131.70, 129.80, 129.25, 128.80, 128.06, 127.05, 126.96, 126.93, 22.22, 21.47. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{27}H_{26}NaSi$: 401.1701, found: 401.1705.

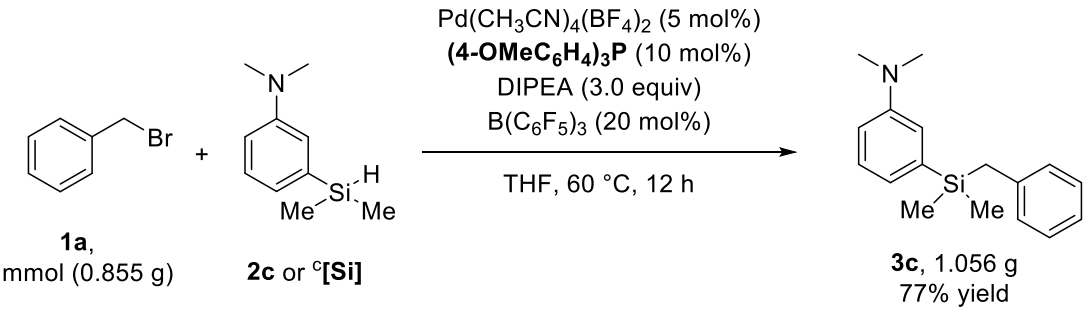


([1,1'-biphenyl]-4-ylmethyl)(cyclopropyl)(phenyl)silane (3af)

Colorless oil (32.5 mg, 52% yield), purified by column chromatography (SiO_2, PE/EA= 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.25-8.17 (m, 4 H), 8.12-7.92 (m, 8 H), 7.80 (d, J = 8.0 Hz, 2 H), 4.84 (q, J = 4 Hz, 1 H), 3.14 (d, J = 4 Hz, 2 H), 1.42-1.29 (m, 2 H), 1.06 - 0.81 (m, 2 H), 0.48 (tt, J_1 = 8, J_2 = 4.0 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.20, 138.59, 137.33, 135.00, 134.42, 129.68, 129.08, 128.80, 127.94, 127.03, 126.94, 126.92, 21.93, 2.30, 2.21, -8.31. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{22}H_{22}NaSi$: 337.1388, found: 337.1392.

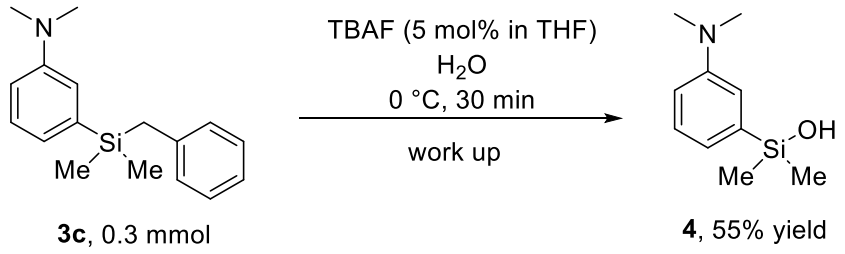
6. Gram-Scale Synthesis and Synthetic Applications

6.1 Gram-scale Synthesis



In a 100-mL Schlenk tube with a magnetic stir bar, $Pd(CH_3CN)_4(BF_4)_2$ (5 mol%, 4.44mg 0.01 mmol), $(4\text{-}OMeC_6H_4)_3P$ (10 mol%, 7.04 mg 0.02 mmol), $B(C_6F_5)_3$ (20 mol%, 20.48 mg, 0.04 mmol) were added. The tube was evacuated and backfilled with N_2. Then, the solvent THF (2 mL) was added to this mixture under N_2. After that, compound **1a** (0.2 mmol, 34 mg), 3-(dimethylsilyl)-*N*, *N*-dimethylaniline **2c** (0.4 mmol, 2 equiv) was added under N_2, along with DIPEA (0.6 mmol, 77.54 mg). The reaction was stirred at room temperature for 12 h. After completion of the reaction, the mixture was cooled to room temperature. It was then diluted with 10 mL of CH_2Cl_2. The combined organic phases were concentrated, and the resulting residue was purified by column chromatography on silica gel (PE/EA = 50:1, to provide the desired product **3c** in good yield.

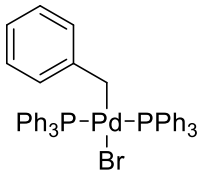
6.2 Synthetic Applications



Following a literature procedure[3],The reaction of **3c** (0.3 mmol) and TBAF (5 mol%) in THF (3 mL) and found that **3c** is converted into **4** as colorless oil (32 mg, 55% yield) within 30 min at 0 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 8 Hz, 1 H), 6.87-6.79 (m, 2 H), 6.67 (dd, J_1 = 8, J_2 = 4 Hz, 1 H), 2.82 (s, 6 H), 2.39 (bs, 1 H), 0.25 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.07,

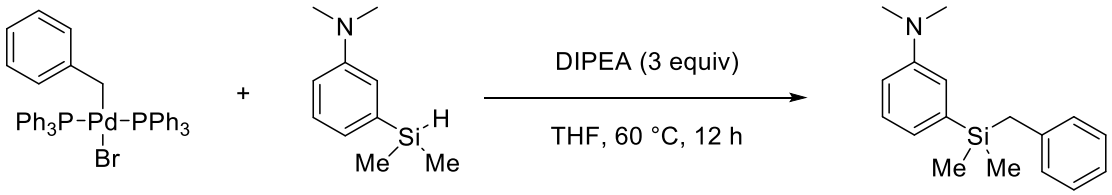
139.76, 128.69, 121.51, 117.15, 114.28, 40.74, 0.00. HRMS (ESI+) m/z: $[M+Na]^+$ calculated for $C_{10}H_{17}NNaOSi$: 218.0977, found: 218.0979.

7. Mechanistic Studies



5

Following a literature procedure[4], a Schlenk tube containing vacuum dried Pd_2dba_3•$CHCl_3$ (100 mg, 0.097 mmol) in dry CH_2Cl_2 (3 mL) under N_2 was used. To this, a solution of PPh_3 (101.4 mg, 0.387 mmol) in dry CH_2Cl_2 (2.5 mL) was added. The mixture was stirred for 0.2 h at room temperature until an orange color persisted. Then, a solution of benzyl bromide (0.5 mmol) in CH_2Cl_2 (2 mL) was added in one portion. The mixture turned to a yellow color after a few minutes, while stirring was continued for 0.5 h. The solution was concentrated in vacuo to one-third of its original volume and petroleum ether added to precipitate the titled complex. The yellow solid was collected by filtration and washed with diethyl ether (**5** (**[Pd/L]-S**), 90 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.45 (m, 10 H), 7.35-7.22 (m, 20 H), 6.99 (t, J = 8.0 Hz, 1 H), 6.84 (t, J = 8 Hz, 2 H), 6.39 (d, J = 8 Hz, 2 H), 2.72 (bs, 2 H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.54 (bs), 23.17(s).



A dry 25-mL Schlenk tube containing a magnetic stirring bar was loaded with compound **5** (**[Pd/L]-S**) (0.2 mmol, 160 mg) and then evacuated and backfilled with N_2. Next, the solvent THF (2 mL) was added into this mixture under N_2. Afterward, hydrosilane (0.4 mmol, 2 equiv) and DIPEA (77.54 mg, 3 equiv) were added under N_2. The reaction was stirred at 60 °C for 12 hours.

Upon completion of the reaction, the mixture was cooled to room temperature. Subsequently, it was diluted with 10 mL of CH_2Cl_2. The combined organic phases were concentrated, and the resulting residue was purified by column chromatography on silica gel (PE/EA = 50:1) to provide the desired product **3c** (21 mg, 38% yield).

8. References

[1] Hirone, N.; Sanjiki, H.; Tanaka, R.; Hata, T.; Urabe, H., Acceleration of the substitution of silanes with Grignard reagents by using either LiCl or YCl_3/MeLi. *Angew. Chem. Int. Ed.*, **2010**, *49*, 7762-7764.

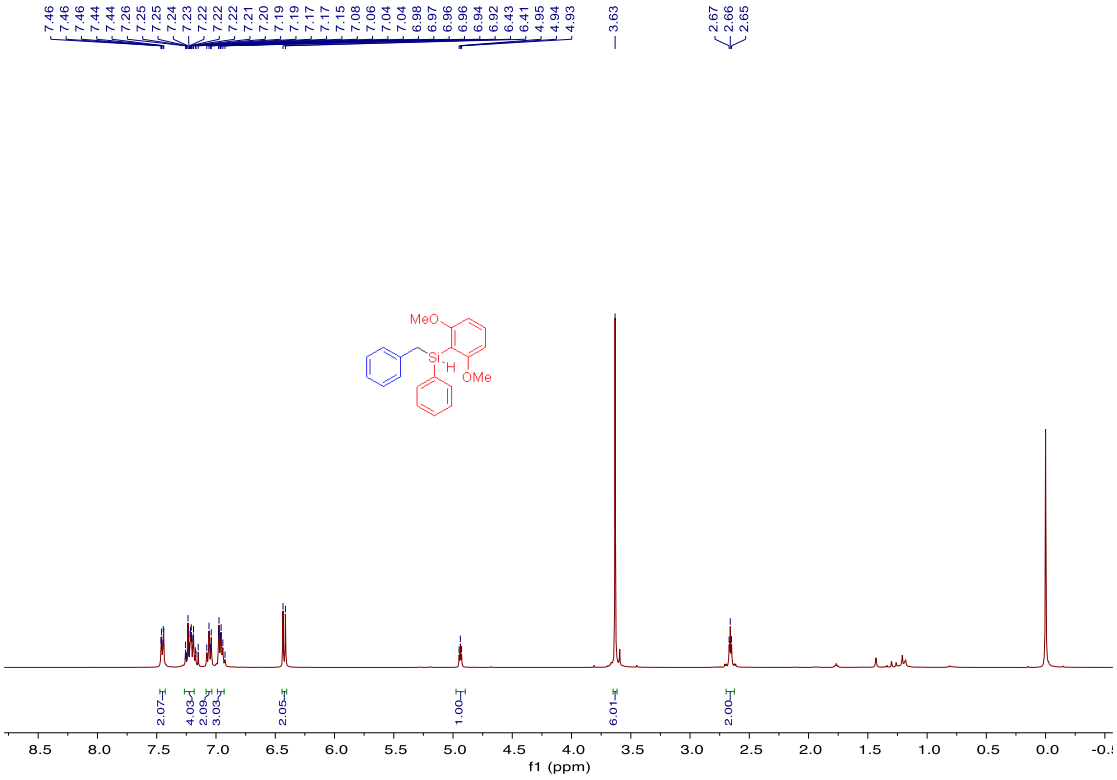
[2] Ma, Y.; Zhang, L.; Luo, Y.; Nishiura, M.; Hou, Z., $B(C_6F_5)_3$-Catalyzed C-Si/Si-H Cross-Metathesis of Hydrosilanes. *J. Am. Chem. Soc.*, **2017**, *139*, 12434-12437.

[3] Han, J.; Qin, Y.; Zhao, D., C(sp3)-H Bond Arylation and Amidation of Sibound Methyl Group via Directing Group Strategy. *ACS Catal.*, **2019**, *9*, 6020-6026.

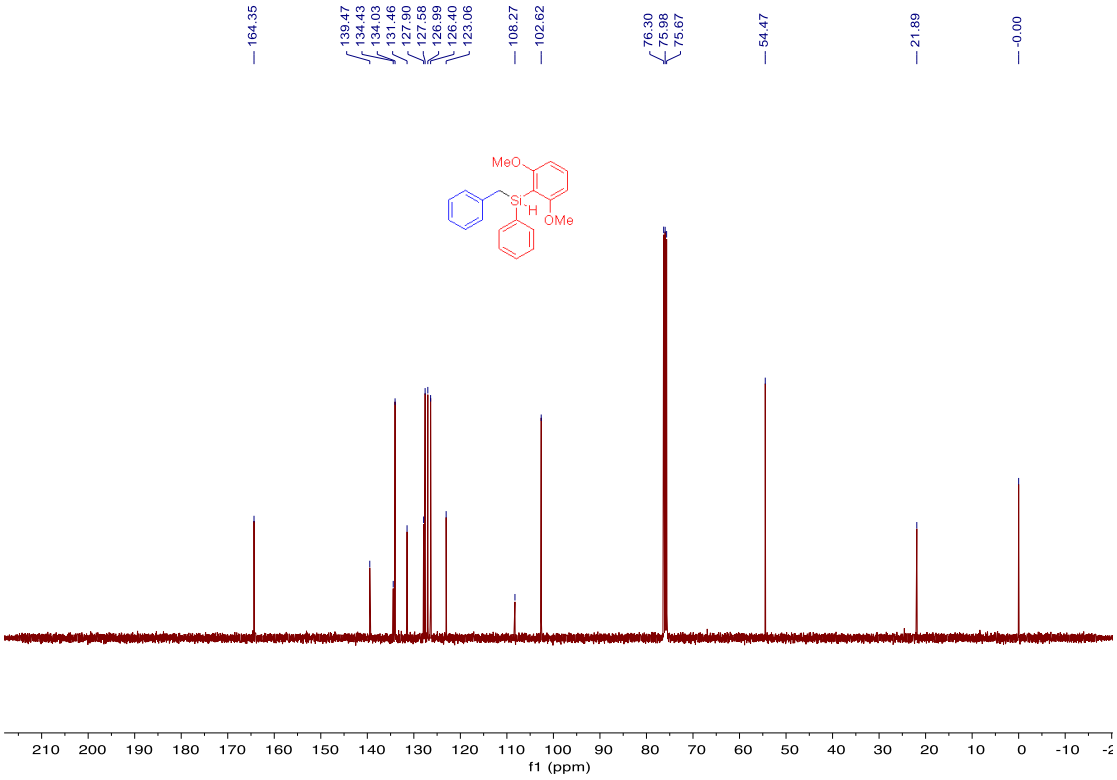
[4] Yu, W.; Tsoi Y.; Zhou, Z.; Chan A., Palladium-catalyzed cross coupling reaction of benzyl bromides with diazoesters for stereoselective synthesis of (*E*)-*α*,*β*-diarylacrylates. *Org. Lett.*, **2008**, *11*, 469-472.

9. Copies of ^{1}H and ^{13}C NMR spectra

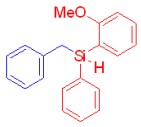
^{1}H NMR of 3a

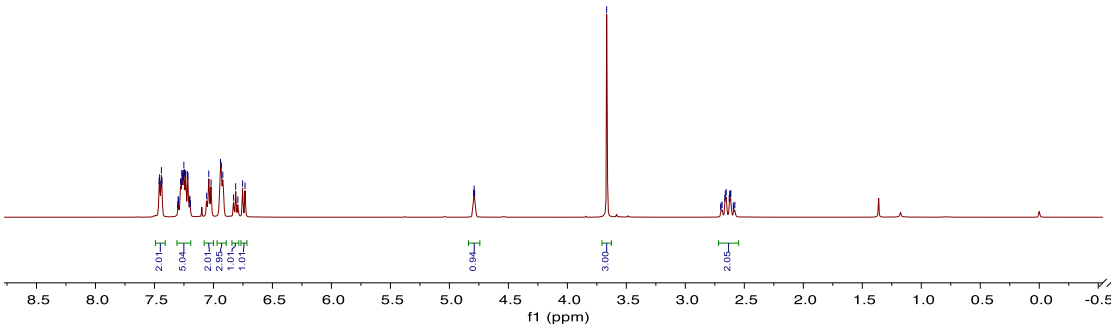


^{13}C NMR of 3a

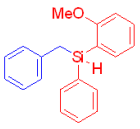


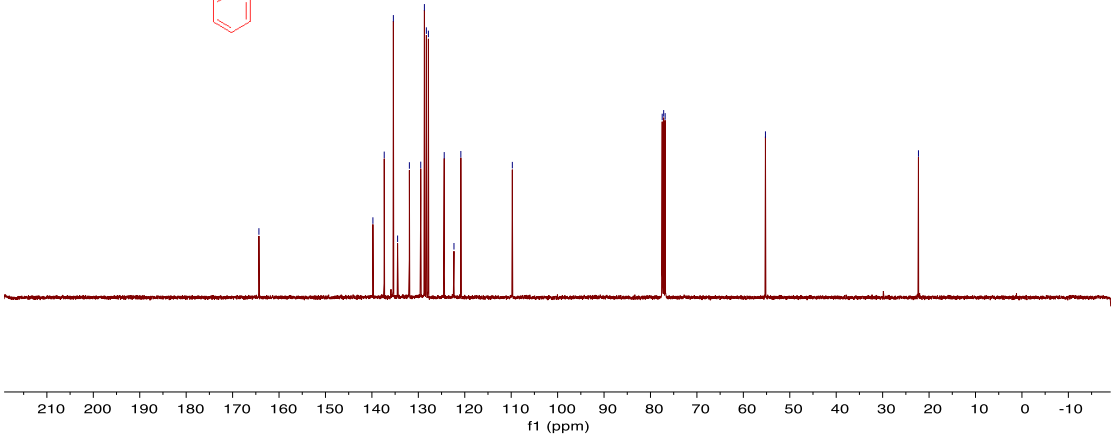
^{1}H NMR of 3b



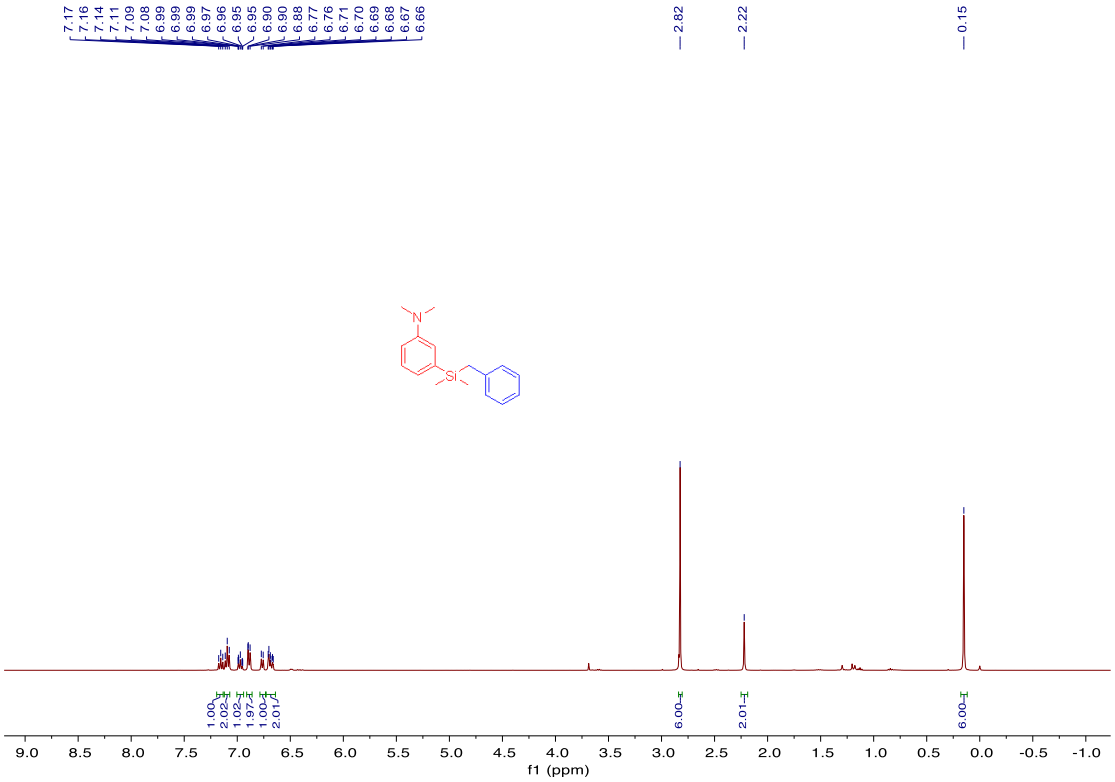


^{13}C NMR of 3b

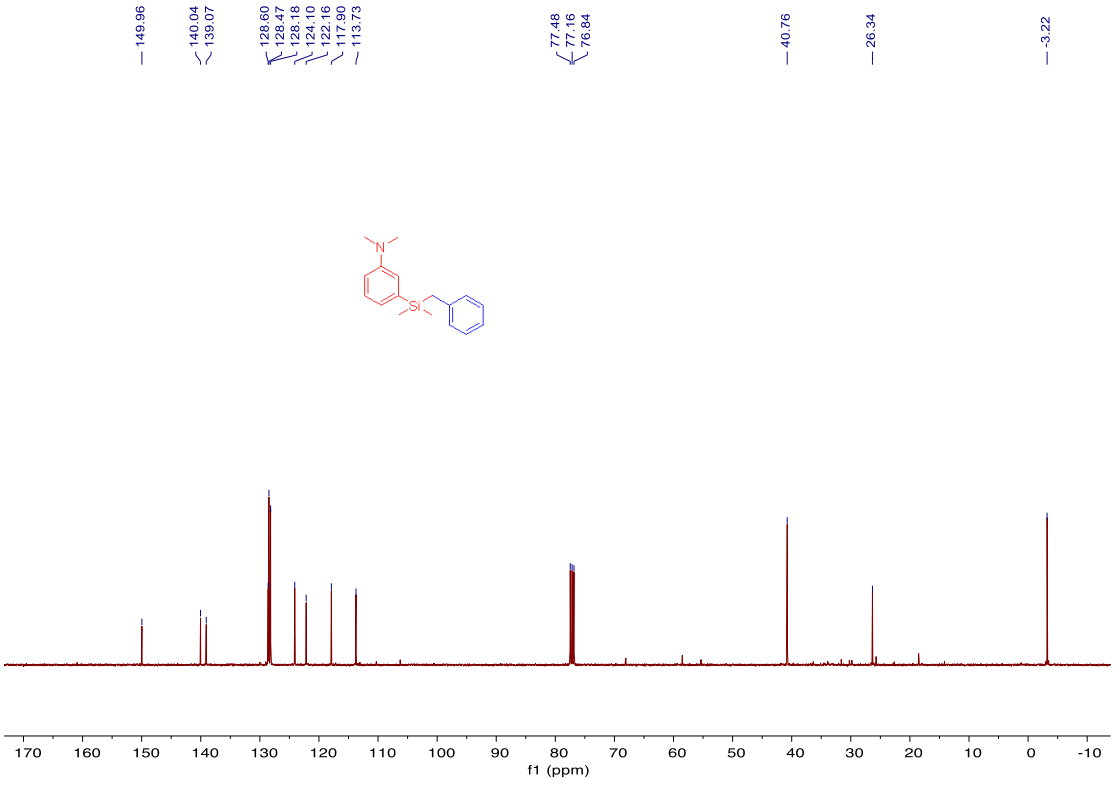




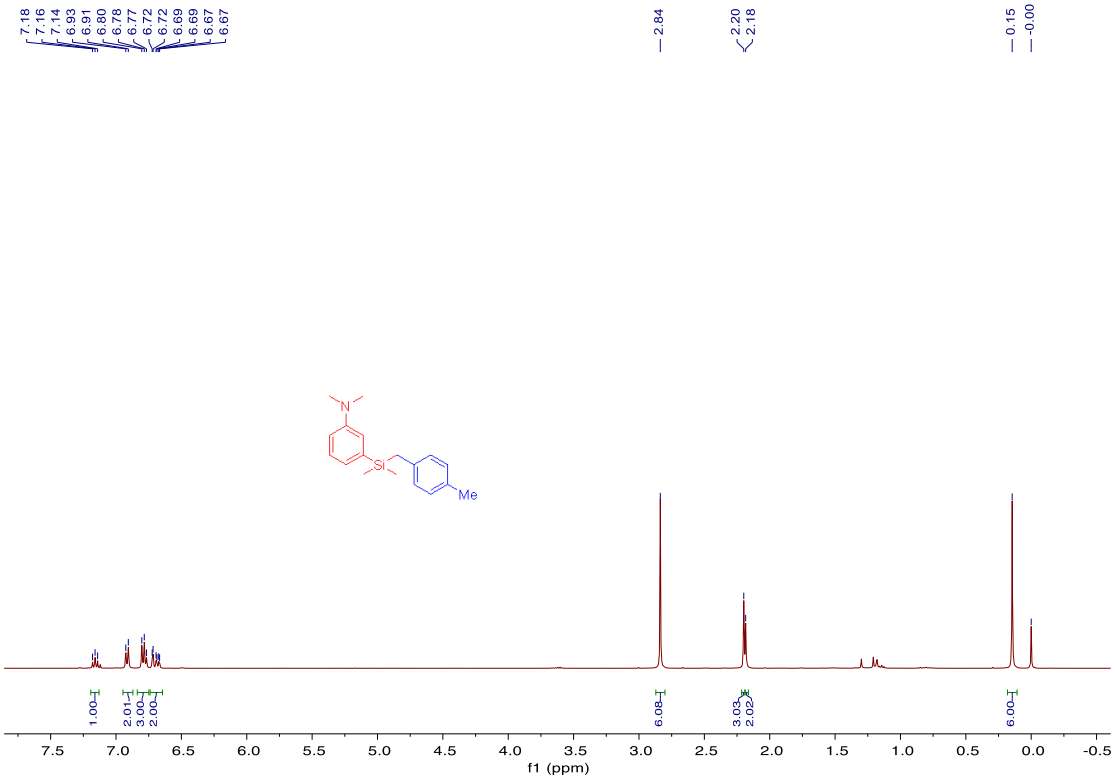
^{1}H NMR of 3c



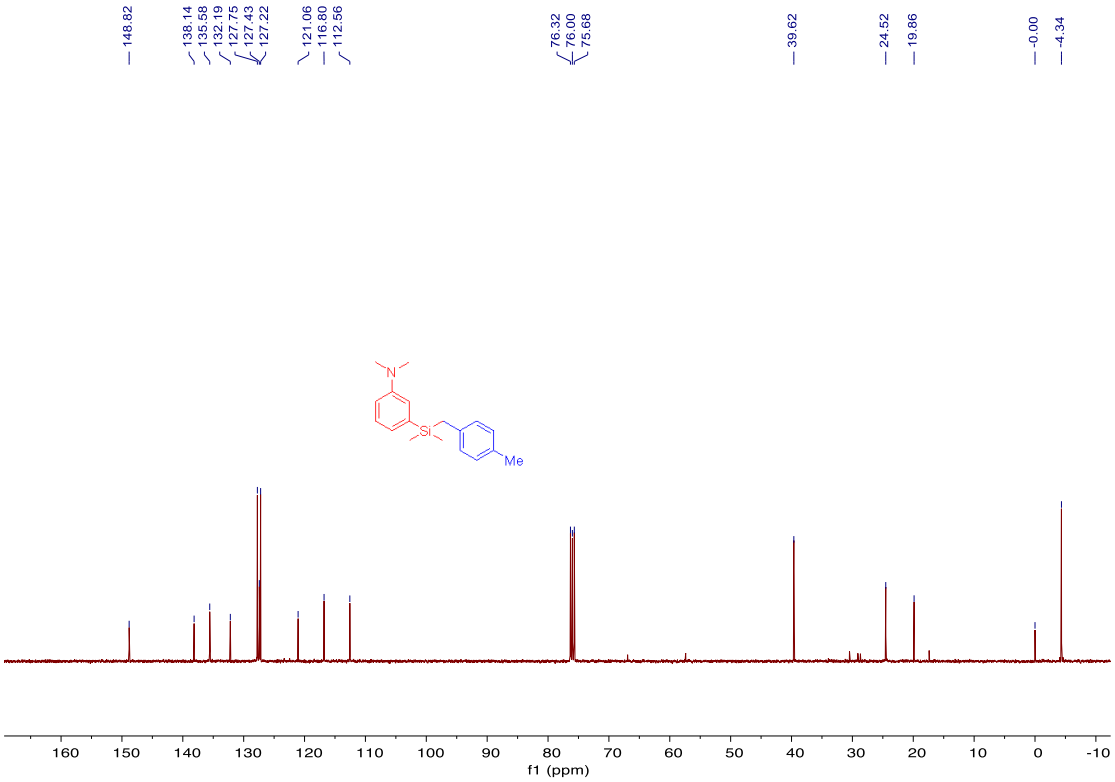
^{13}C NMR of 3c



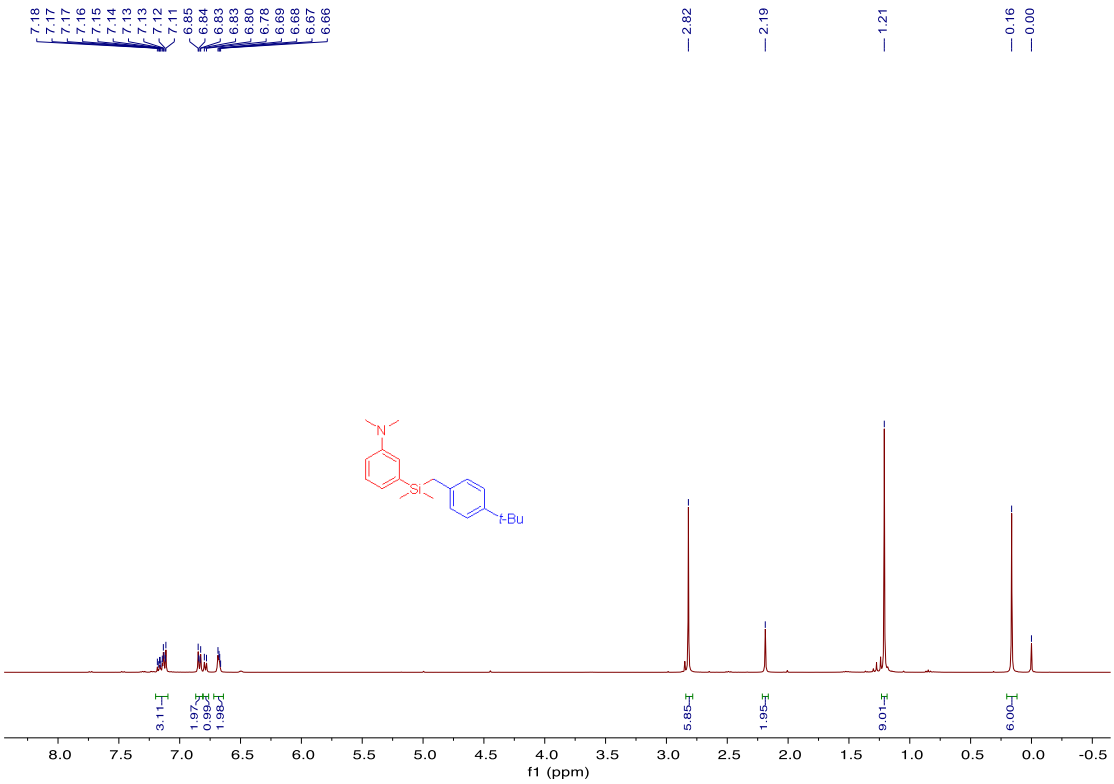
^{1}H NMR of 3d



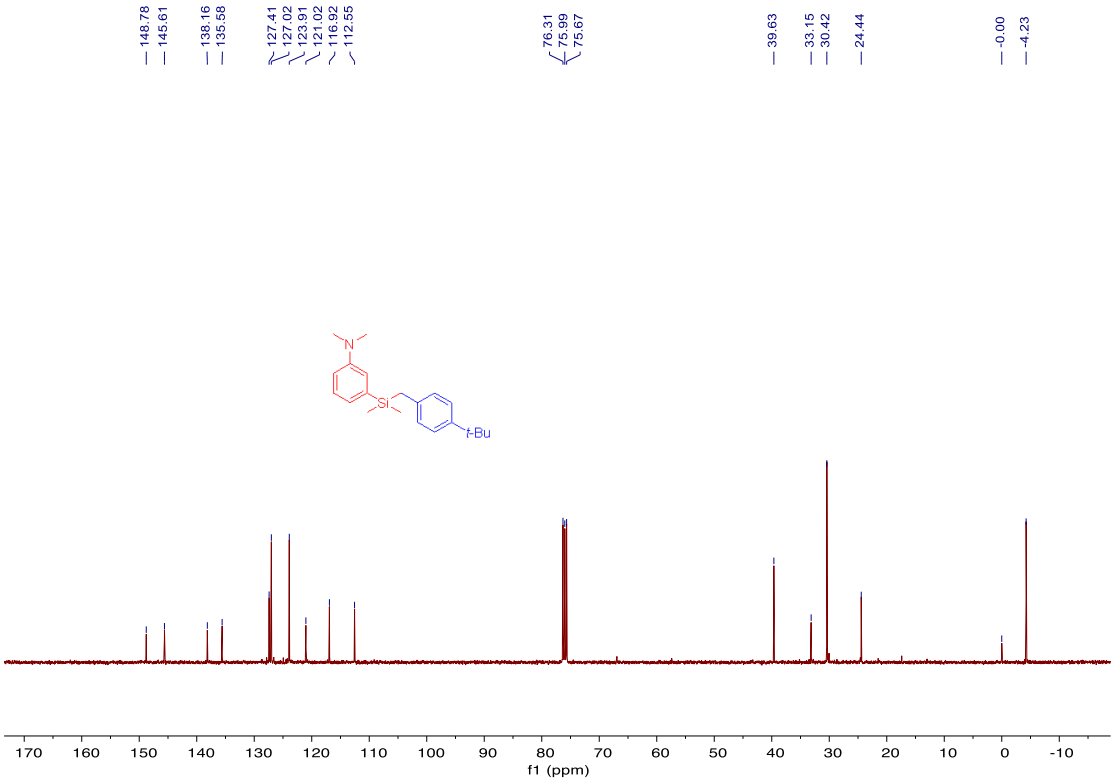
^{13}C NMR of 3d



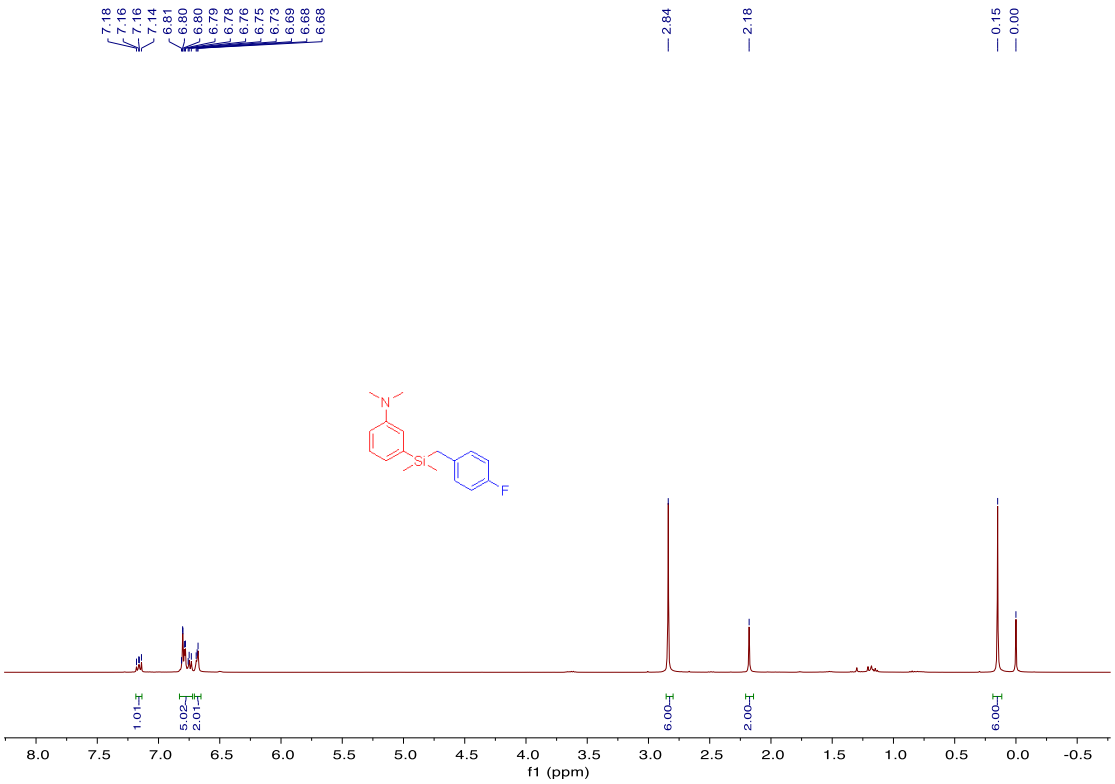
^{1}H NMR of 3e



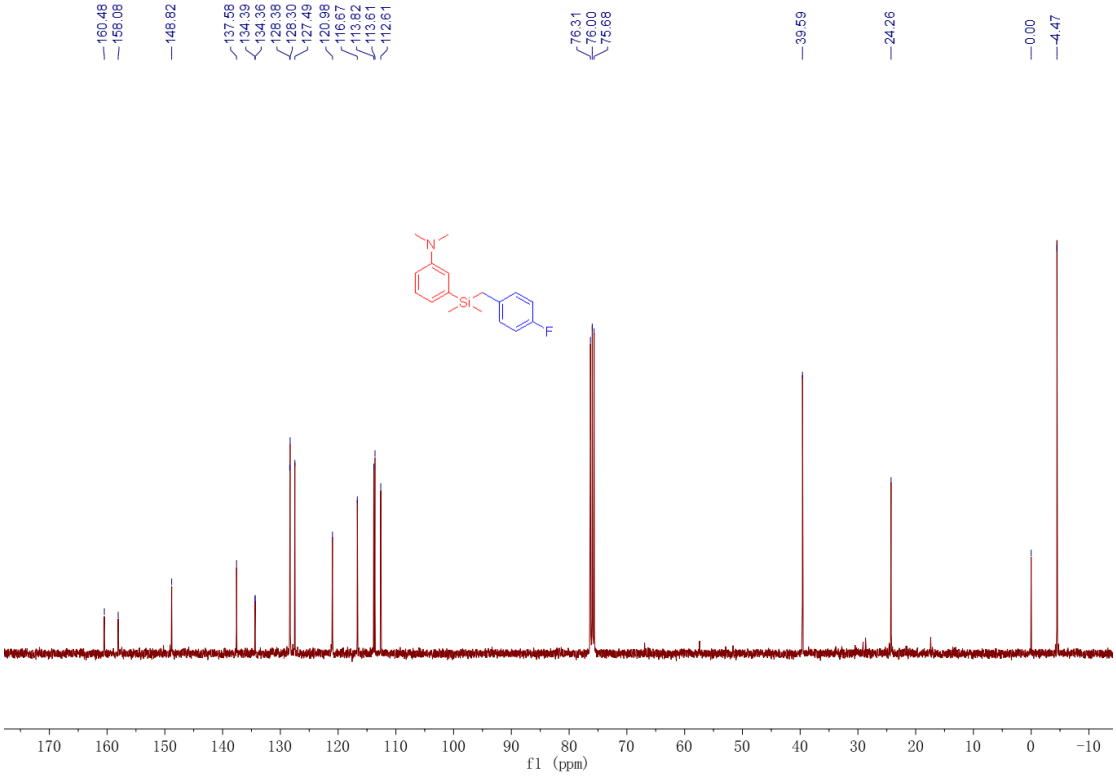
^{13}C NMR of 3e



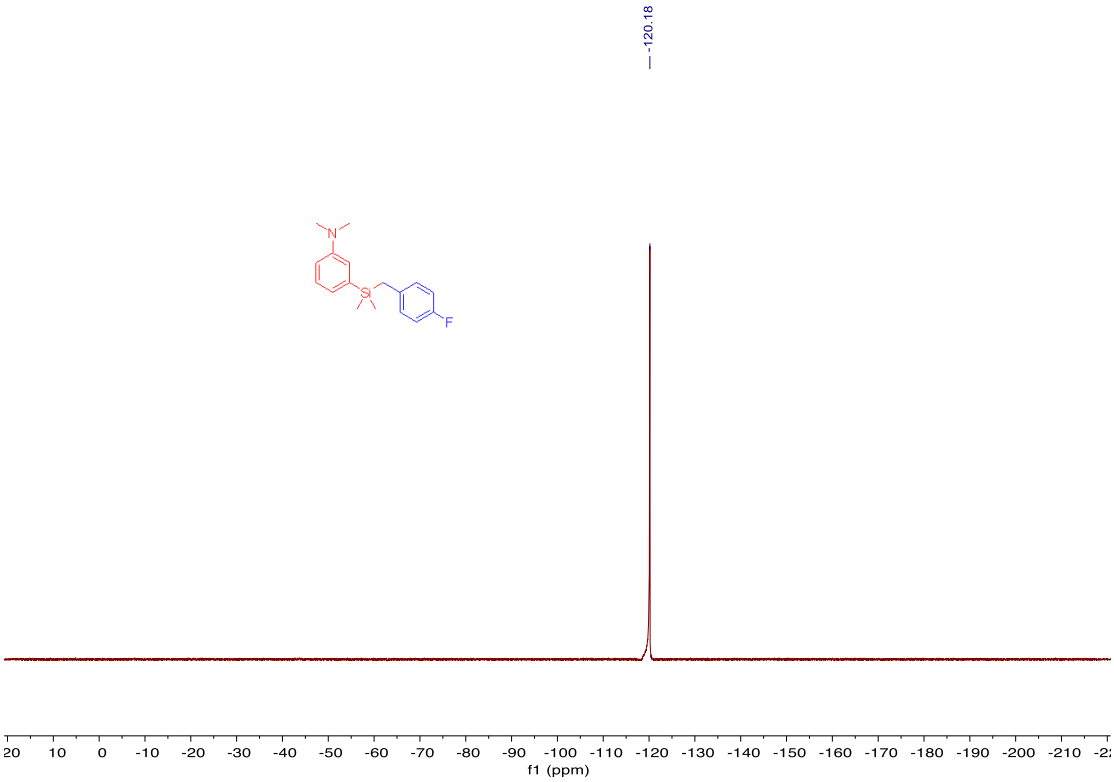
^{1}H NMR of 3f



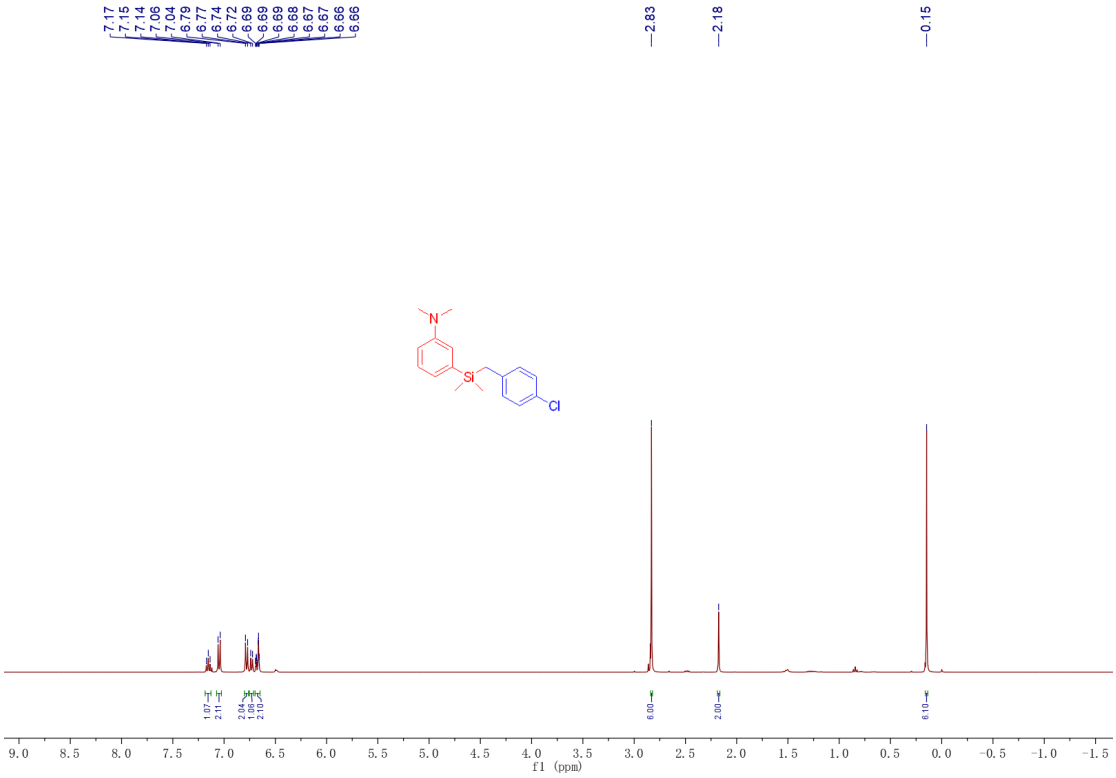
^{13}C NMR of 3f



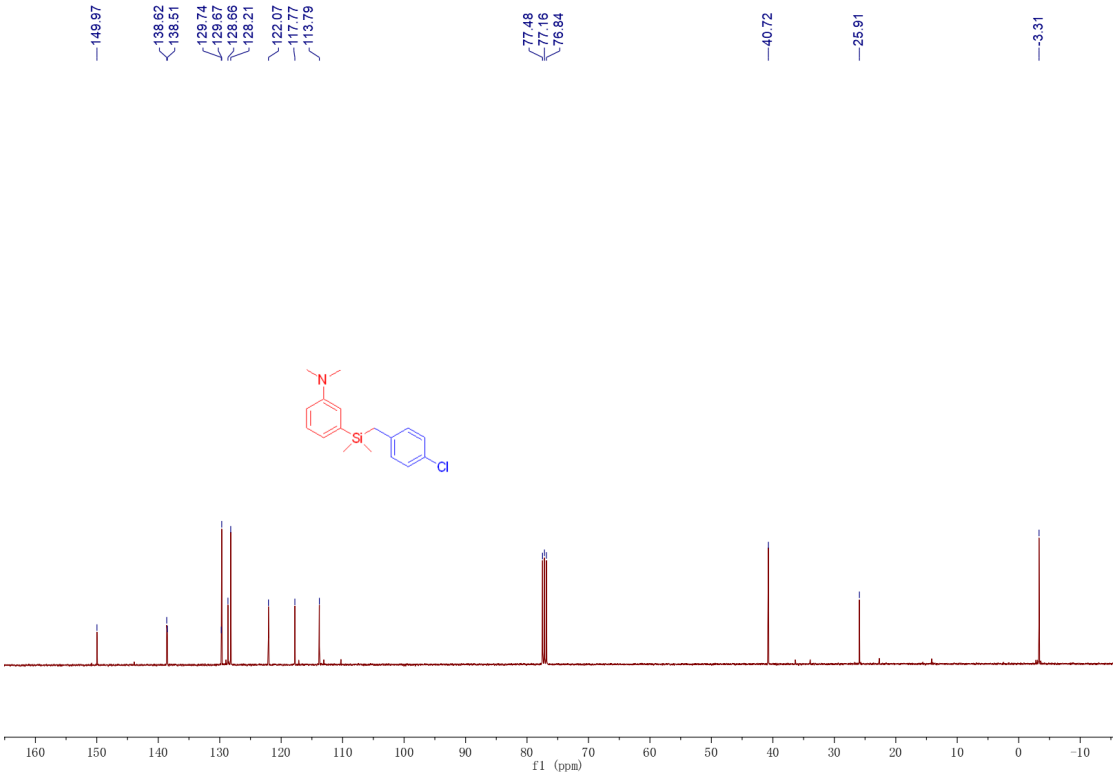
^{19}F NMR of 3f


-120.18
N
Si
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

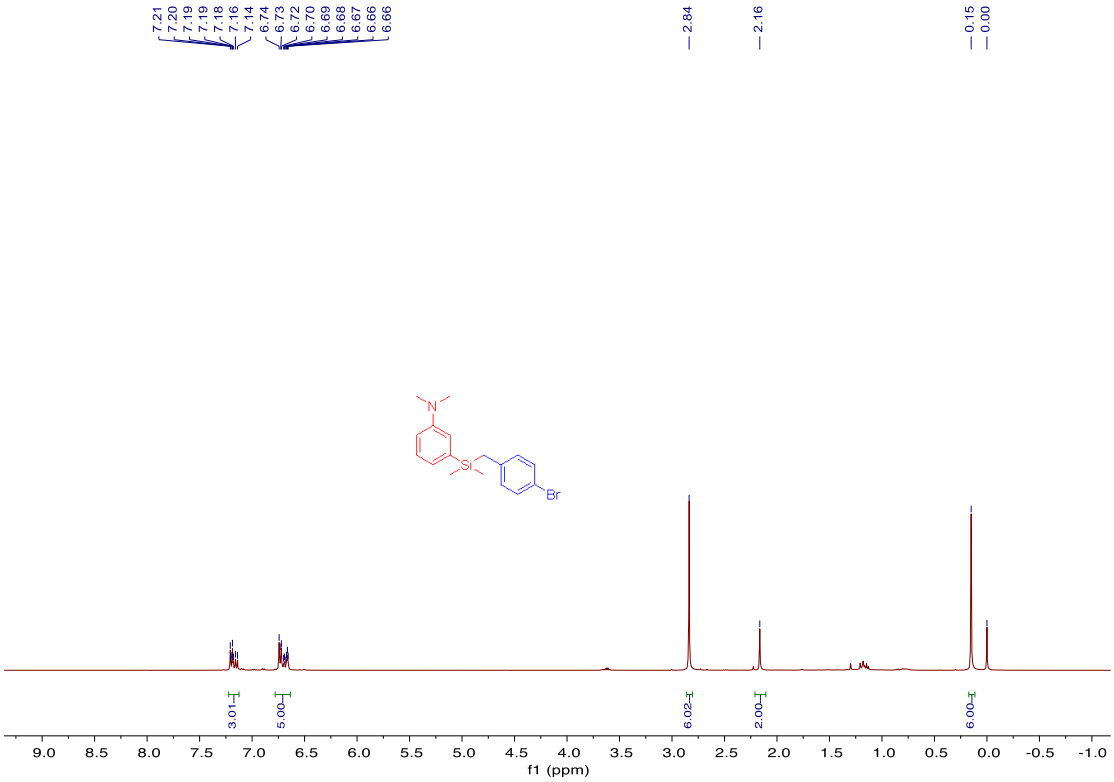
^{1}H NMR of 3g



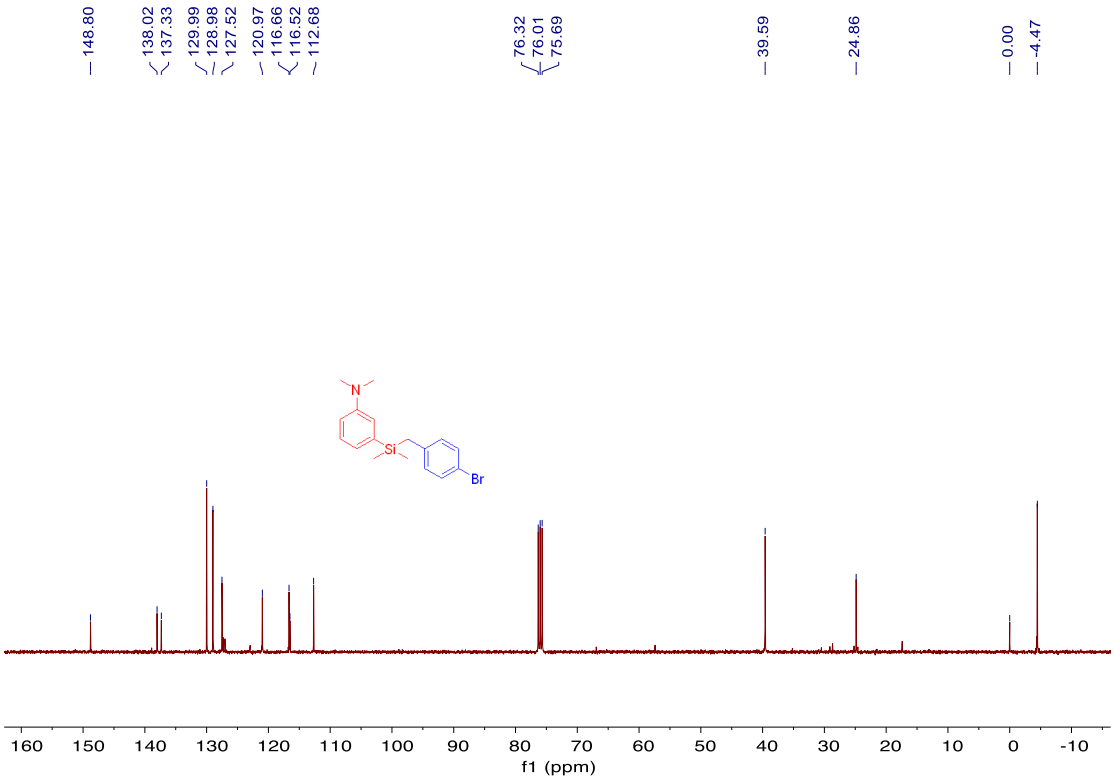
^{13}C NMR of 3g



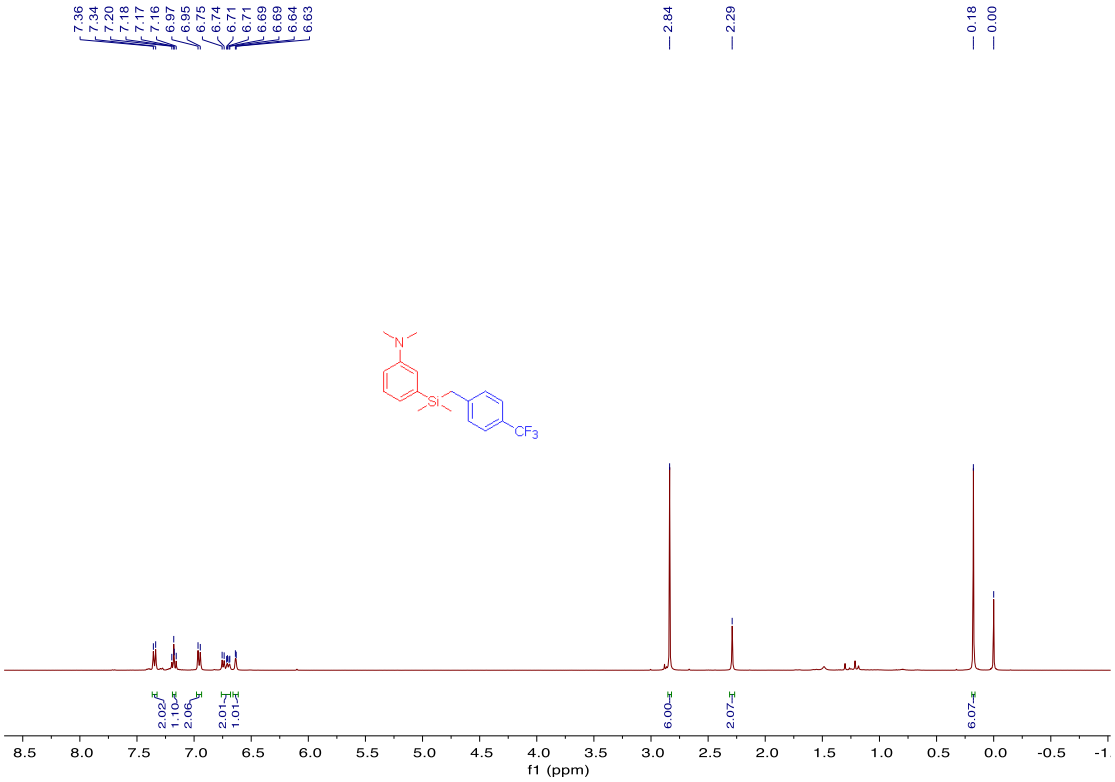
^{1}H NMR of 3h



^{13}C NMR of 3h



^{1}H NMR of 3i



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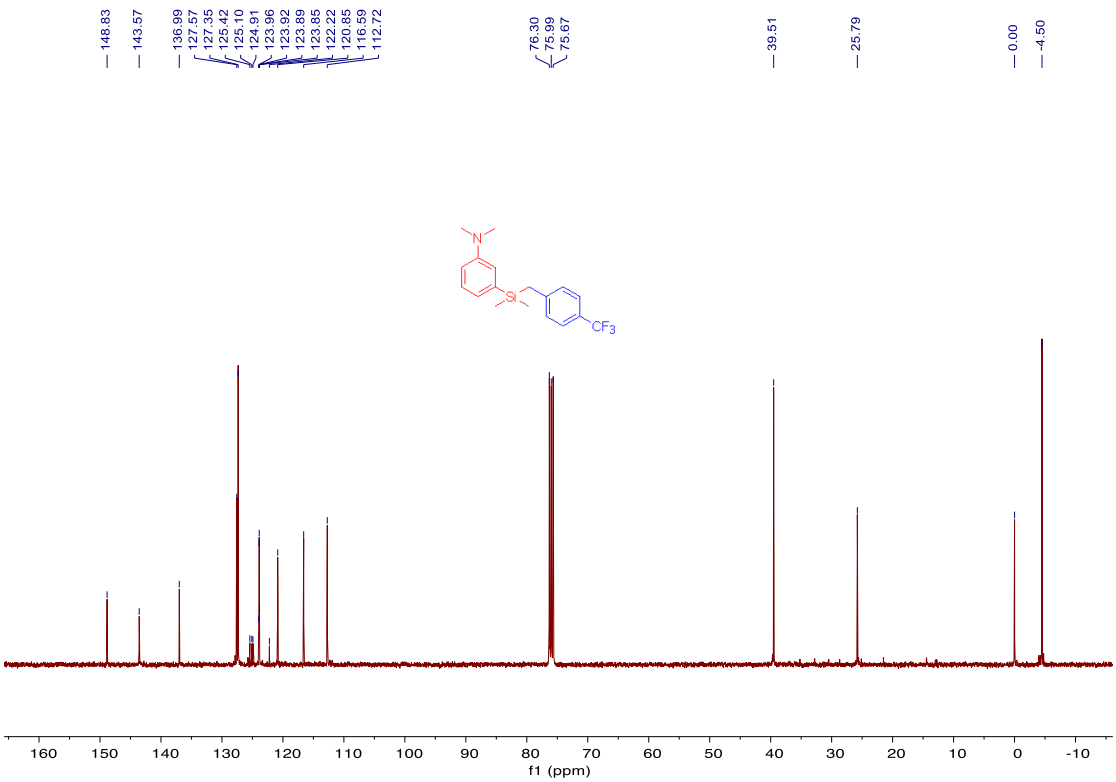
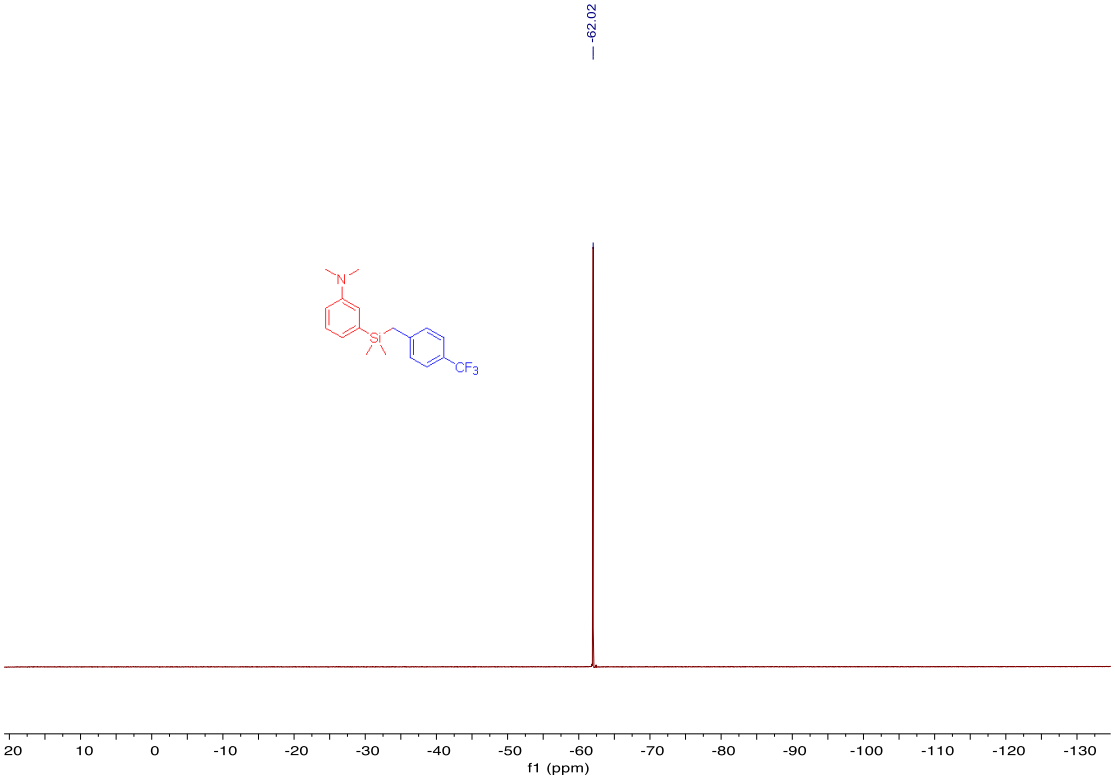


^{19}F NMR of 3i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Si
CF3
20
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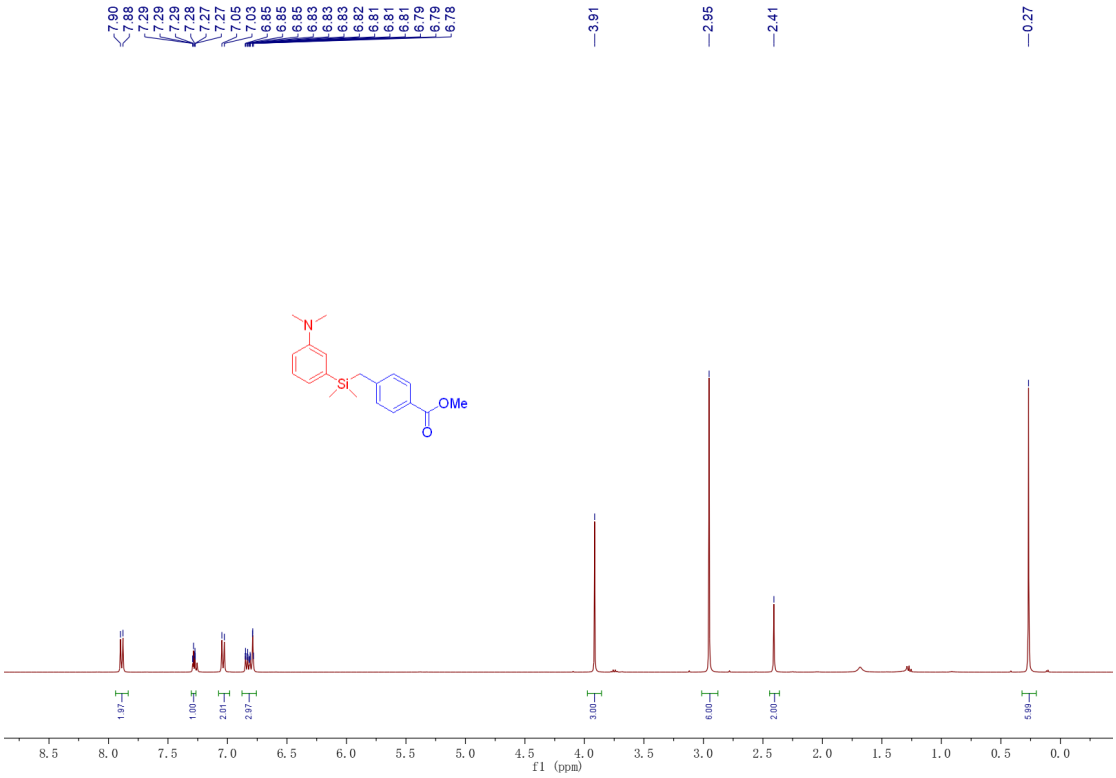
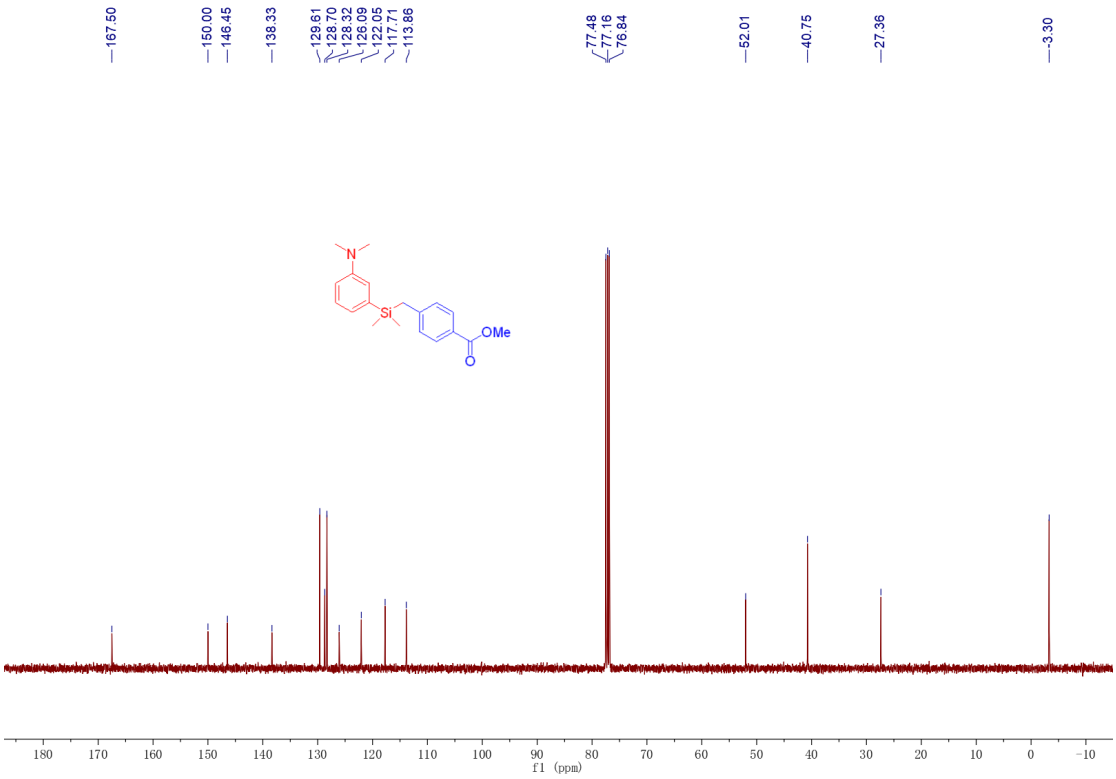
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
f1 (ppm)

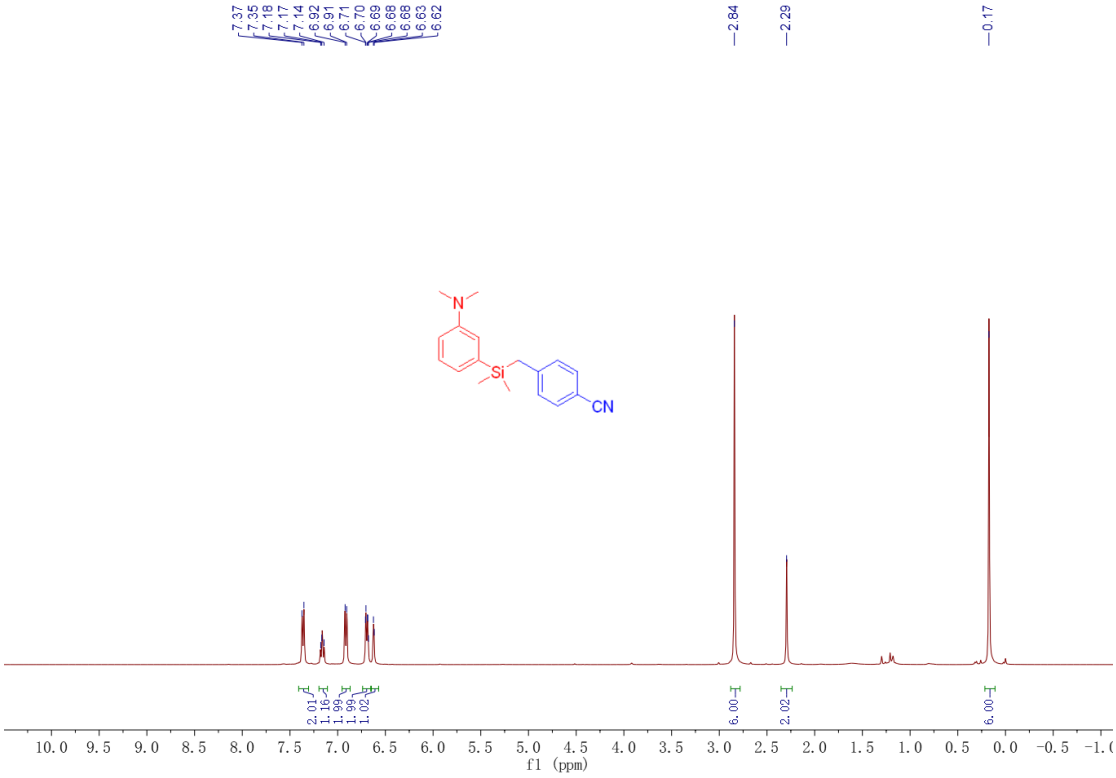
^{1}H NMR of 3j



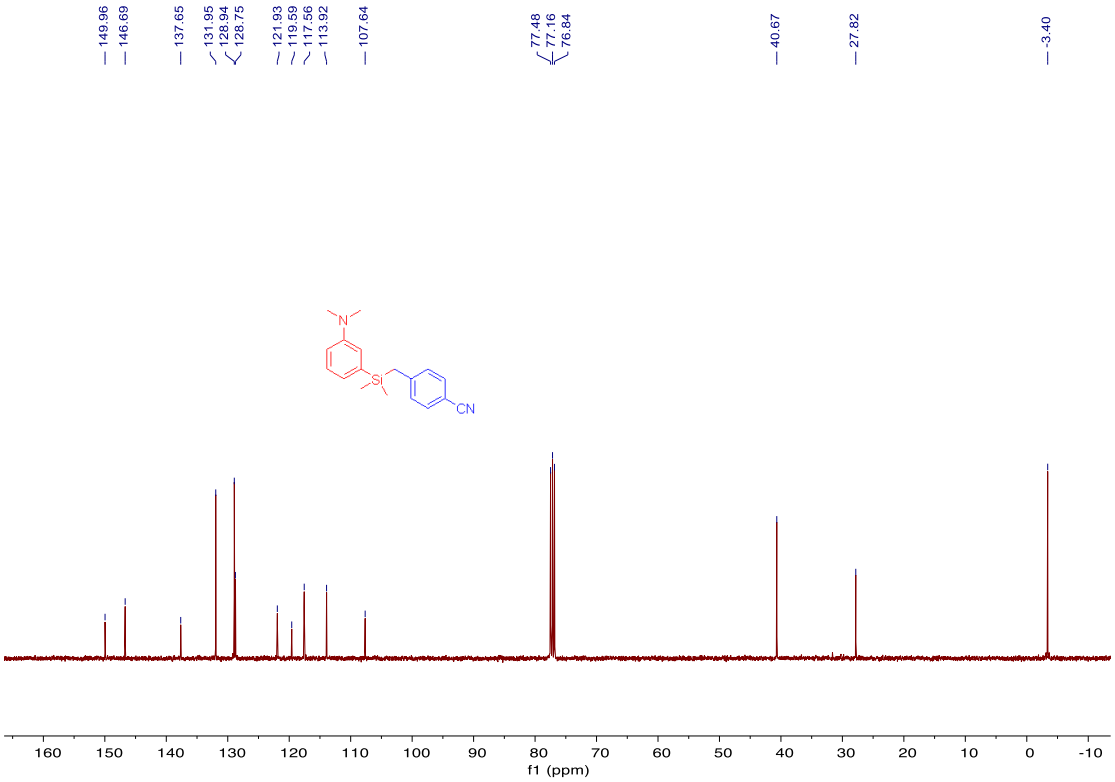
^{13}C NMR of 3j



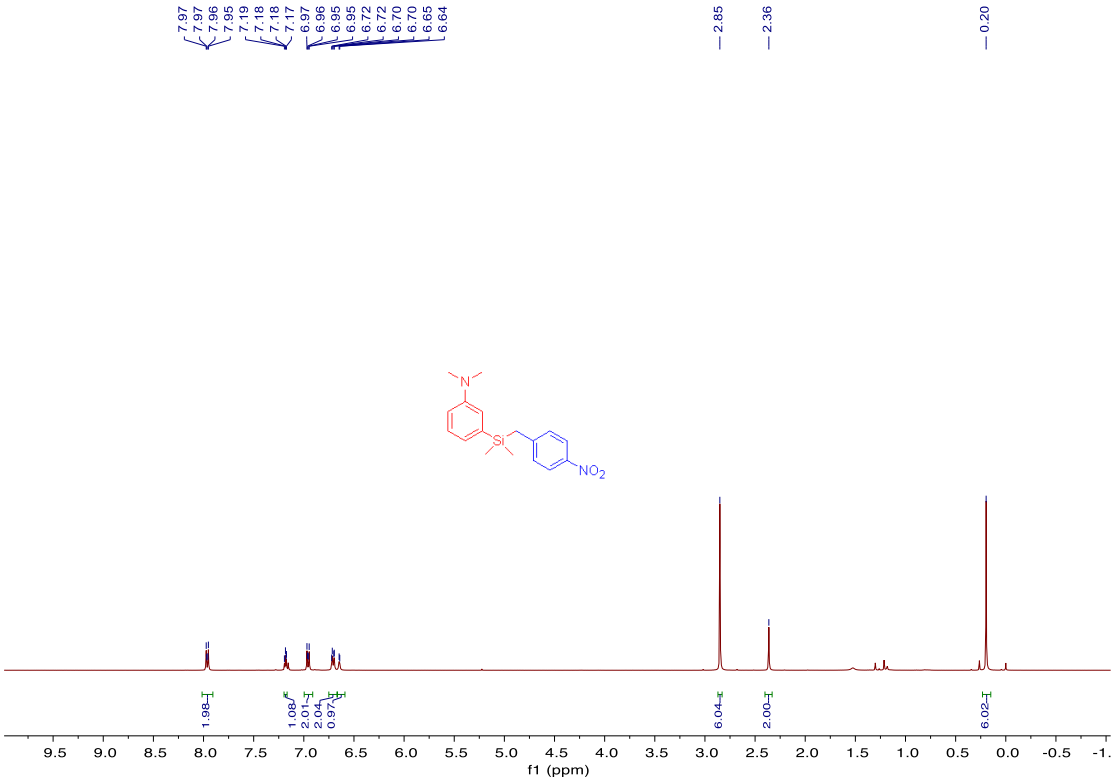
^{1}H NMR of 3k



^{13}C NMR of 3k



^{1}H NMR of 3l



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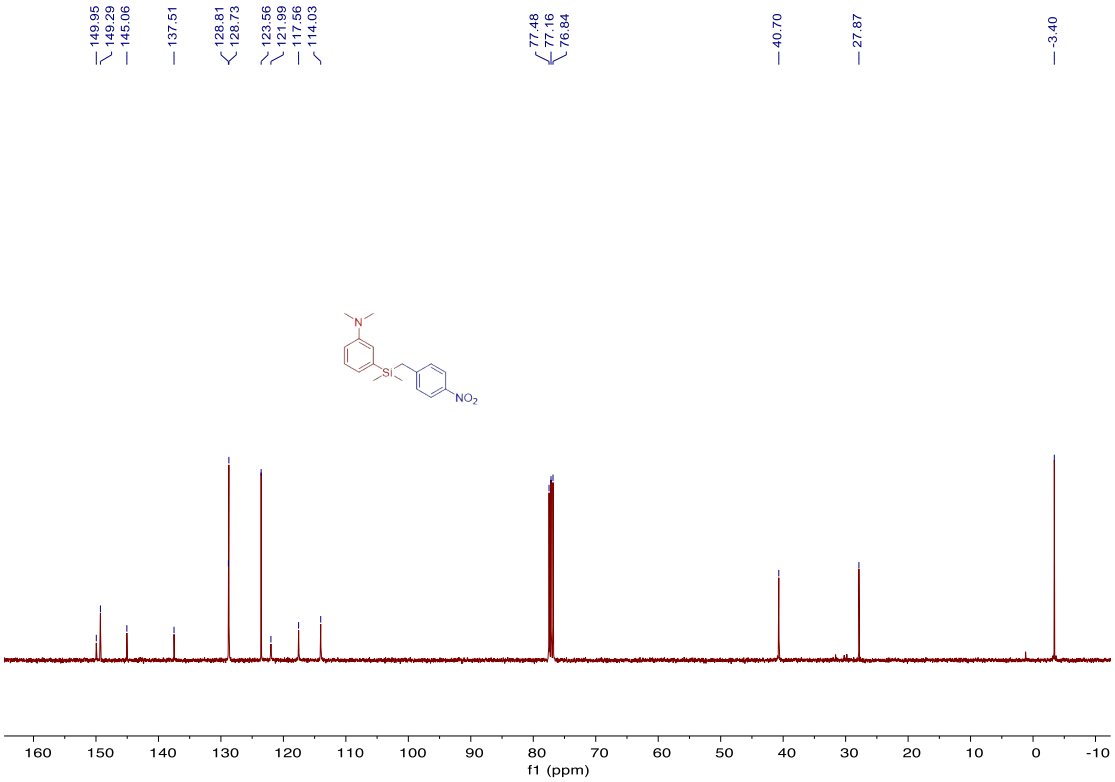
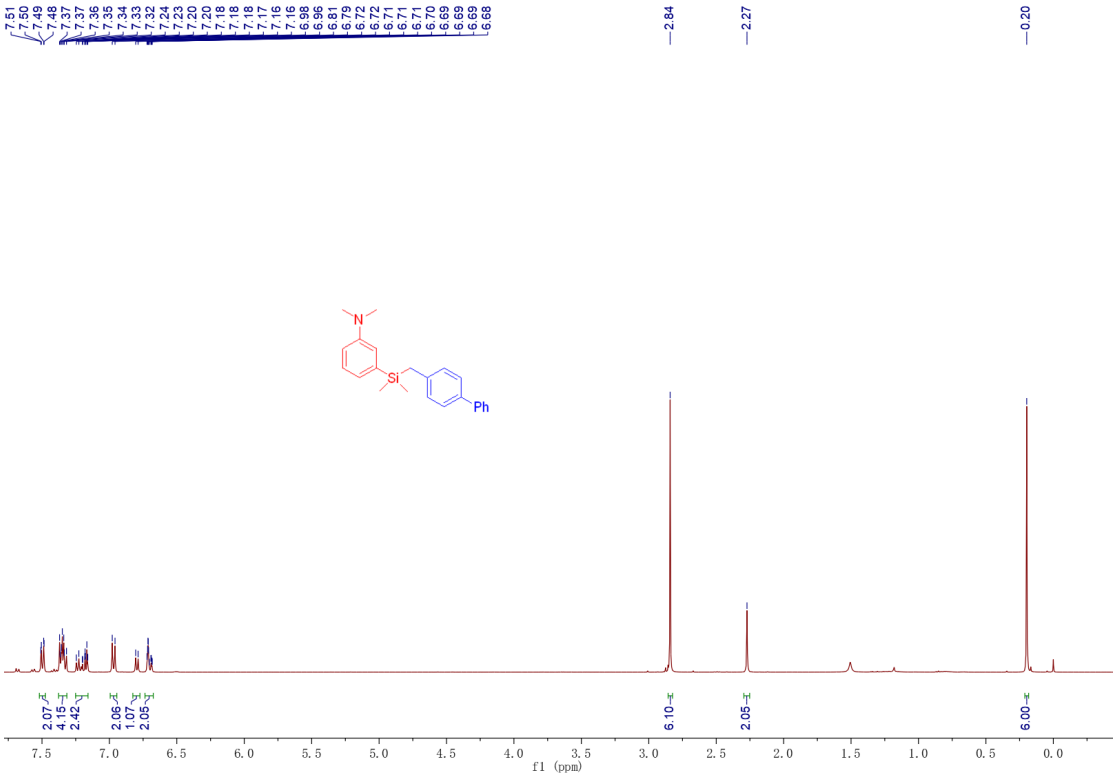
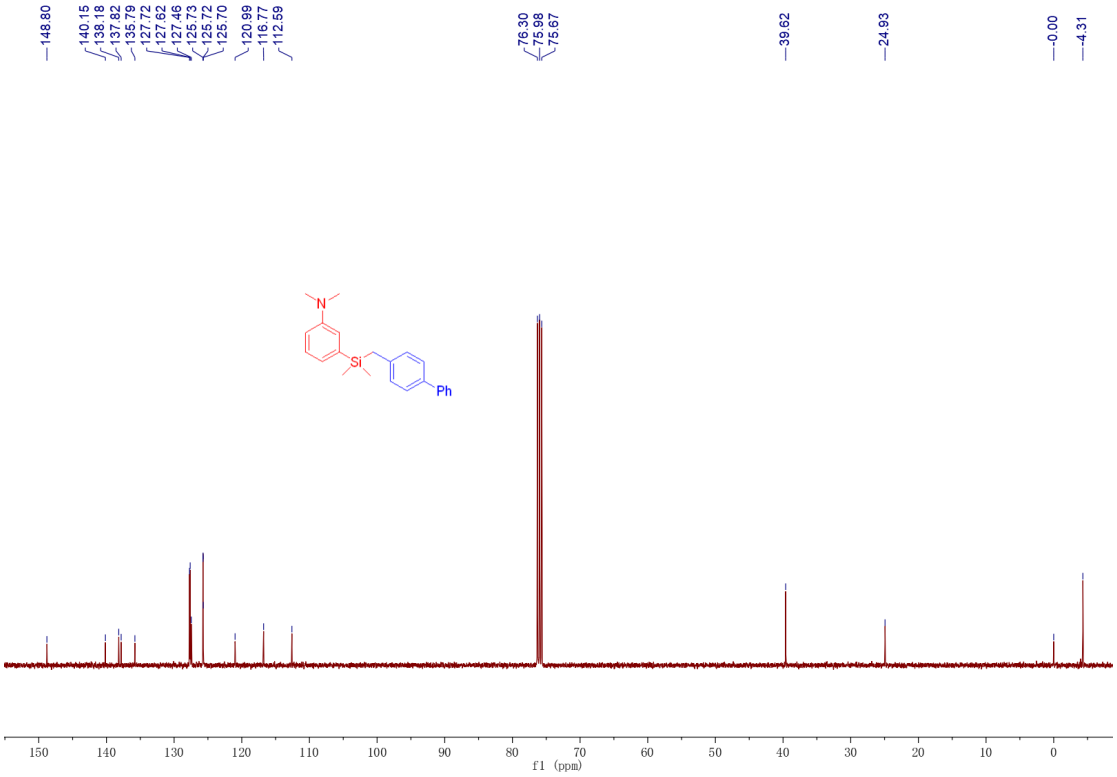


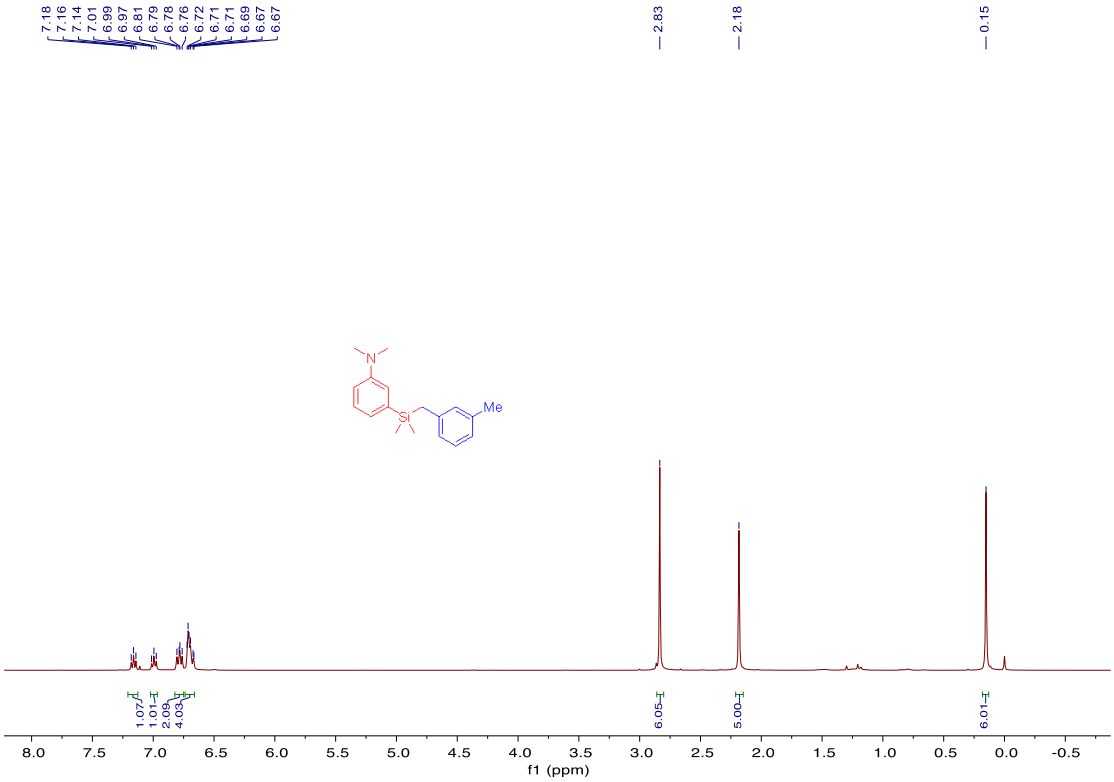
^{1}H NMR of 3m



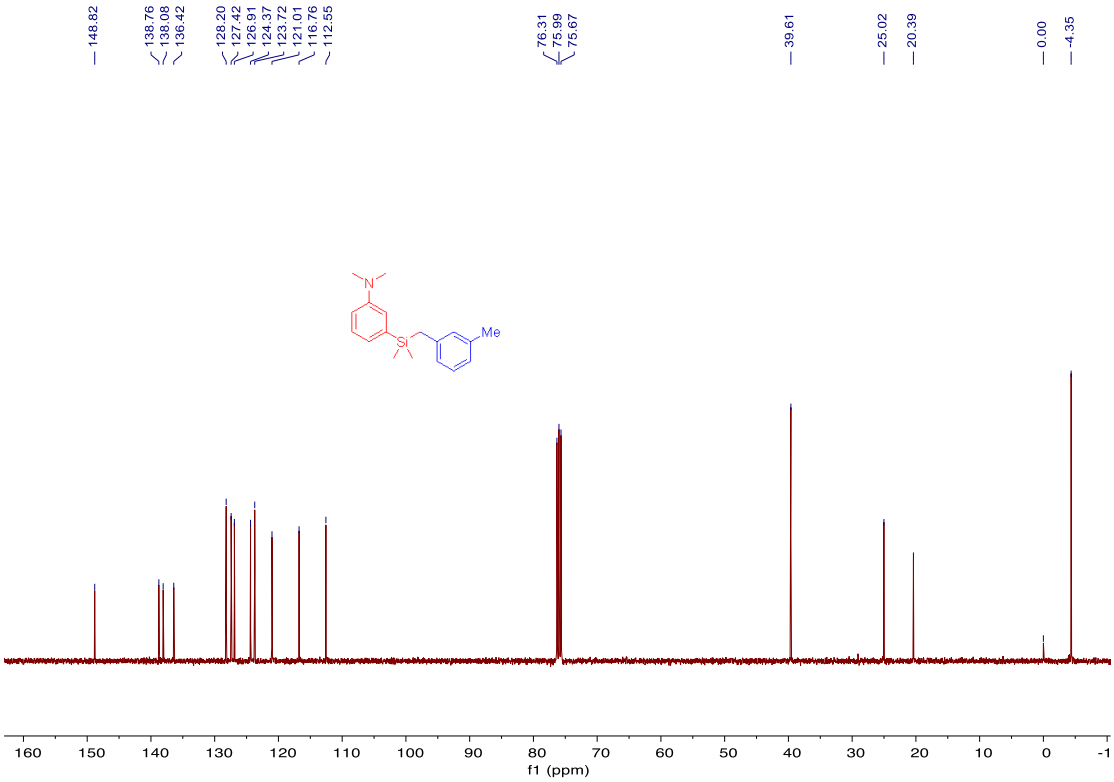
^{13}C NMR of 3m



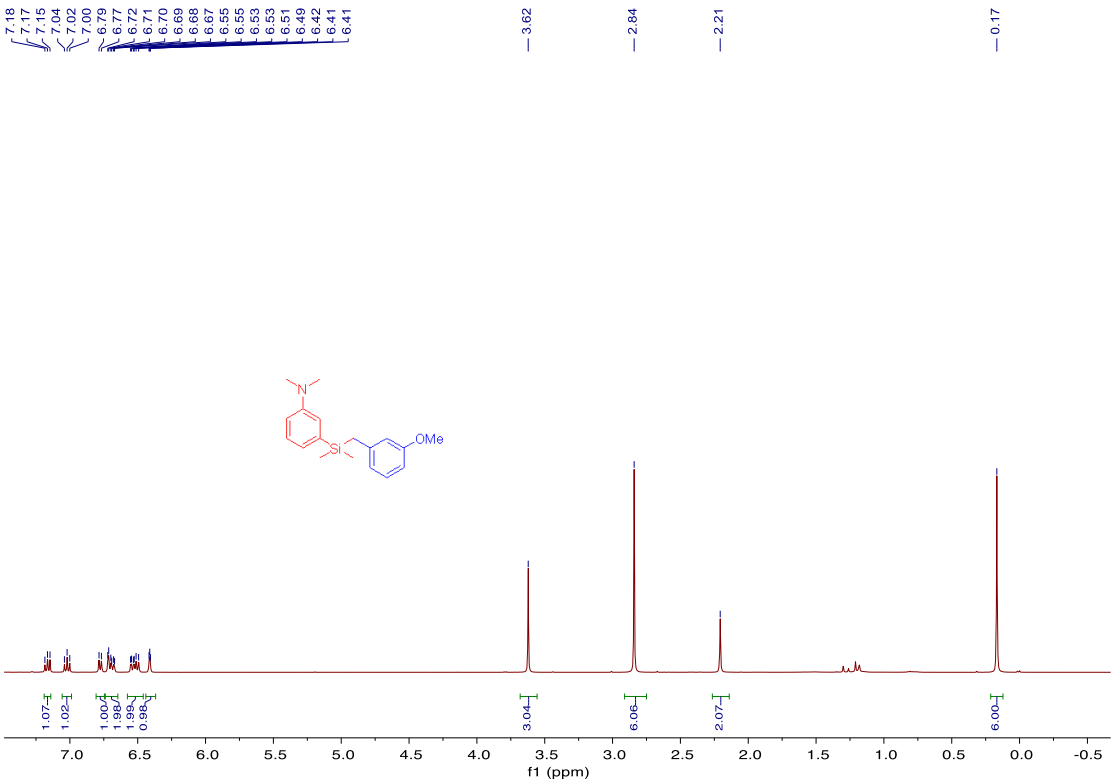
^{1}H NMR of 3n



^{13}C NMR of 3n



^{1}H NMR of 3o



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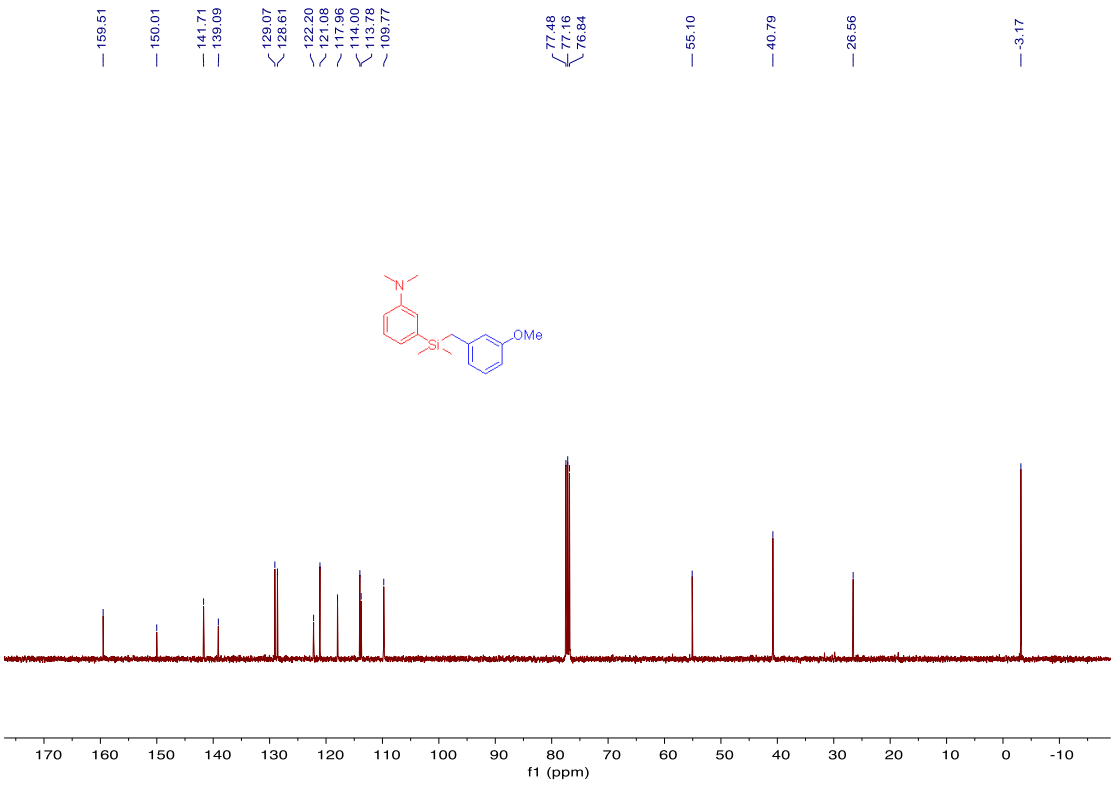

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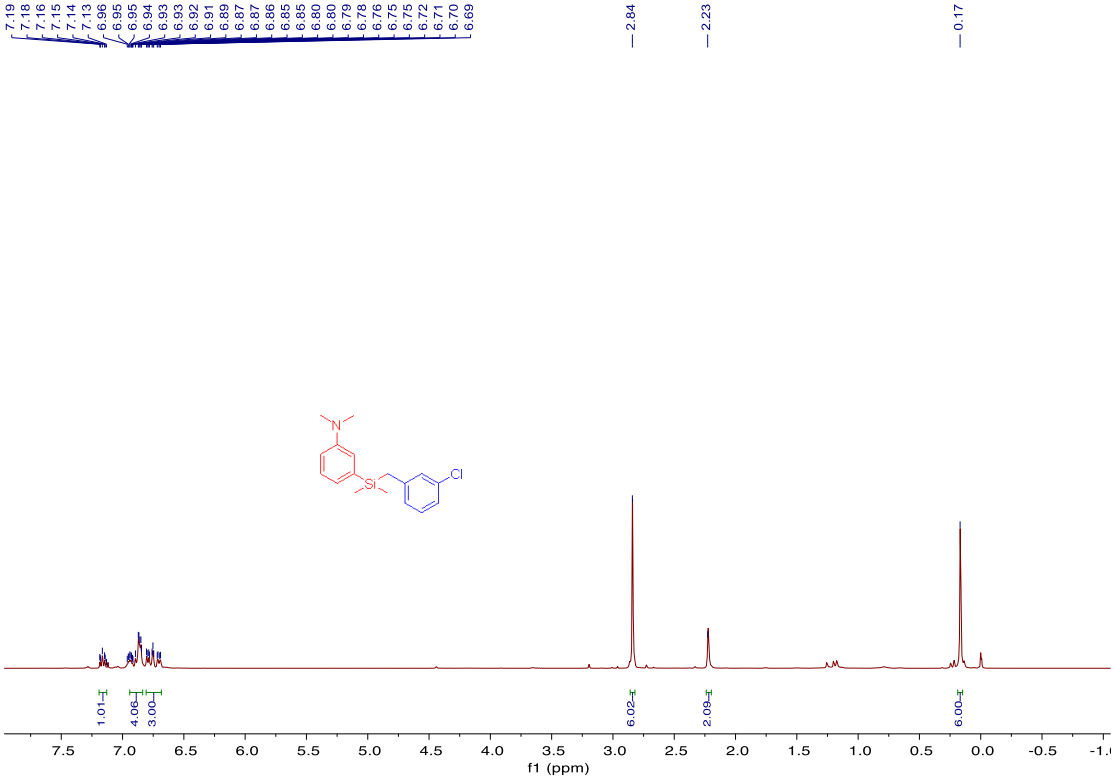

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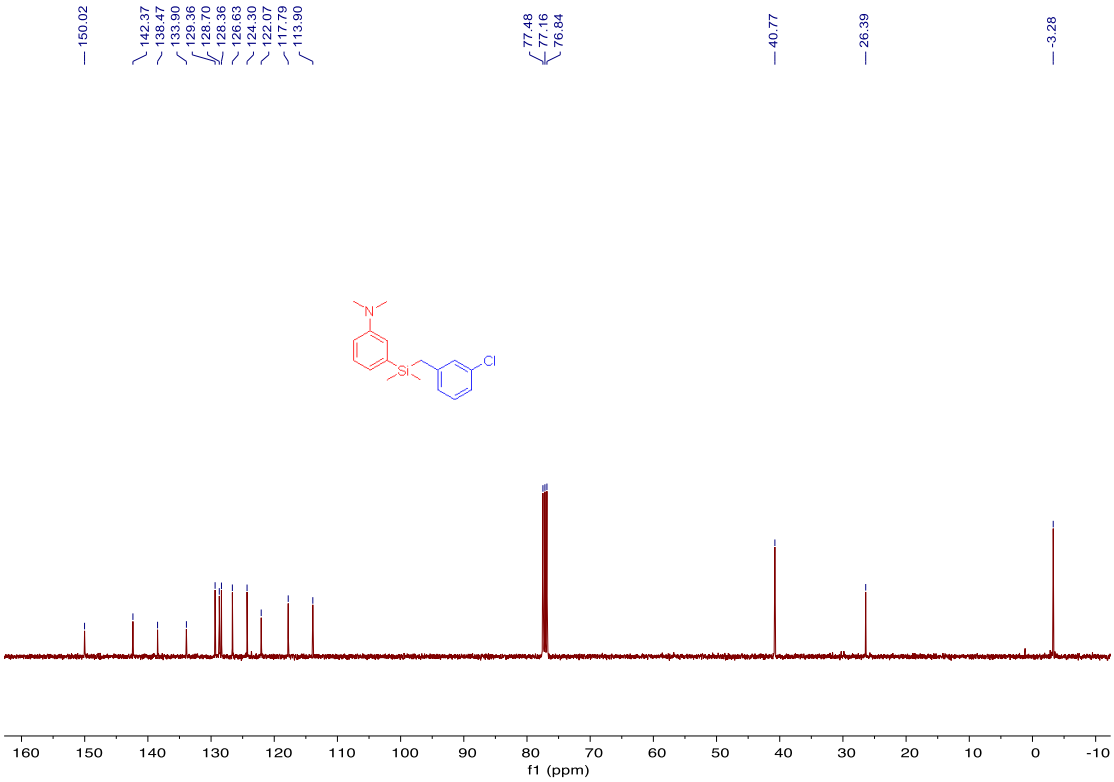
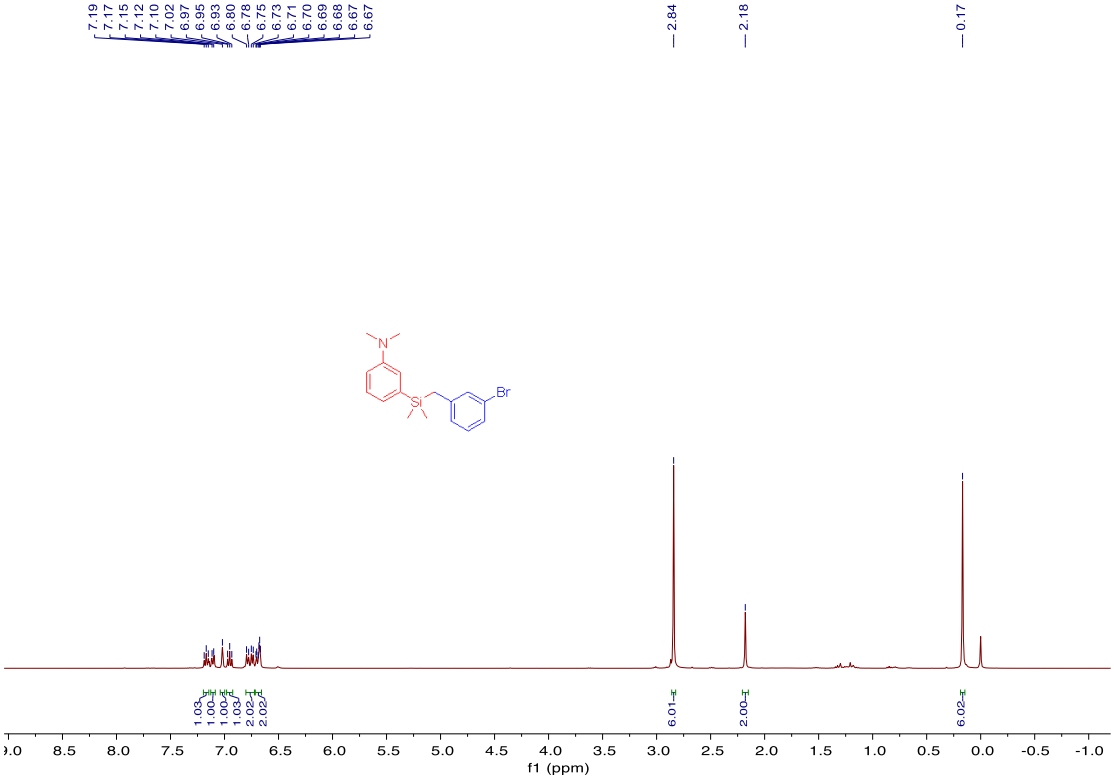
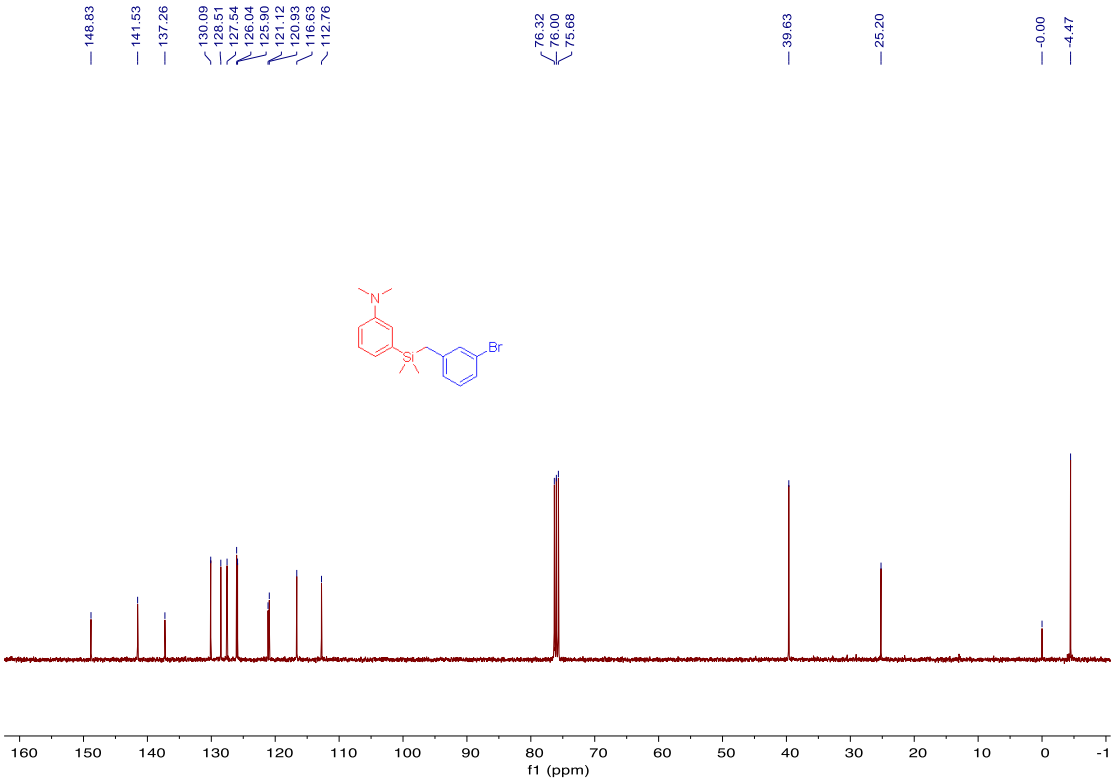


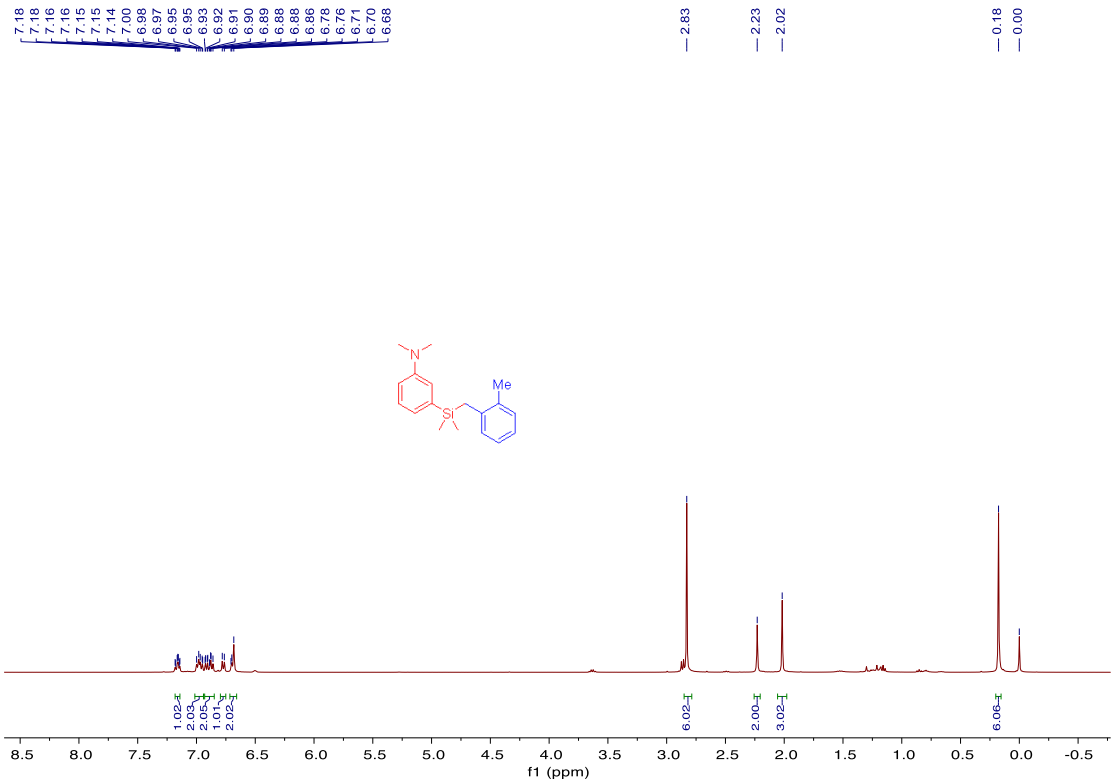
^{1}H NMR of 3q



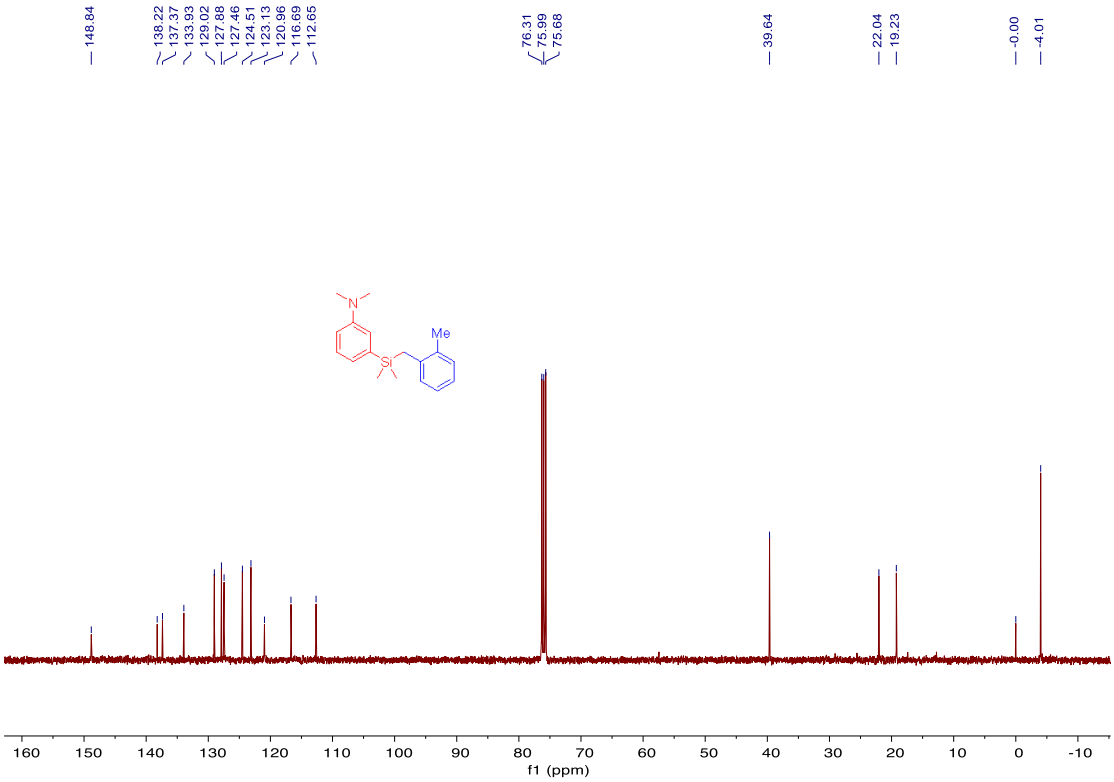
^{13}C NMR of 3q



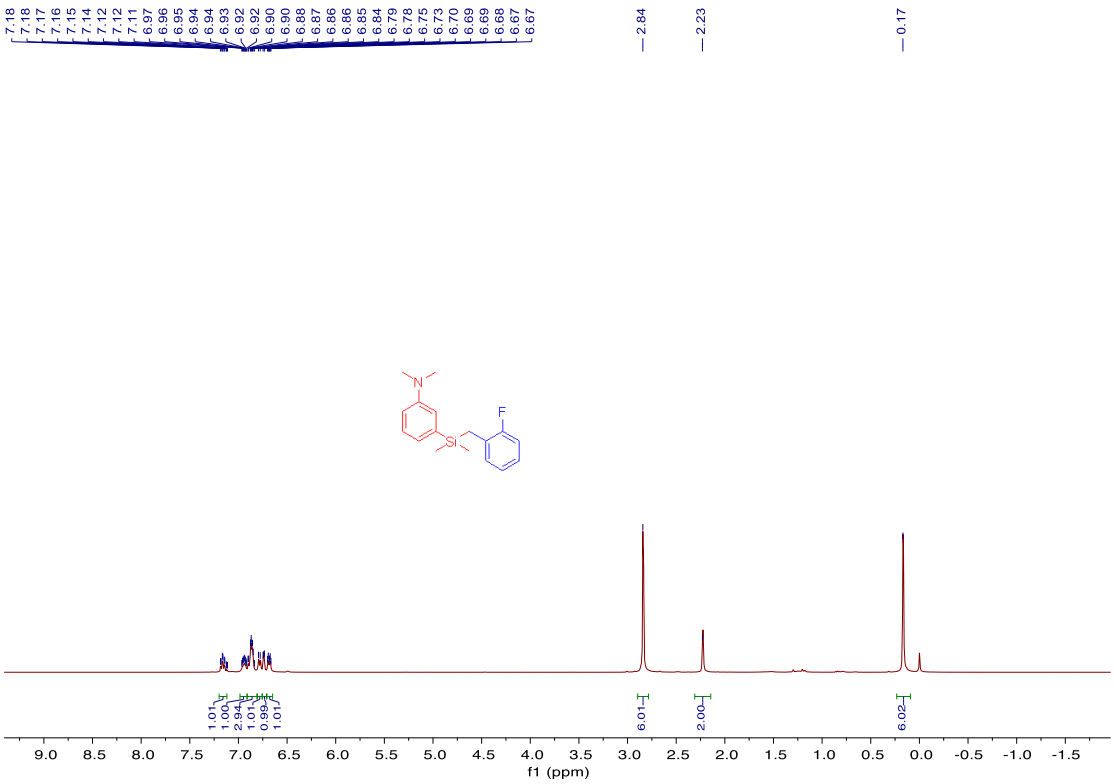
^{1}H NMR of 3r



^{13}C NMR of 3r



^{1}H NMR of 3s



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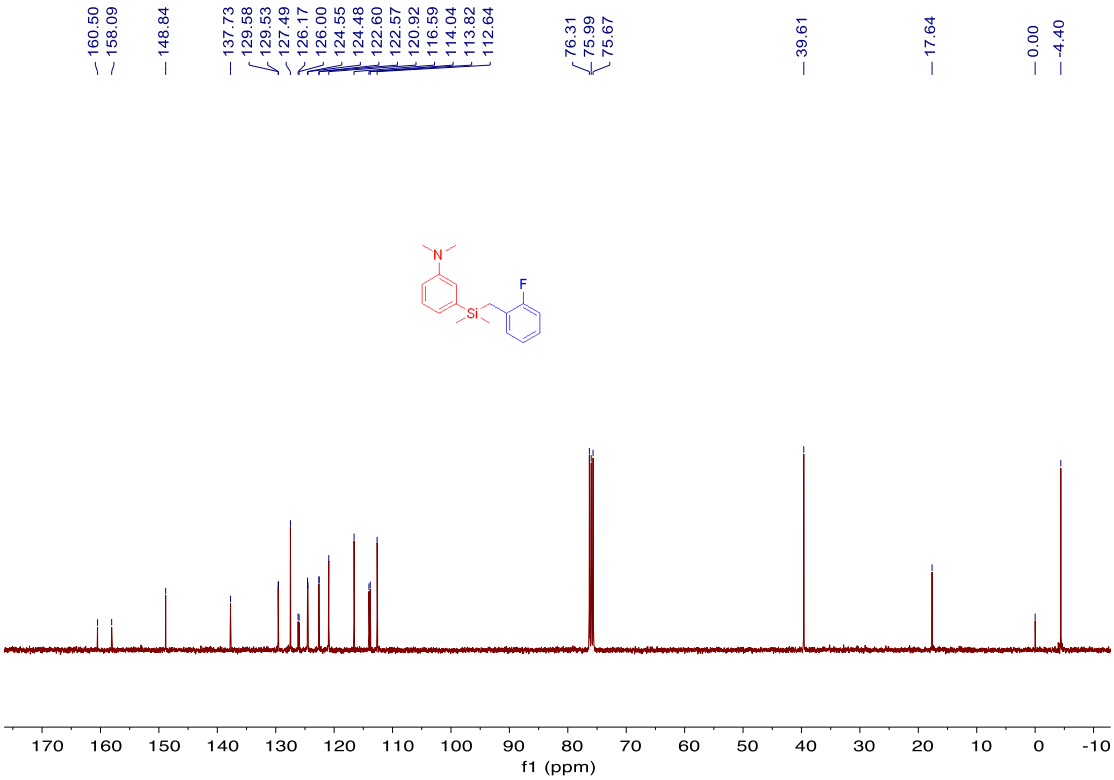

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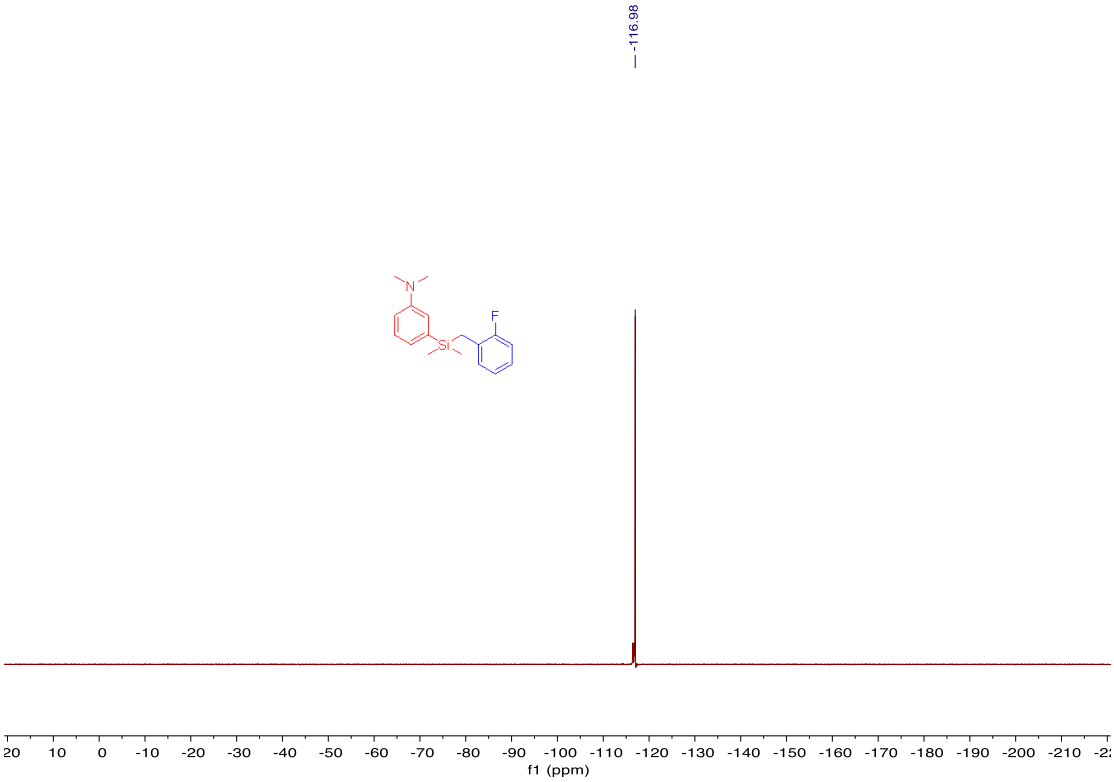
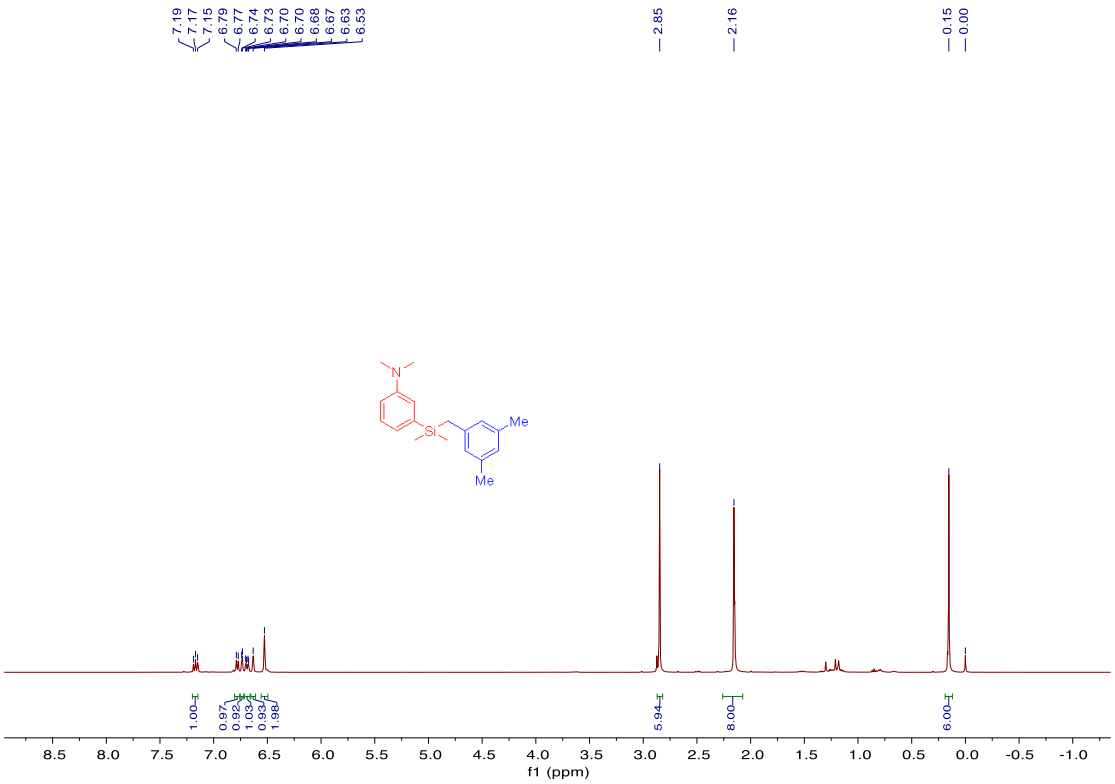

-116.98
N
Si
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

^{1}H NMR of 3t



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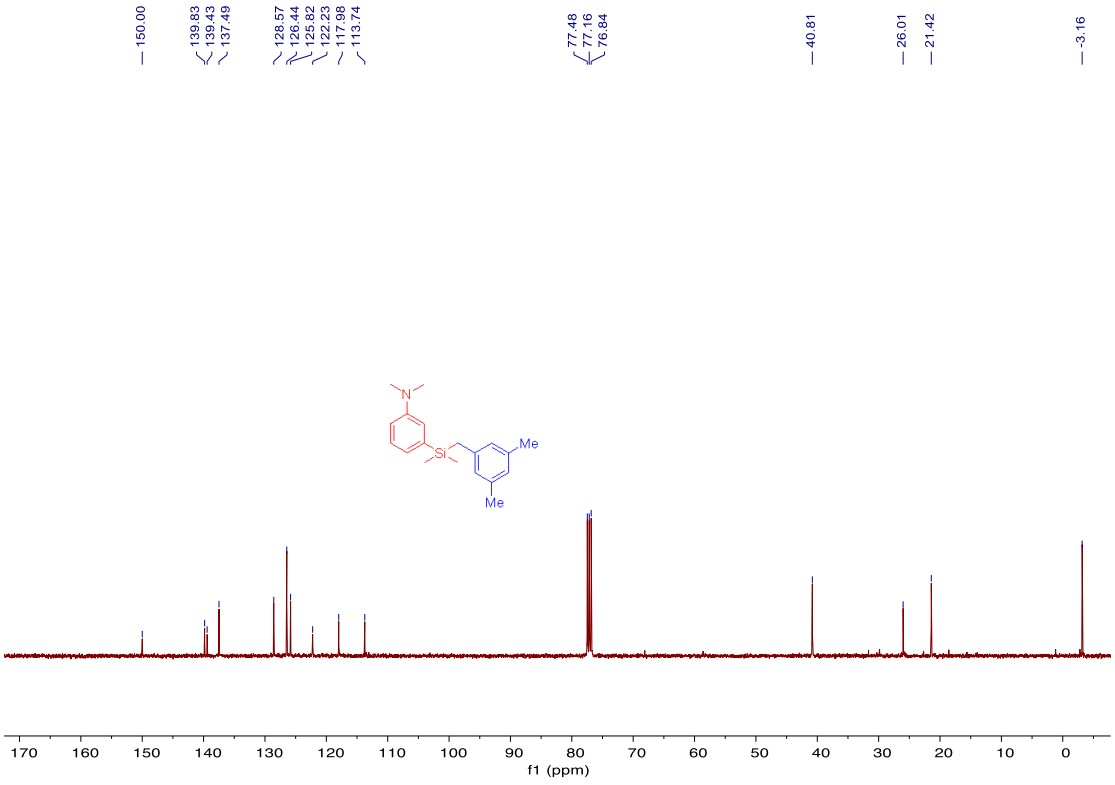
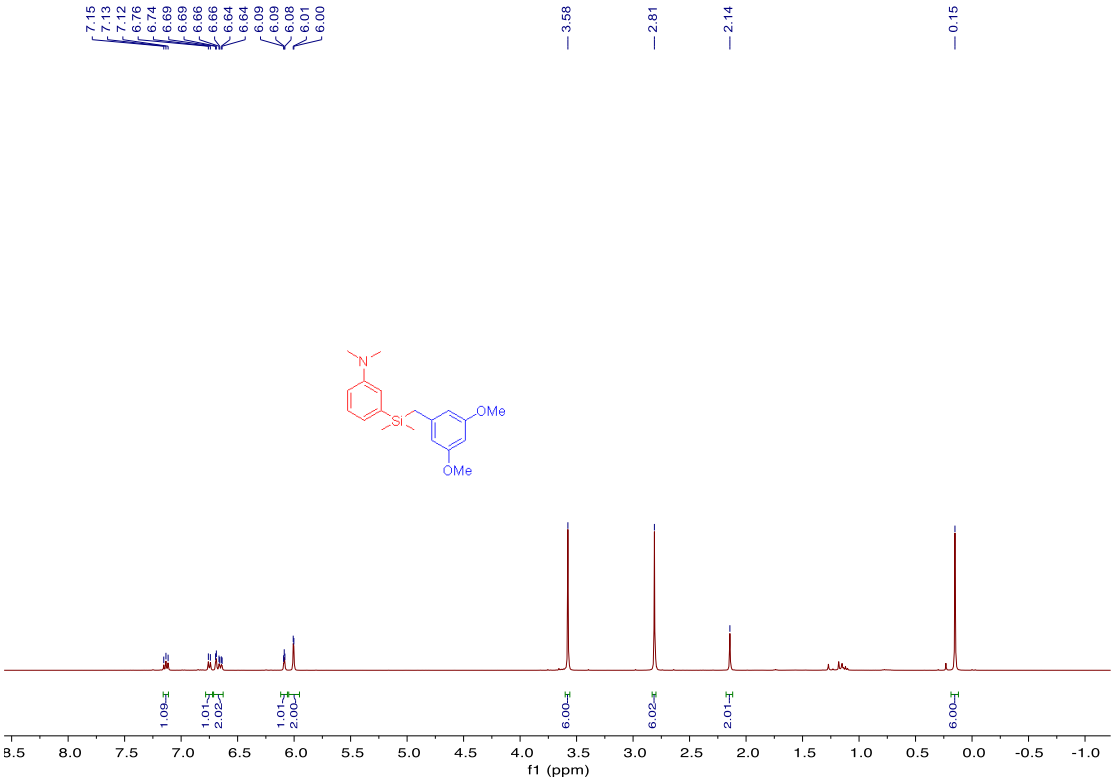
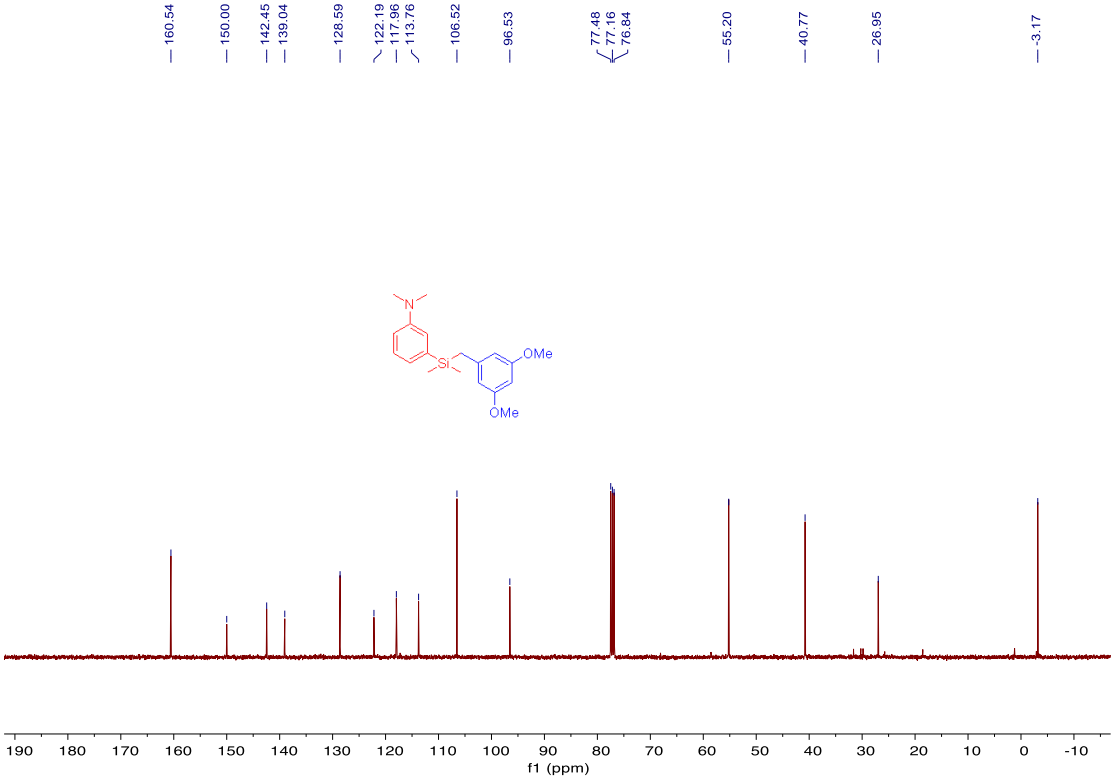


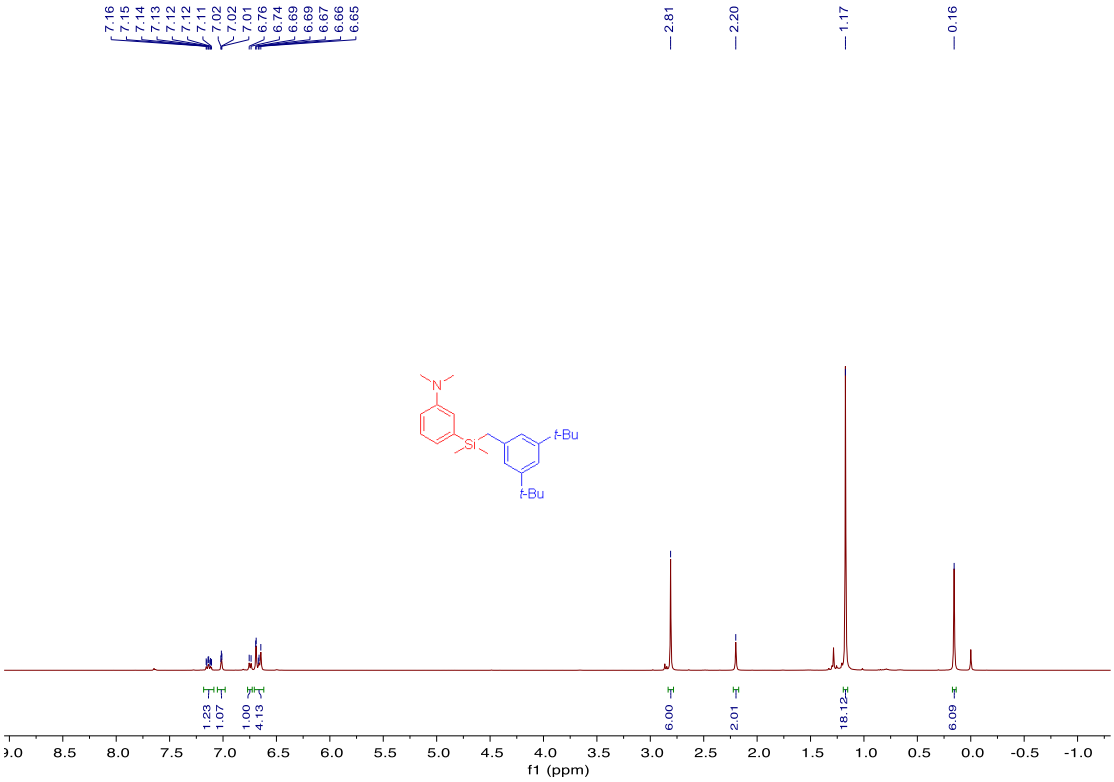
^{1}H NMR of 3u



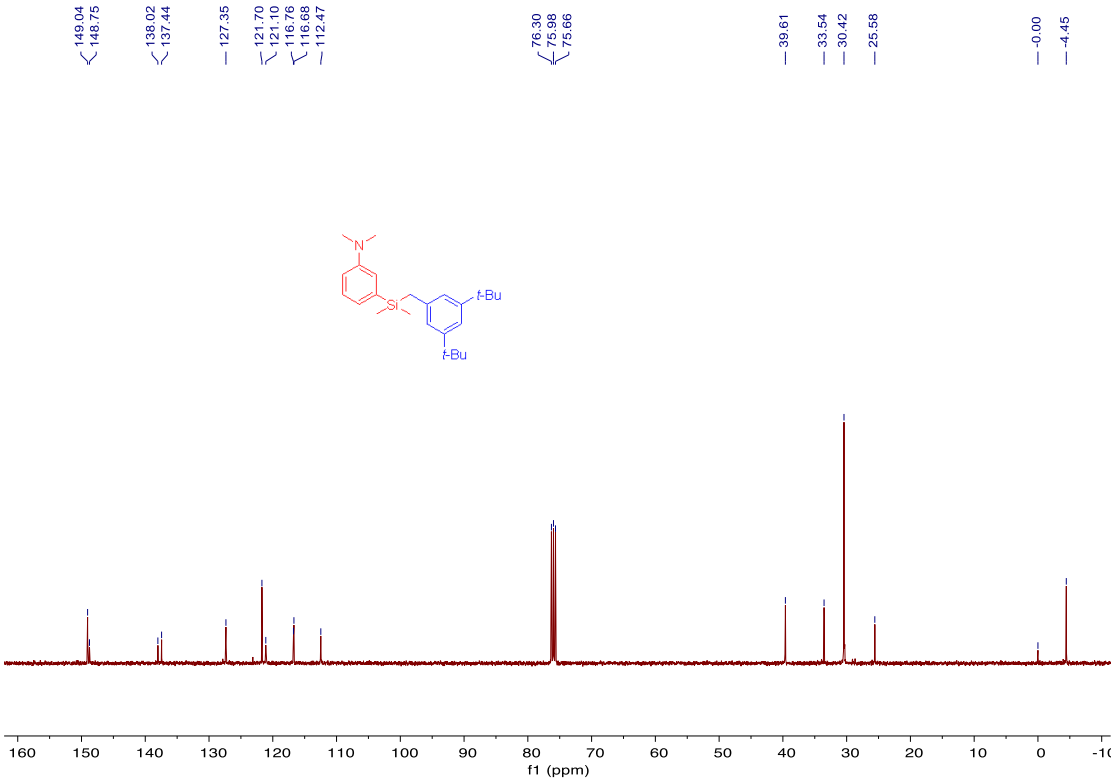
^{13}C NMR of 3u



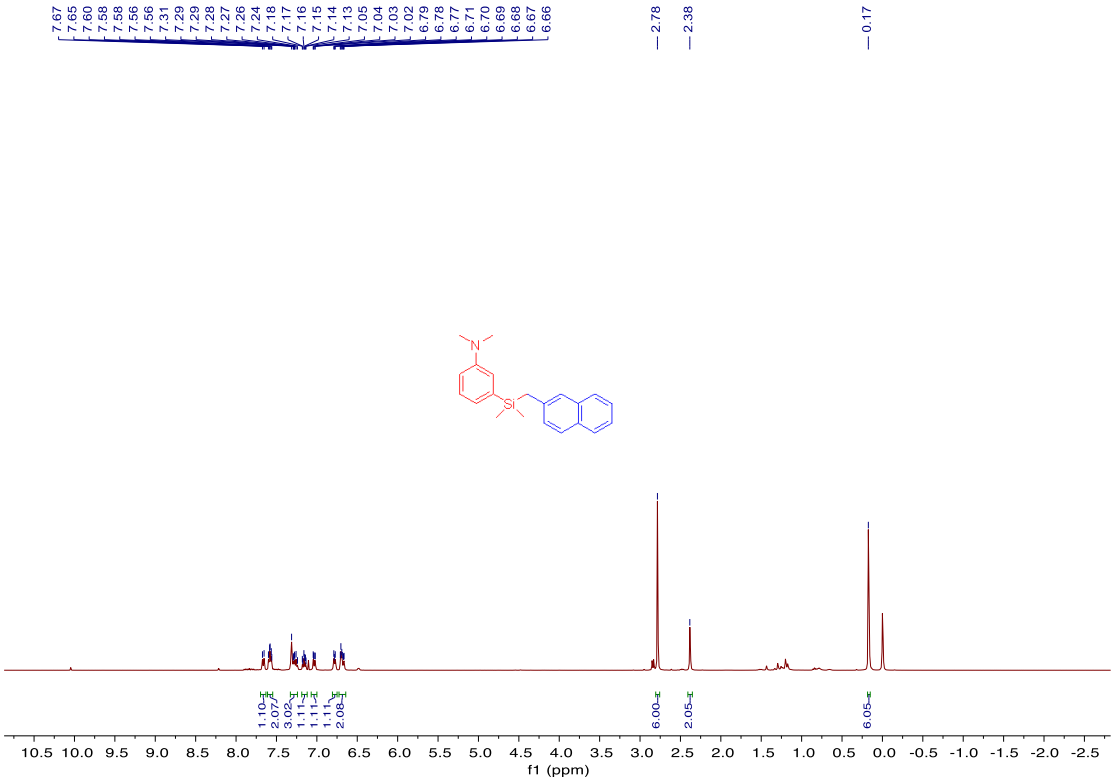
^{1}H NMR of 3v



^{13}C NMR of 3v



^{1}H NMR of 3w



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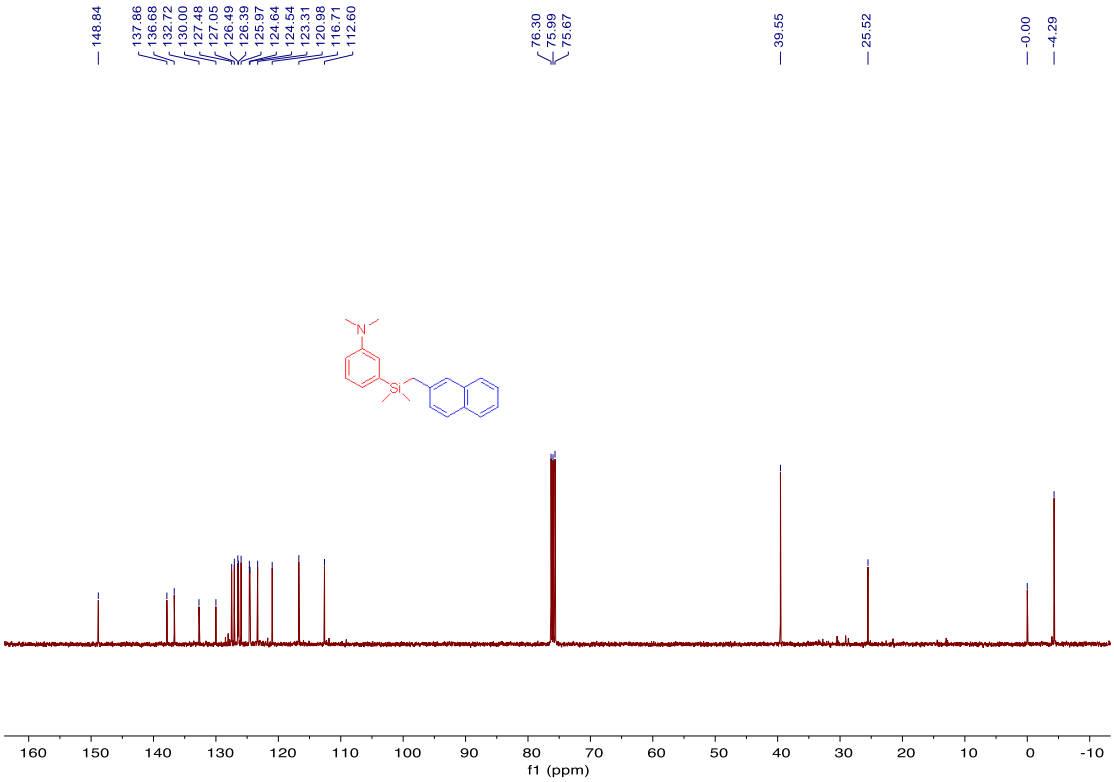
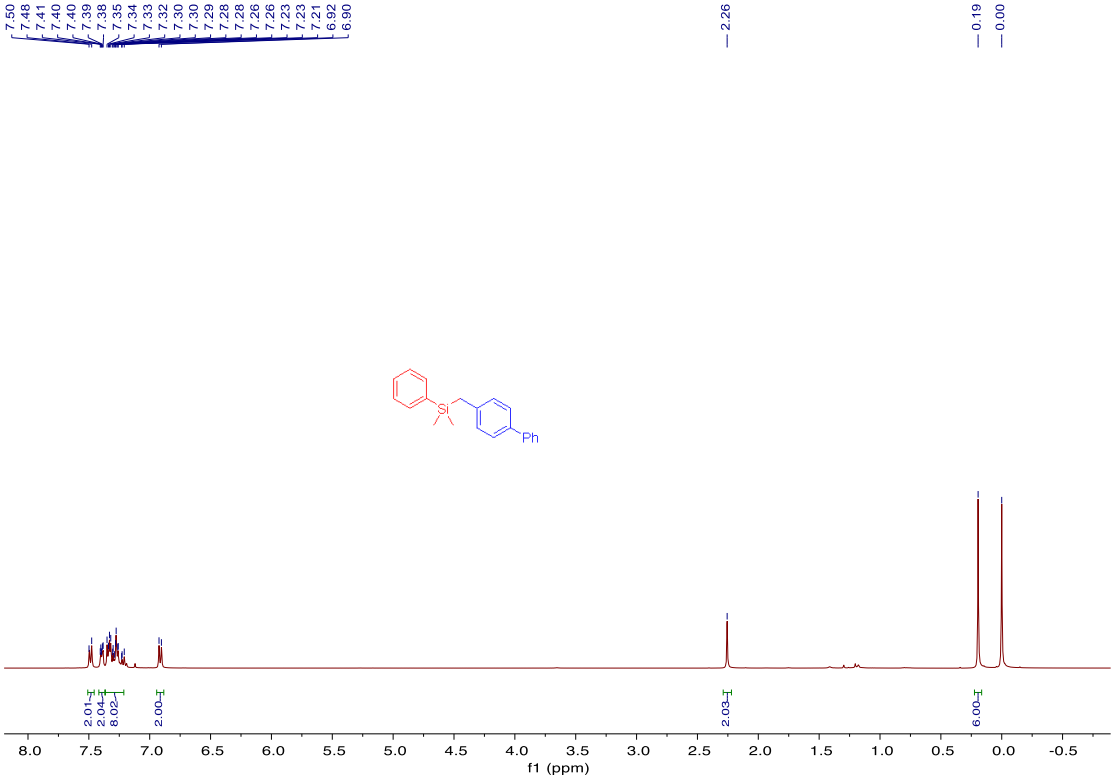
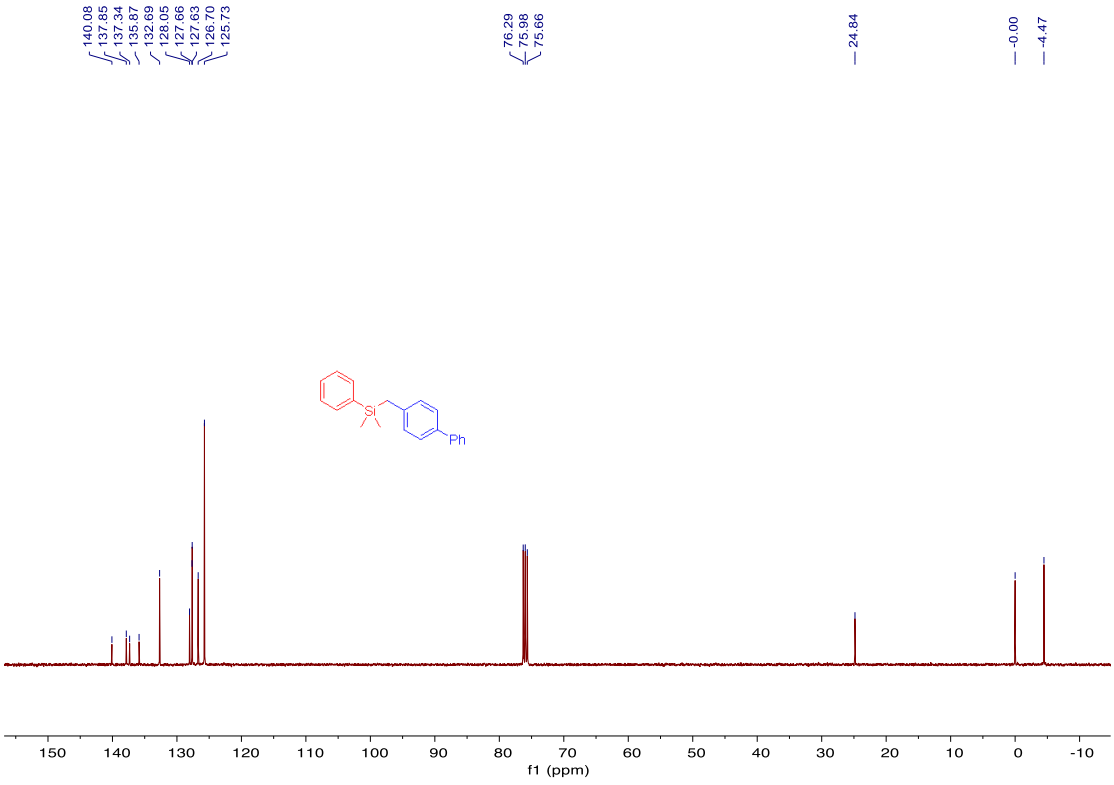


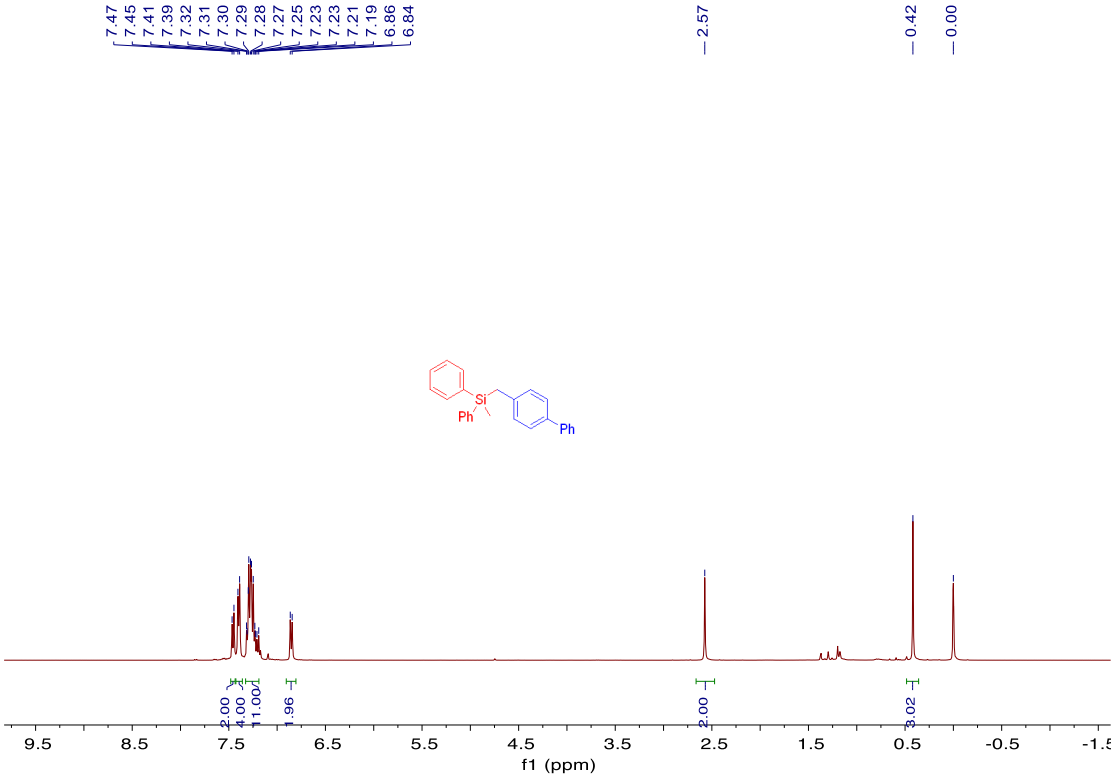
^{1}H NMR of 3x



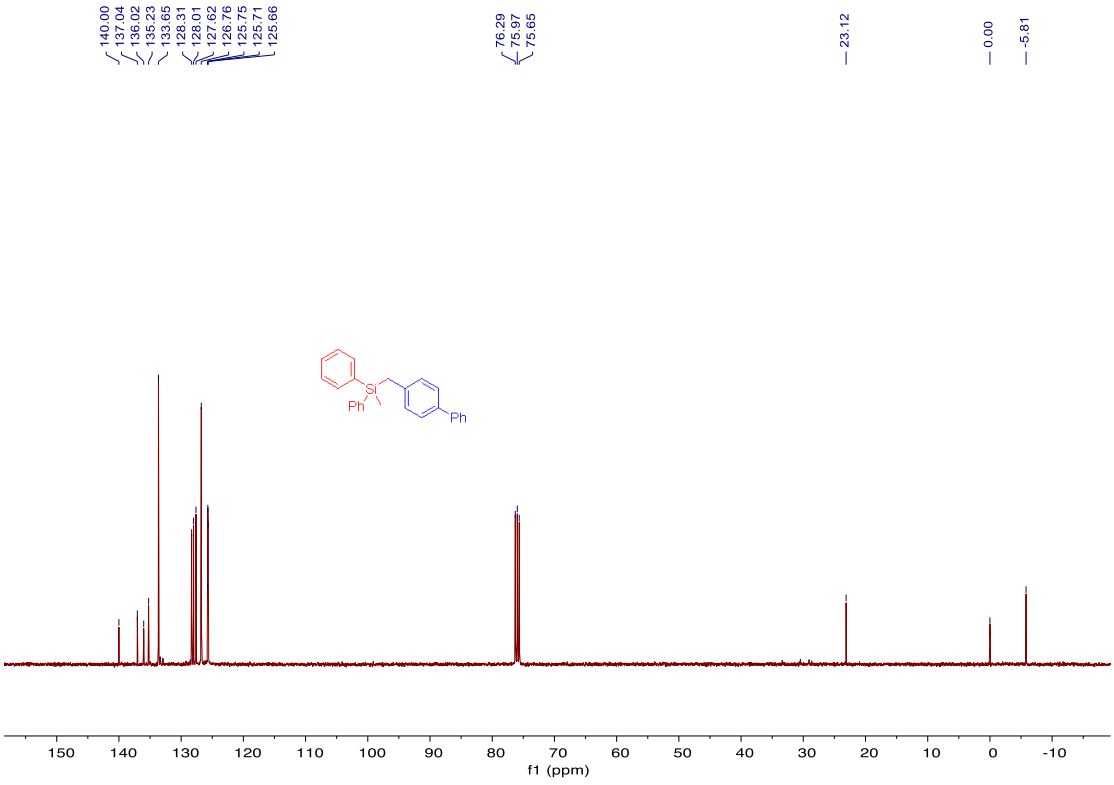
^{13}C NMR of 3x



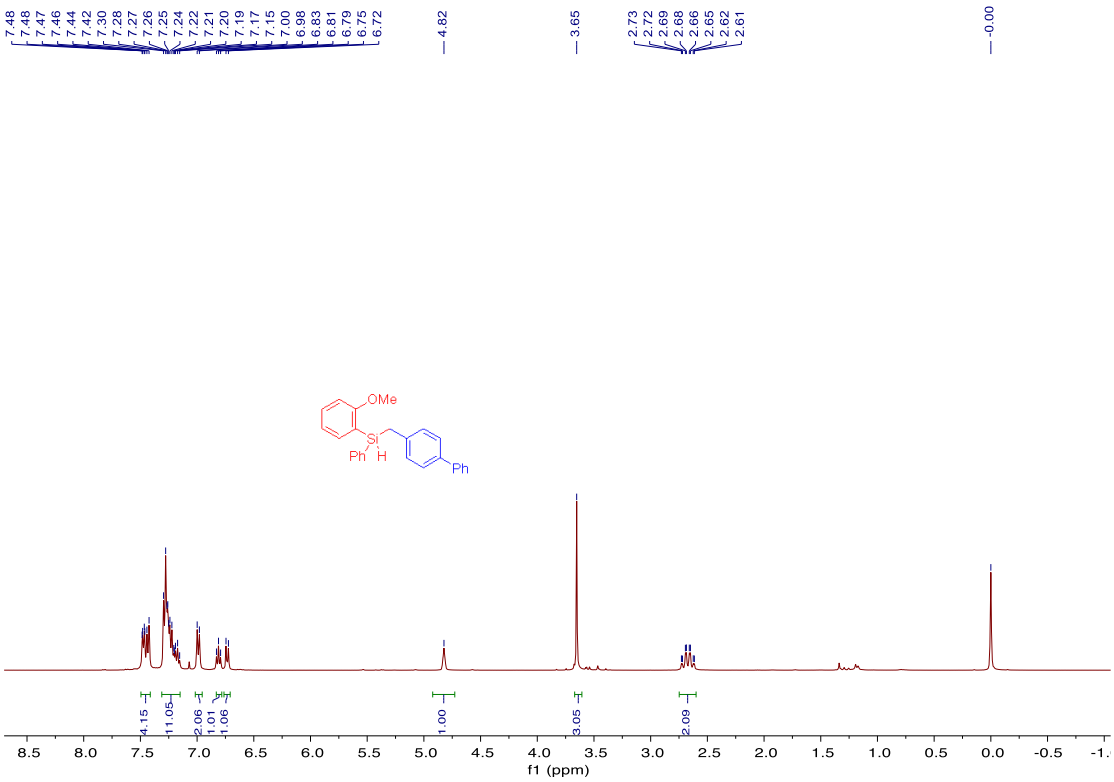
^{1}H NMR of 3y



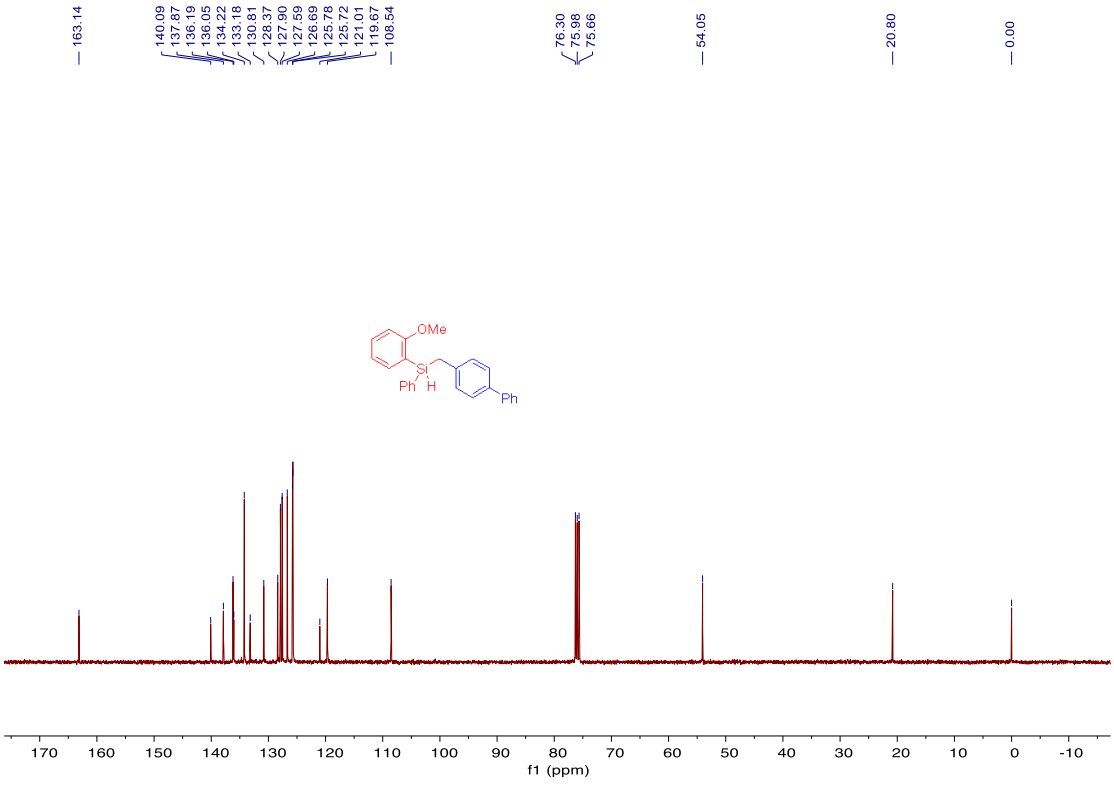
^{13}C NMR of 3y



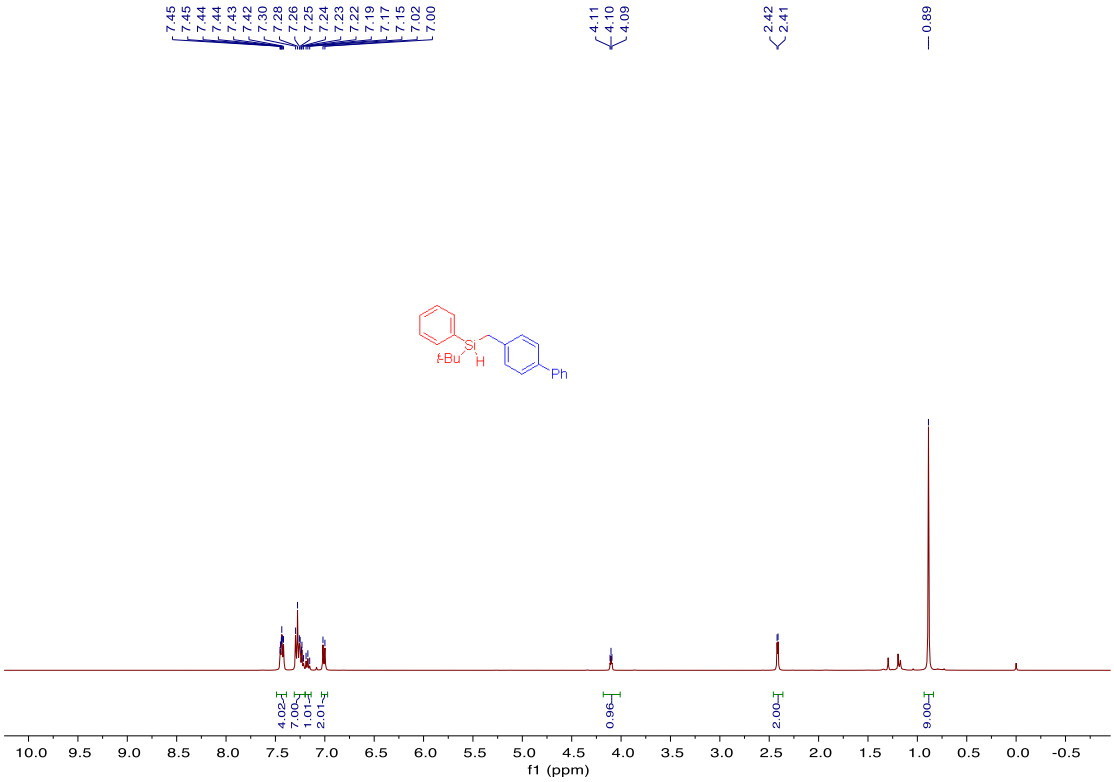
^{1}H NMR of 3z



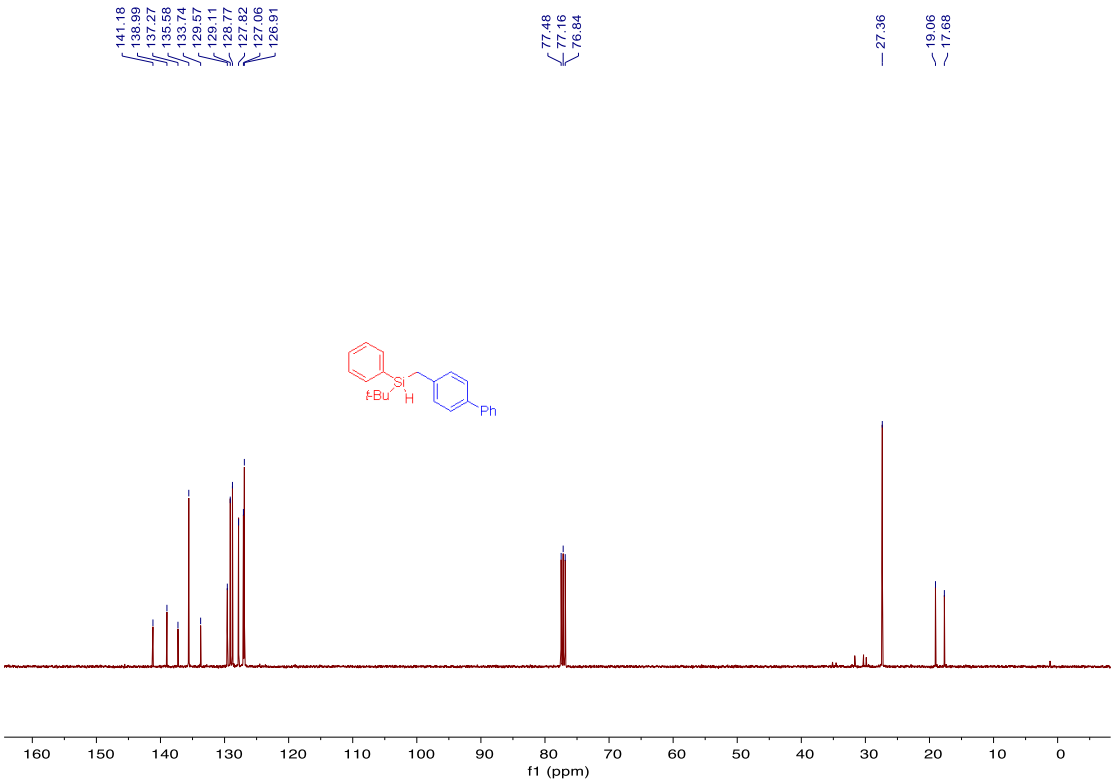
^{13}C NMR of 3z



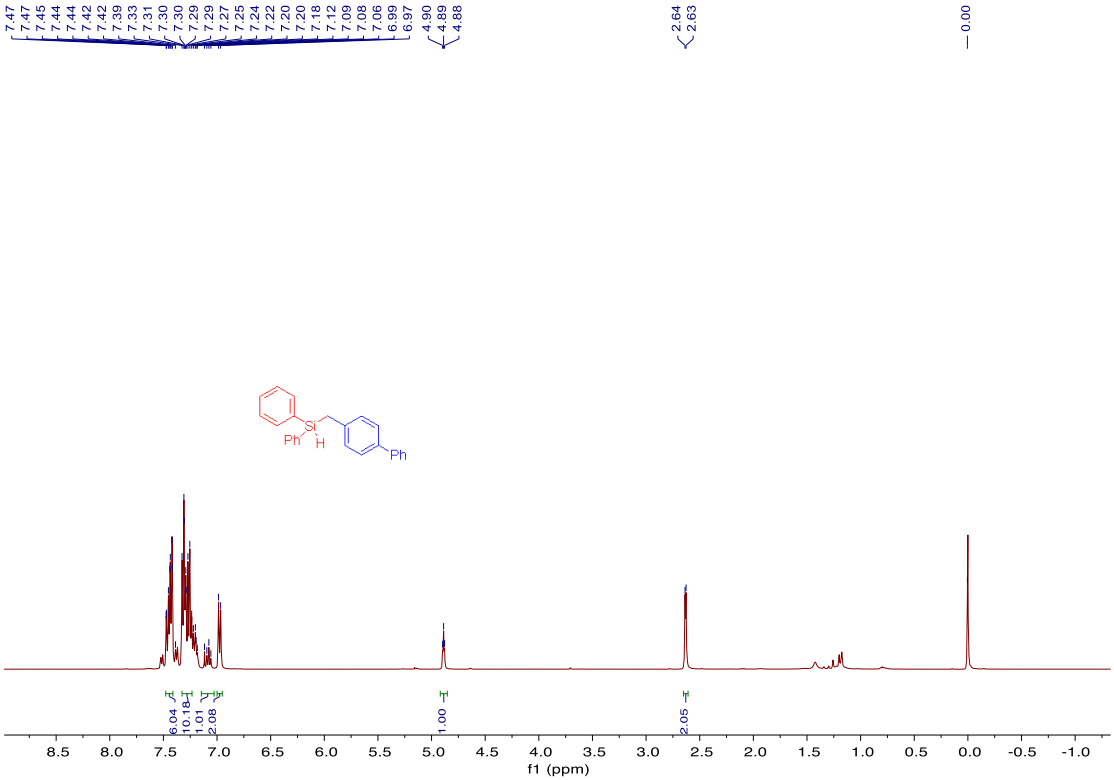
^{1}H NMR of 3aa



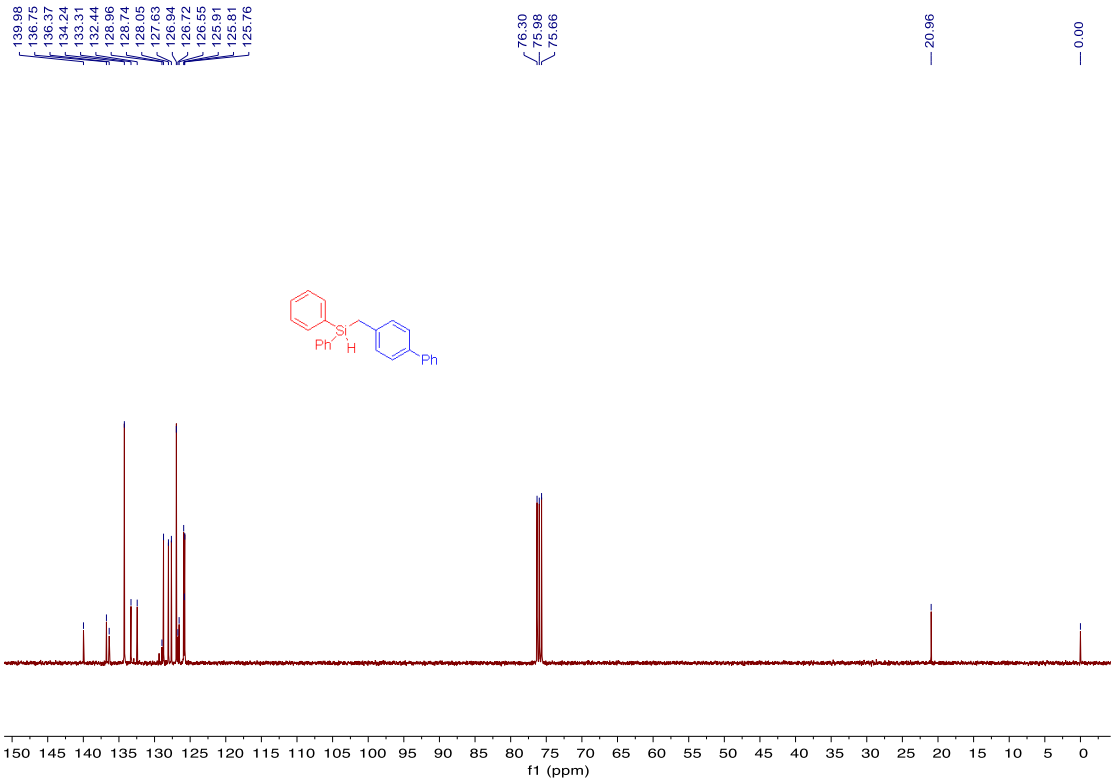
^{13}C NMR of 3aa



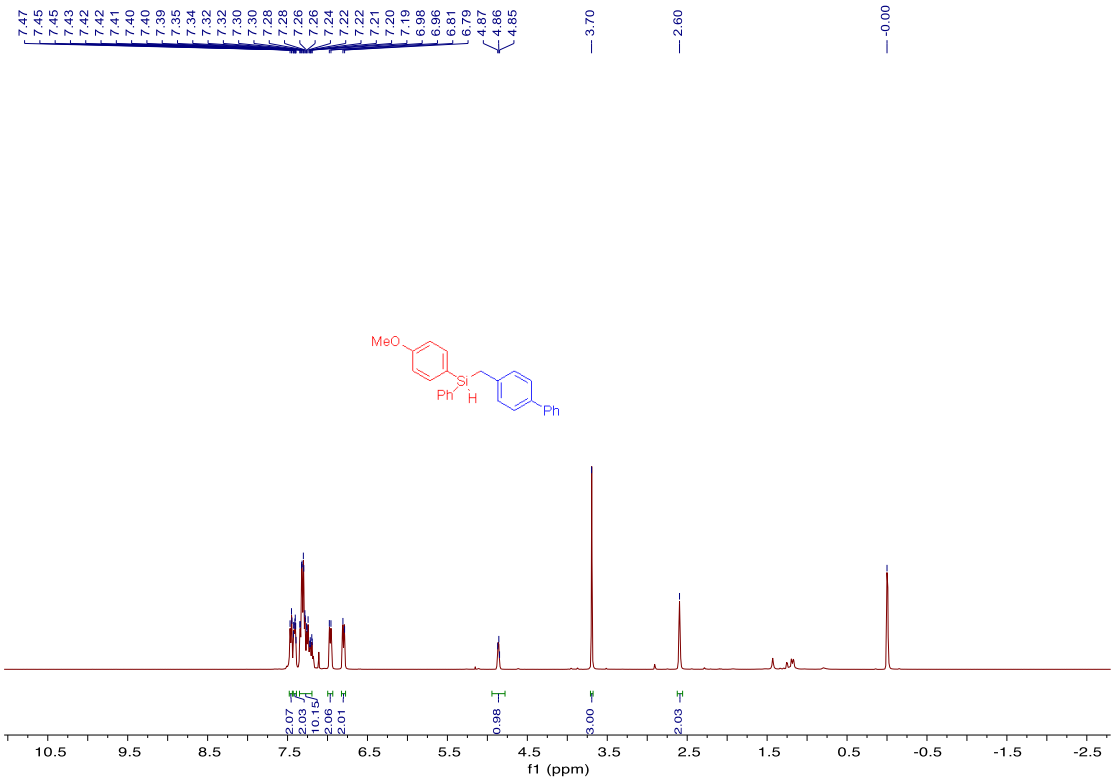
^{1}H NMR of 3ab



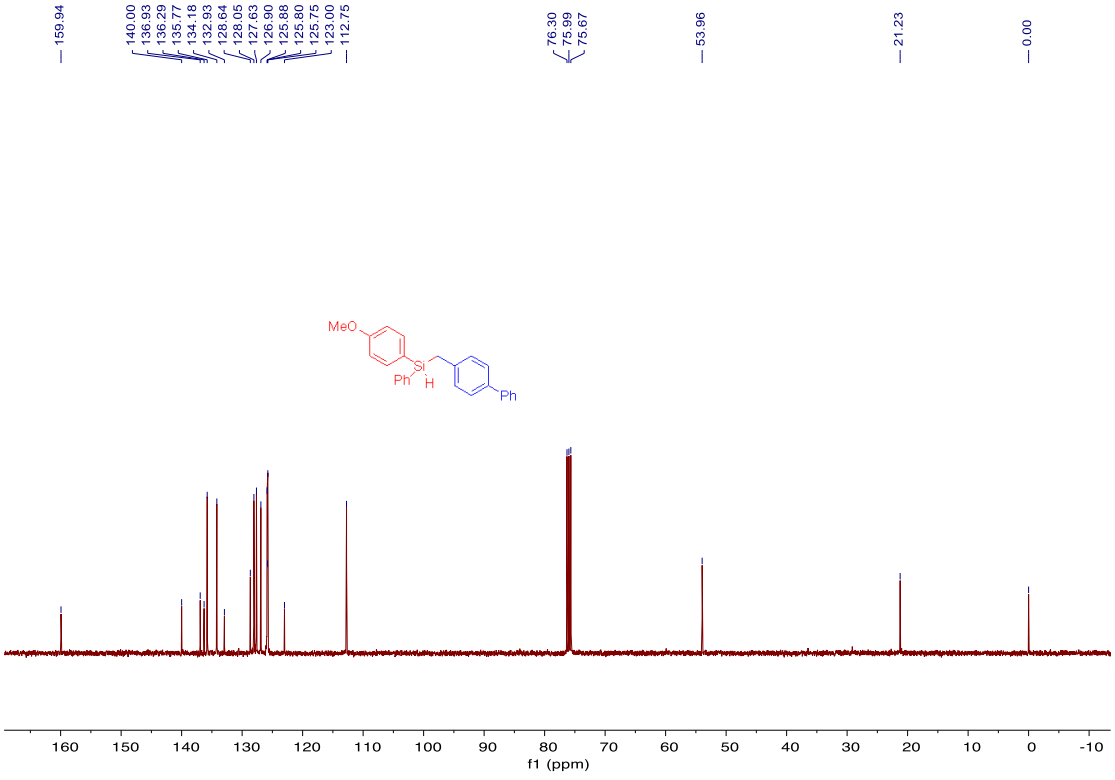
^{13}C NMR of 3ab



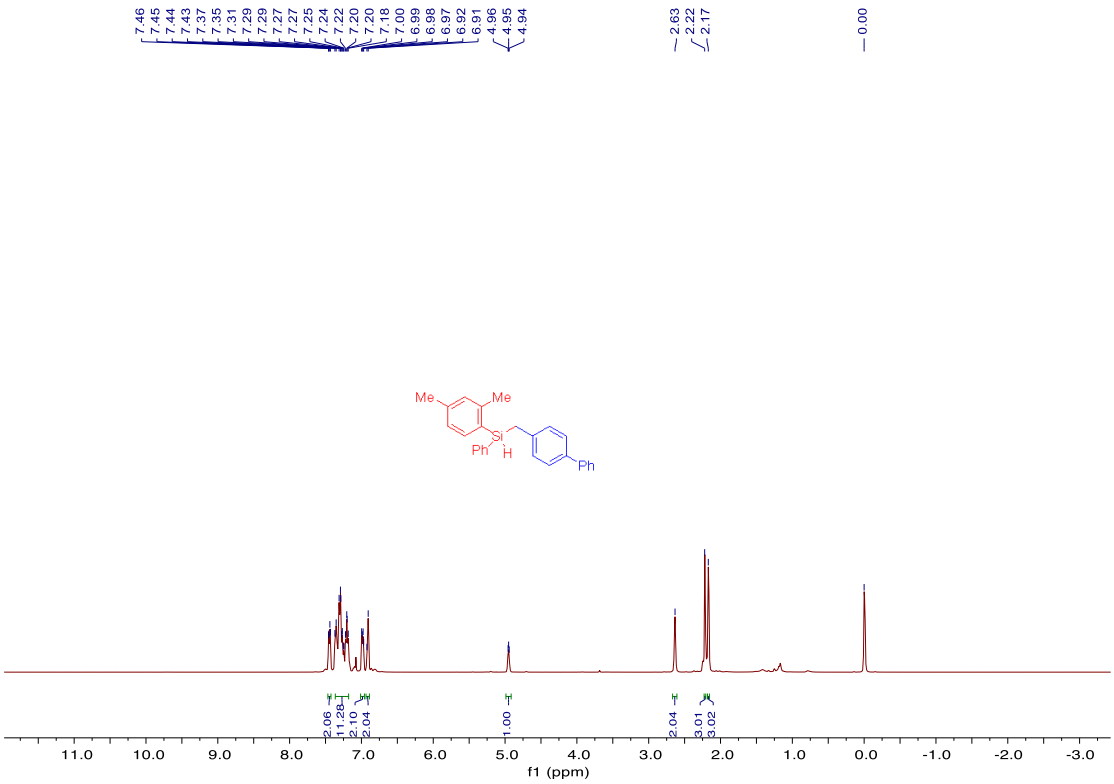
^{1}H NMR of 3ac



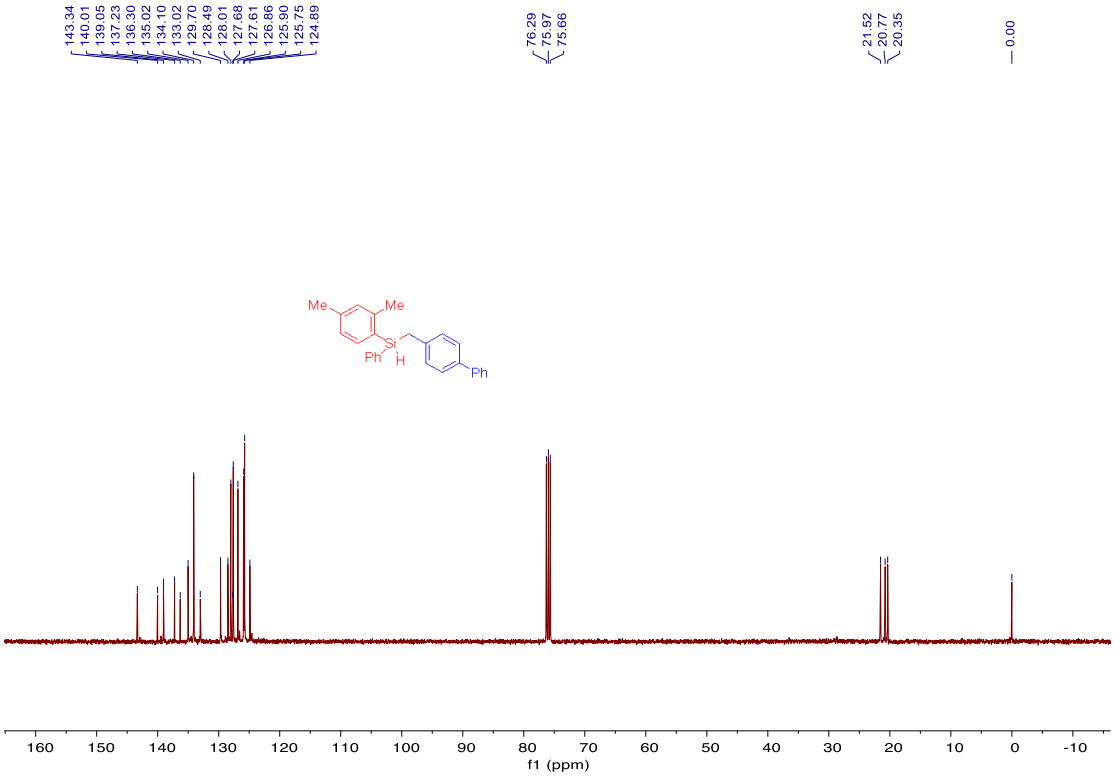
^{13}C NMR of 3ac



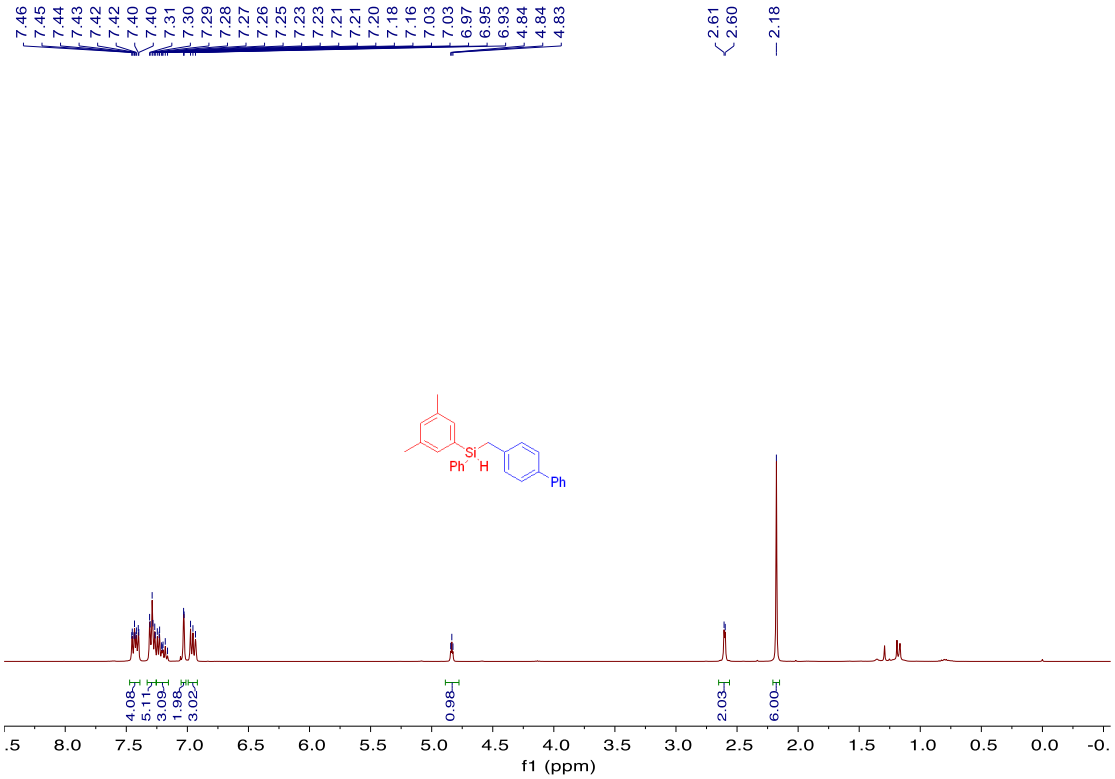
^{1}H NMR of 3ad



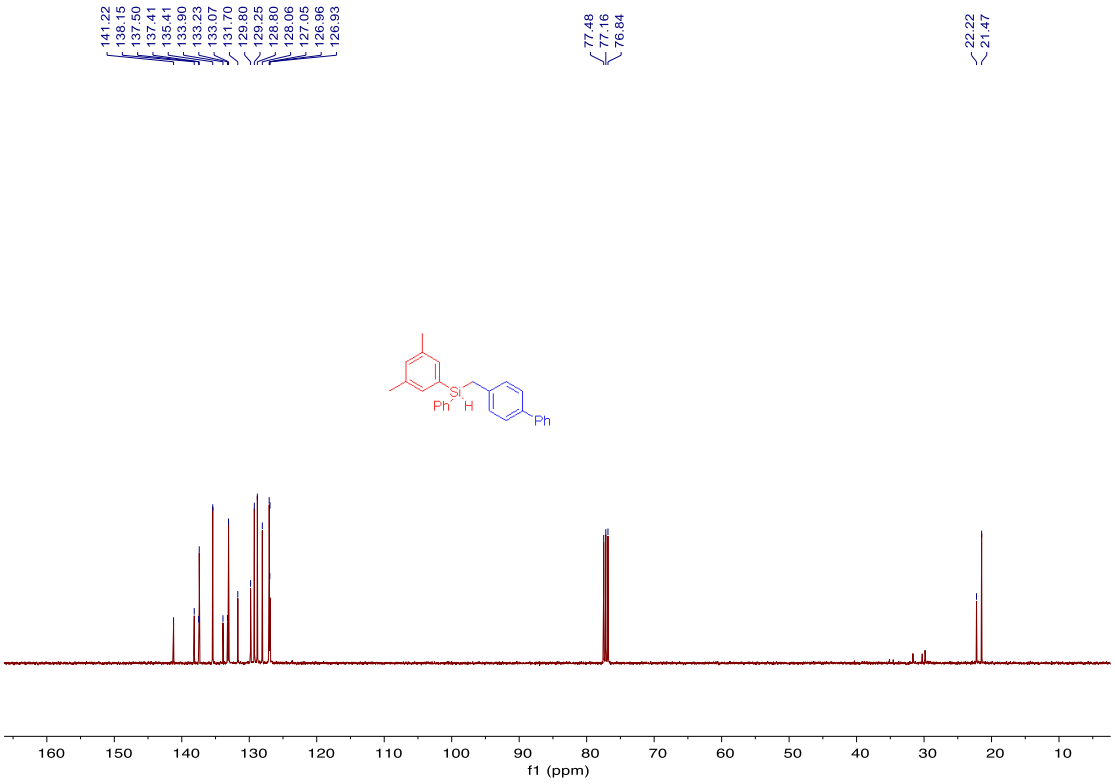
^{13}C NMR of 3ad



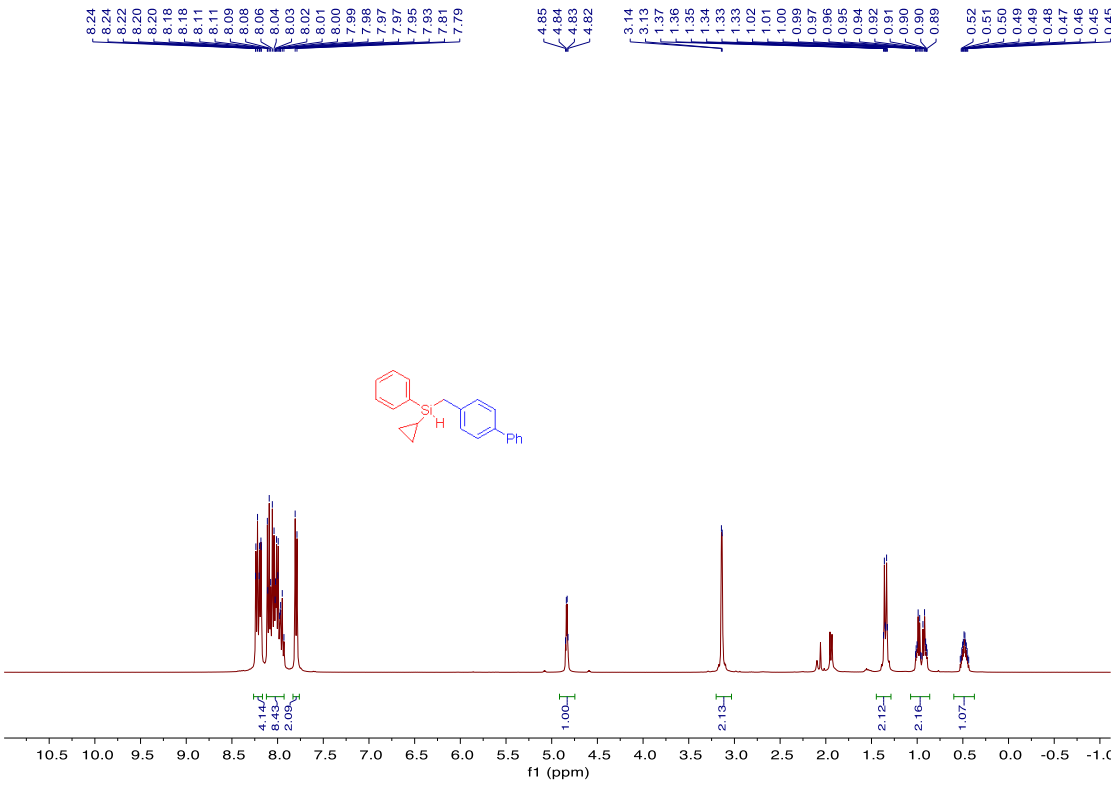
^{1}H NMR of 3ae



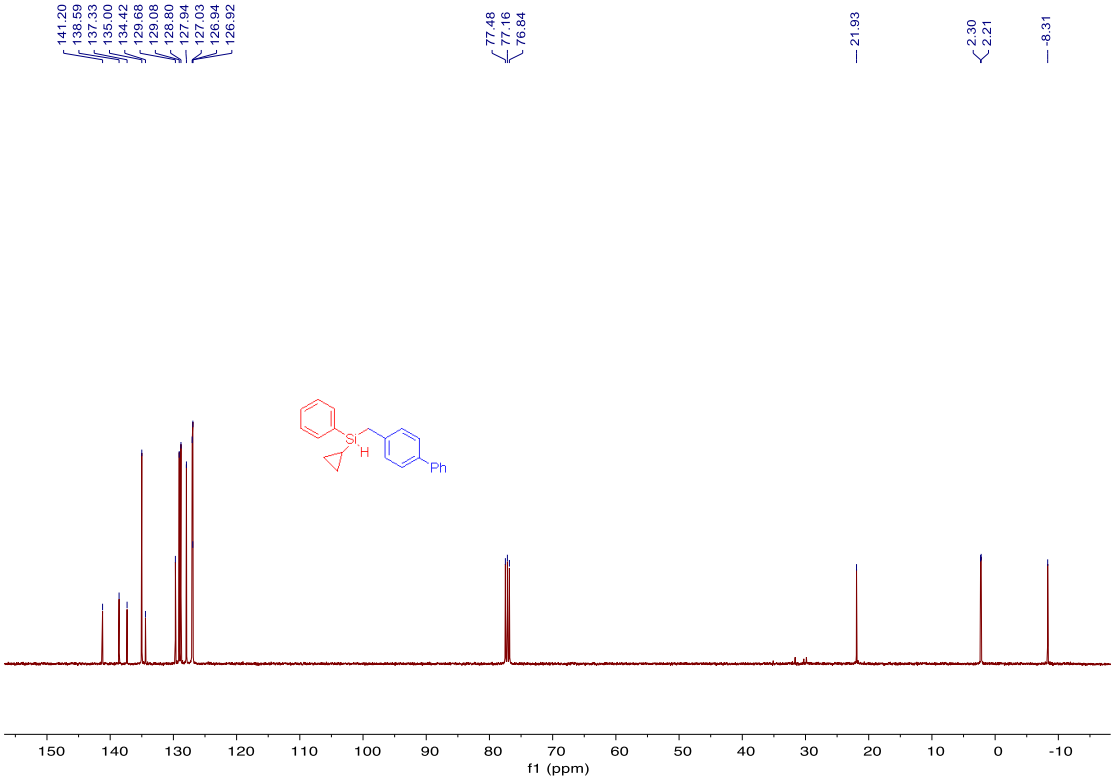
^{13}C NMR of 3ae



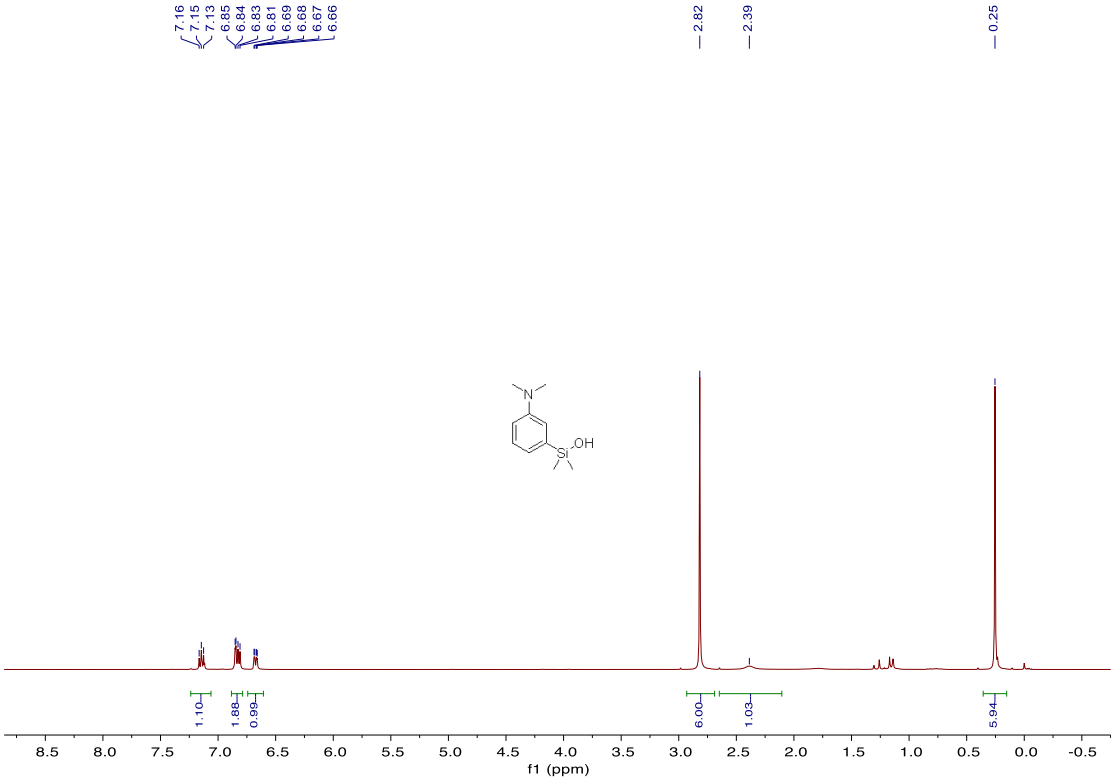
^{1}H NMR of 3af



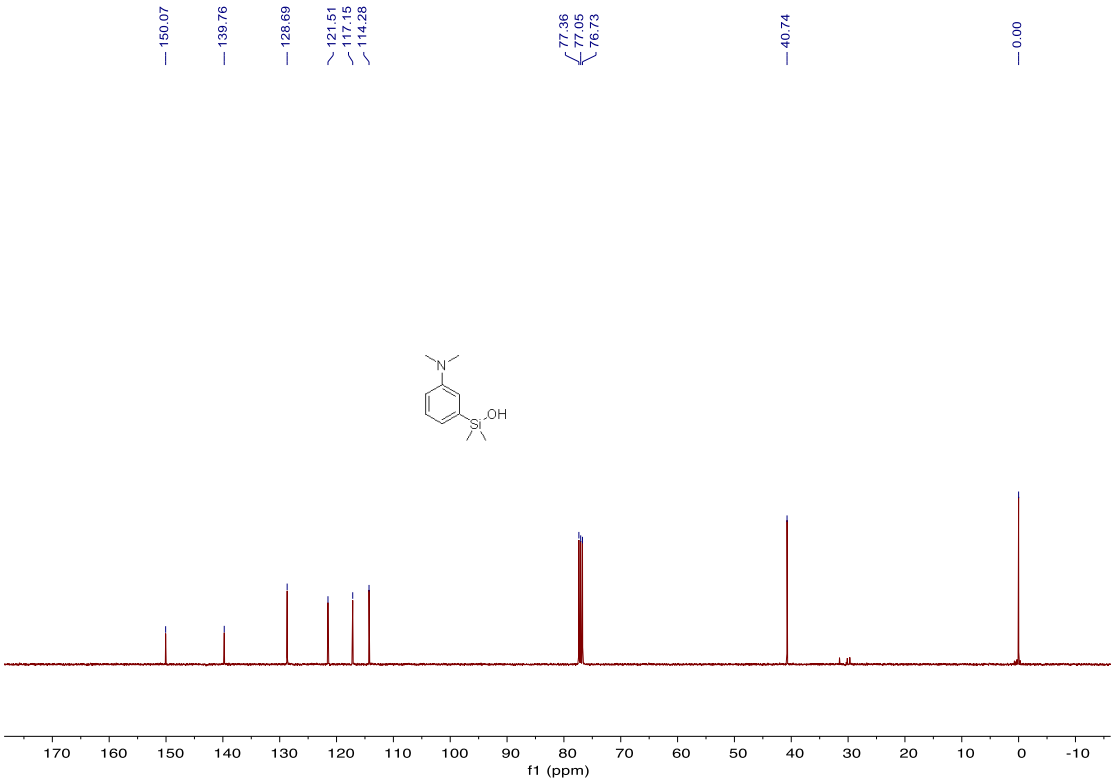
^{13}C NMR of 3af



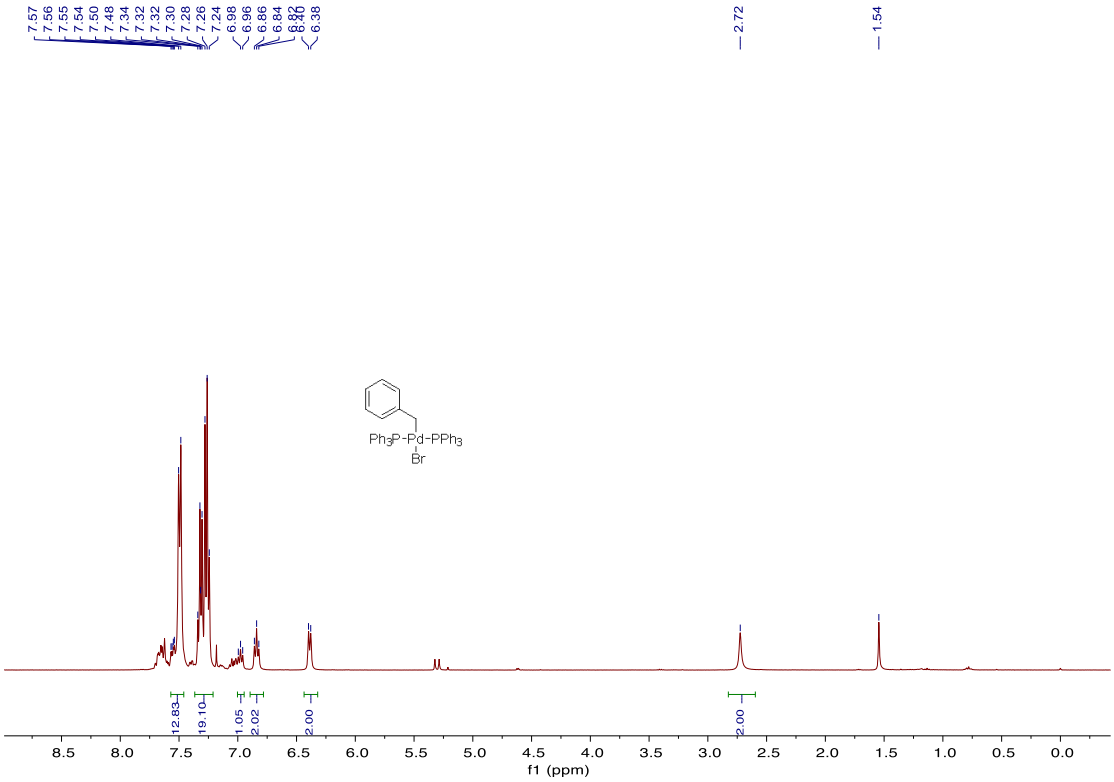
^{1}H NMR of 4



^{13}C NMR of 4



^{1}H NMR of 5



^{31}P NMR of 5