Metal-free enantioselective addition of nucleophilic silicon to aromatic aldehydes catalyzed by a [2.2]Paracyclophane-Based N-Heterocyclic carbene catalyst

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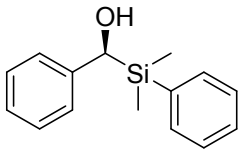
1, General Information

Commercially available reagents were used without further purification unless otherwise noted. Solvents were reagent grade and purified by standard techniques. Purification of the reaction products was carried out by chromatography on silicagl (200-400 mesh). Optical rotations were taken on a polarimeter with a wavelength of 589 nm. The concentration "*c*" had units of g/100 mL (or 10 mg/mL). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE-300 spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to the internal solvent for ^{1}H NMR and ^{13}C NMR spectra. Mass spectra were recorded on an Agilent Technologies 6510 Q-Tof LC/MS. Enantiomeric ratio was determined using HPLC on Chiralpak IA chiral column Chiralpak IB chiral column.

2, General procedure for the synthesis of α-hydroxysilanes

Under an N_2 atmosphere, triazolium salt (*S*,S_p)-**4** (2.0 mg, 5×10^{-3}mmol) was added to 0.20 mL of anhydrous THF in an oven-dried vial equipped with a stir bar. $PhMe_2SiB(pin)$ (0.15 mmol, 1.5 equiv) and freshly distilled aldehyde (0.1 mmol, 1 equiv) were added to the vial. Anhydrous MeOH (60 equiv) was added and immediately followed by addition of H_2O (2 equiv). The mixture was allowed to stir at room temperature for 2 hours before adding KF (1.7 mg, 0.03 mmol). Then, the mixture was stirred at room temperature for 24 hours (Table 3, **1 k-n** at 60 ^{o}C). The solvent was removed in vacuum and the crude product was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:20-1:10) to afford the corresponding product.

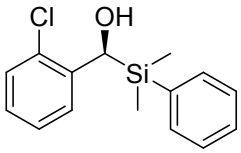
(*S*)-(Dimethyl(phenyl)silyl)(phenyl)methanol (3 d)



Colorless oil, 22.0 mg (91% yield). Enantiomeric ratio: 84.5:15.5. The enantiomeric ratio was determined by HPLC using CHIRALPAK IA column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 25.417 (major), t_R = 29.873 (minor)). $[\alpha]_D^{20}$ = -45.2 (*c* 0.21, CH_2Cl_2). The absolute configuration was assigned as *S* by the comparison of its optical rotation with the value reported by Riant's group (lit.[1] : $[\alpha]_D^{20}$ = -63.0 (*c*

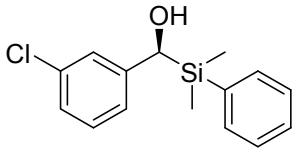
0.0125, CH_2Cl_2), 99% ee (*S*)).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 –7.46 (m, 2H), 7.40 – 7.32 (m, 3H), 7.29 – 7.24 (m, 2H), 7.18 –7.13 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 4.70 (s, 1H), 1.97 (s, 1H), 0.29 (s, 3H), 0.26 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.47, 135.94, 134.36, 129.48, 128.06, 127.79, 125.92, 125.17, 70.02, -5.39, -6.28. Spectral data are identical to those reported in the literature [1].

(*S*)-(2-Chlorophenyl)(dimethyl(phenyl)silyl)methanol (3 b)



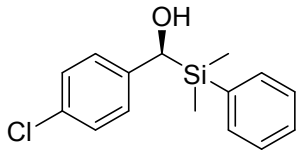
Colorless oil, 25.1 mg (91% yield). Enantiomeric ratio: 77.2:22.8. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 15.533 (minor), t_R = 18.870 (major)). $[\alpha]_D^{20}$ = -48.0 (c 0.25, CH_2Cl_2).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 –7.55 (m, 2H), 7.46 – 7.27 (m, 6H), 7.17 –7.11 (m, 1H), 5.26 (s, 1H), 1.71 (s, 1H), 0.37 (s, 3H), 0.35 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 141.46, 135.80, 134.38, 130.69, 129.59, 129.08, 127.83, 127.38, 126.90, 126.77, 65.66, -4.58, -6.35. HRMS (ESI) m/z calcd for $[M + Na]^+$ ($C_{15}H_{17}ClOSi$): 299.0629, found: 299.0648.

(*S*)-(3-Chlorophenyl)(dimethyl(phenyl)silyl)methanol (3 c)



Colorless oil, 26.2 mg (95% yield). Enantiomeric ratio: 81.8:18.2. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 26.663 (major), t_R = 32.417 (minor)). $[\alpha]_D^{20}$ = -48.4 (c 0.15, CH_2Cl_2).
^{1}H NMR (300 MHz, CDCl3) δ 7.50 – 7.34 (m, 5H), 7.21 – 7.04 (m, 3H), 6.92 (d, J = 6.9 Hz, 1H), 4.68 (s, 1H), 1.70 (s, 1H), 0.31 (s, 3H), 0.28 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.71, 135.32, 134.32, 134.10, 129.70, 129.21, 127.88, 125.94, 125.12, 123.16, 69.50, -5.59, -6.33. Spectral data are identical to those reported in the literature [2].

(*S*)-(4-Chlorophenyl)(dimethyl(phenyl)silyl)methanol (3 a)

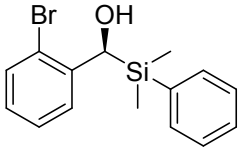


Colorless oil, 27.1 mg (98% yield). Enantiomeric ratio: 88.5:11.5. The enantiomeric ratio was determined by HPLC using CHIRALPAK IA column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 31.283 (major), t_R = 33.967 (minor)). $[\alpha]_D^{20}$ = -48.1 (c 0.27, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 –7.44, (m, 2H), 7.40 –7.32, (m, 3H), 7.25 –7.19, (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.66 (s, 1H), 1.72 (s, 1H), 0.29 (s, 3H), 0.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.99, 135.41, 134.34, 131.39, 129.65, 128.14, 127.88, 126.40, 69.44, -5.59, -6.29. Spectral data are identical to those reported in the literature [1].

(*S*)-(2-Bromophenyl)(dimethyl(phenyl)silyl)methanol (3 e)

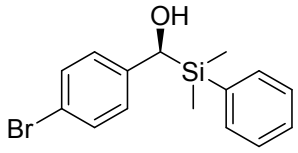


Colorless oil, 29.5 mg (92% yield). Enantiomeric ratio: 76.5:23.5. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 100/1, 0.5 mL/min, 254 nm, t_R = 23.099 (minor), t_R = 29.636 (major)). $[\alpha]_D^{20}$ = -56.0 (c 0.12, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.26 (m, 6H), 5.19 (s, 1H), 1.70 (s, 1H), 0.35 (s, 3H), 0.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.04, 135.82, 134.41, 132.40, 129.59, 127.83, 127.73, 127.37, 127.33, 121.16, 68.05, -4.34, -6.23. Spectral data are identical to those reported in the literature [2].

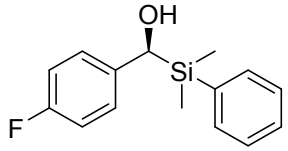
(*S*)-(4-Bromophenyl)(dimethyl(phenyl)silyl)methanol (3 f)



Colorless oil, 24.5 mg (76% yield). Enantiomeric ratio: 88.1:11.9. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 100/1, 0.5 mL/min, 254 nm, t_R = 51.783 (major), t_R = 56.597 (minor)). $[\alpha]_D^{20}$ = -64.6 (c 0.24, CH_2Cl_2).

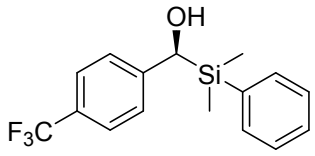
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.32 (m, 5H), 6.94 (d, *J* = 8.2 Hz, 2H), 4.66 (s, 1H), 1.69 (s, 1H), 0.29 (s, 3H), 0.27 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.53, 135.37, 134.34, 131.05, 129.66, 127.88, 126.78, 119.40, 69.46, 0.02, -5.60, -6.31. Spectral data are identical to those reported in the literature [1].

(*S*)-(Dimethyl(phenyl)silyl)(4-fluorophenyl)methanol (3 g)



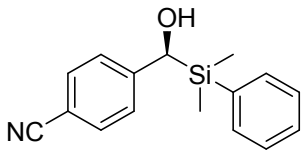
Colorless oil, 17.7 mg (68% yield). Enantiomeric ratio: 87.9:12.1. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 100/1, 0.5 mL/min, 254 nm, t_R = 33.043 (major), t_R = 35.660 (minor)). $[\alpha]_D^{20}$ = -41.2 (c 0.10, CH_2Cl_2).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.41 – 7.31 (m, 3H), 7.06 – 6.89 (m, 4H), 4.68 (s, 1H), 1.66 (s, 1H), 0.30 (s, 3H), 0.27 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.89, 159.66, 139.05, 135.60, 134.32, 129.57, 127.83, 126.61, 126.50, 114.98, 114.70, 69.40, -5.57, -6.29. Spectral data are identical to those reported in the literature [2].

(*S*)-(Dimethyl(phenyl)silyl)(4-(trifluoromethyl)phenyl)methanol (3 h)



Colorless oil, 29.1 mg (94% yield). Enantiomeric ratio: 84.6:15.4. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 70/1, 0.5 mL/min, 254 nm, t_R = 46.293 (minor), t_R = 49.360 (major)). $[\alpha]_D^{20}$ = -38.1 (c 0.21, CH_2Cl_2).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.34 (m, 7H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.77 (s, 1H), 1.72 (s, 1H), 0.30 (s, 3H), 0.28 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 147.72, 135.10, 134.30, 129.76, 127.92, 125.09, 124.95, 124.89, 69.73, -5.66, -6.33. Spectral data are identical to those reported in the literature [2].

(*S*)-4-((Dimethyl(phenyl)silyl)(hydroxy)methyl)benzonitrile (3 i)

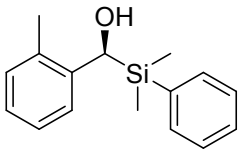


Colorless oil, 22.6 mg (85% yield). Enantiomeric ratio: 84.1:15.9. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 20/1, 0.5 mL/min, 220 nm, t_R = 45.600 (major), t_R = 48.297 (minor)). $[\alpha]_D^{20}$ = -51.5 (c 0.07, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.32 (m, 5H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.77 (s, 1H), 1.76 (s, 1H), 0.31 (s, 3H), 0.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.33, 134.64, 134.26, 131.81, 129.91, 127.98, 125.40, 109.31, 69.89, -0.01, -5.84, -6.26. Spectral data are identical to those reported in the literature [2].

(*S*)-(Dimethyl(phenyl)silyl)(o-tolyl)methanol (3 j)

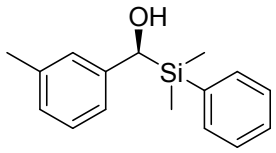


Colorless oil, 15.6 mg (61% yield). Enantiomeric ratio: 79.9:20.1. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 26.967 (major), t_R = 30.210 (minor)). $[\alpha]_D^{20}$ = -40.0 (c 0.20, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.42 – 7.31 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 2H), 4.67 (s, 1H), 2.29 (s, 3H), 1.65 (s, 1H), 0.31 (s, 3H), 0.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.40, 137.60, 136.06, 134.38, 129.45, 127.93, 127.74, 126.67, 125.94, 122.27, 69.98, 21.47, -5.39, -6.29. Spectral data are identical to those reported in the literature [2].

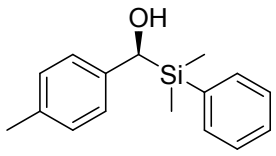
(*S*)-(Dimethyl(phenyl)silyl)(m-tolyl)methanol (3 k)



Colorless oil, 18.2 mg (71% yield). Enantiomeric ratio: 85.5:14.5. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 15.557 (minor), t_R = 20.343 (major)). $[\alpha]_D^{20}$ = -50.0 (c 0.07, CH_2Cl_2).

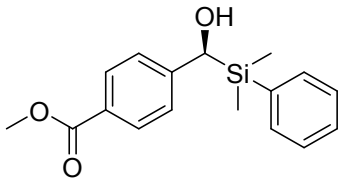
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.40 – 7.29 (m, 4H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.13 – 7.01 (m, 2H), 4.95 (s, 1H), 1.99 (s, 3H), 1.61 (s, 1H), 0.39 (s, 3H), 0.27 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 141.87, 136.28, 134.27, 133.44, 130.01, 129.47, 127.76, 125.97, 125.81, 125.77, 65.65, 29.73, 19.53, -5.22, -5.97. HRMS (ESI) m/z calcd for $[M + H]^+$ ($C_{16}H_{20}OSi$): 257.1356, found: 257.1352.

(*S*)-(Dimethyl(phenyl)silyl)(p-tolyl)methanol (3 l)



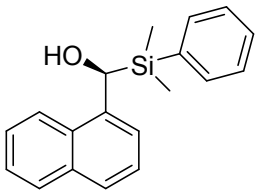
Colorless oil, 24.1 mg (94% yield). Enantiomeric ratio: 83.3:16.7. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 100/1, 0.5 mL/min, 254 nm, t_R = 28.047 (major), t_R = 32.143 (minor)). $[\alpha]_D^{20}$ = -58.7 (c 0.23, CH_2Cl_2).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.41 – 7.32 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 4.68 (s, 1H), 2.33 (s, 3H), 1.64 (s, 1H), 0.30 (s, 3H), 0.26 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 140.40, 136.28, 136.16, 135.45, 134.37, 129.43, 128.77, 127.77, 125.20, 116.66, 69.84, 21.06, -5.29, -6.29. Spectral data are identical to those reported in the literature [2].

(*S*)-Methyl 4-((dimethyl(phenyl)silyl)(hydroxy)methyl)benzoate (3 m)



Colorless oil, 20.2 mg (67% yield). Enantiomeric ratio: 86.0:14.0. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 49.190 (minor), t_R = 56.397 (major)). $[\alpha]_D^{20}$ = -30.6 (c 0.05, CH_2Cl_2).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.42 – 7.34 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.78 (s, 1H), 3.90 (s, 3H), 1.74 (s, 1H), 0.30 (s, 3H), 0.28 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 167.15, 149.09, 135.16, 134.31, 129.72, 129.38, 127.90, 127.66, 124.77, 70.01, 51.97, -0.01, -5.63, -6.28.$[M+H]^+$ 301.1260, found 301.1317.

(*S*)-(Dimethyl(phenyl)silyl)(naphthalen-1-yl)methanol (3 n)



Colorless oil, 12.6 mg (43% yield). Enantiomeric ratio: 75.0:25.0. The enantiomeric ratio was determined by HPLC using CHIRALPAK IB column (hexane/i-PrOH : 40/1, 0.5 mL/min, 254 nm, t_R = 37.410 (major), t_R = 43.917 (minor)). $[\alpha]_D^{20}$ = -70.8 (c 0.12, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 –7.78 (m, 2H), 7.71 –7.68 (m, 1H), 7.53 – 7.28 (m, 9H), 5.60 (s, 1H), 1.74 (s, 1H), 0.30 (s, 3H), 0.21 (s, 3H).

^{13}C NMR (75 MHz, CDCl3) δ 139.89, 136.22, 134.33, 133.49, 129.90, 129.49, 128.66, 127.79, 126.34, 125.49, 125.34, 125.14, 123.49, 122.82, 65.92, -4.43, -5.91. Spectral data are identical to those reported in the literature [2].

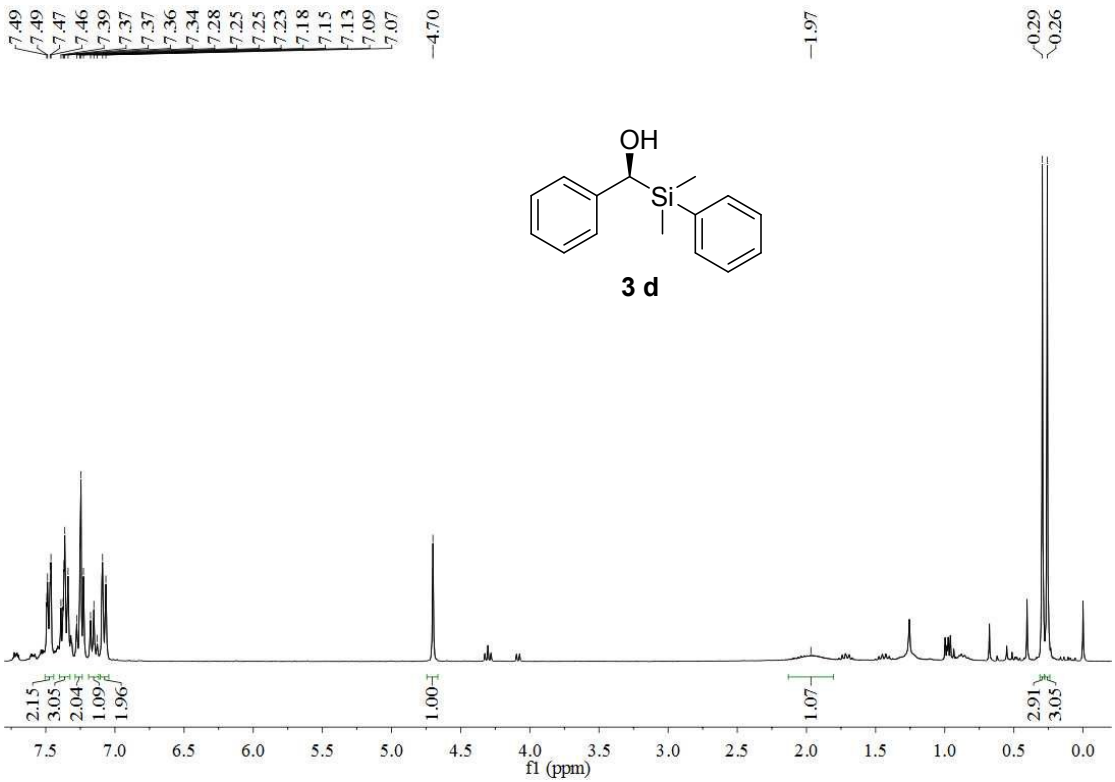
3, References

1, C. Kleeberg, E. Feldmann, E. Hartmann, D. J. Vyas and M. Oestreich, *Chem. Eur. J.* 2011, **17**, 13538.

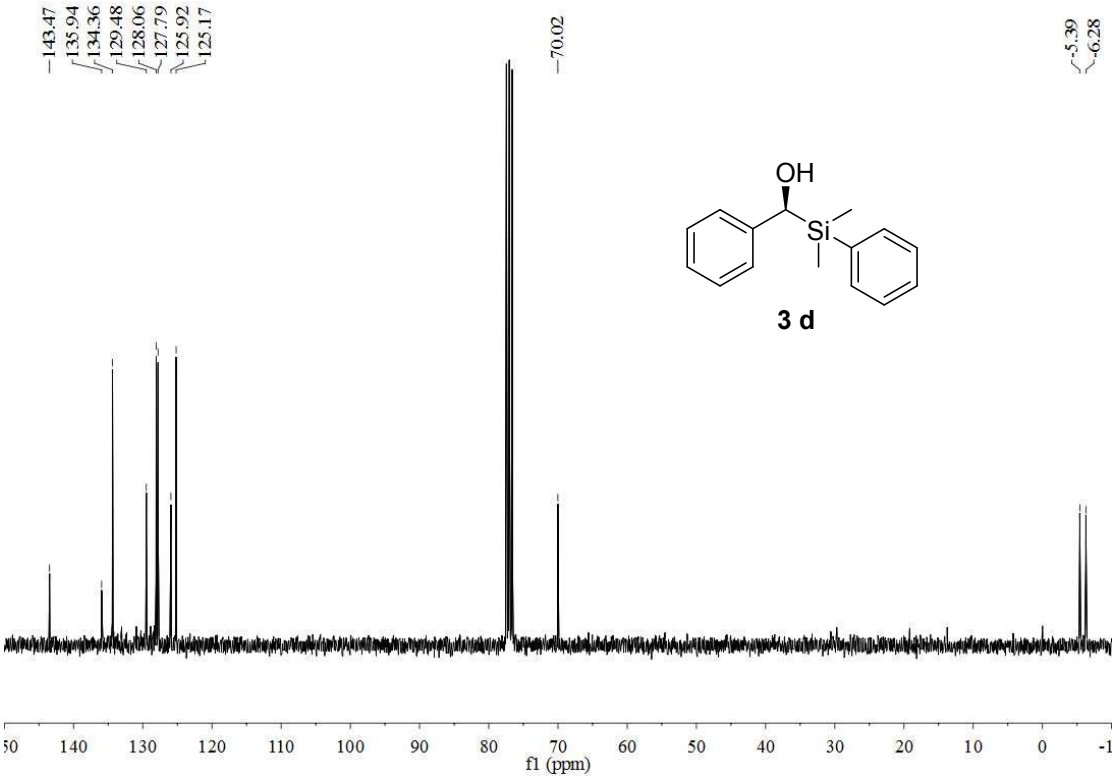
2, V. Cirriez, C. Rasson, T. Hermant, J. Petrignet, J. D. Alvarez, K. Robeyns and O. Riant, *Angew. Chem. Int. Ed.*, 2013, **52**, 1785.

4, Copies of NMR spectra

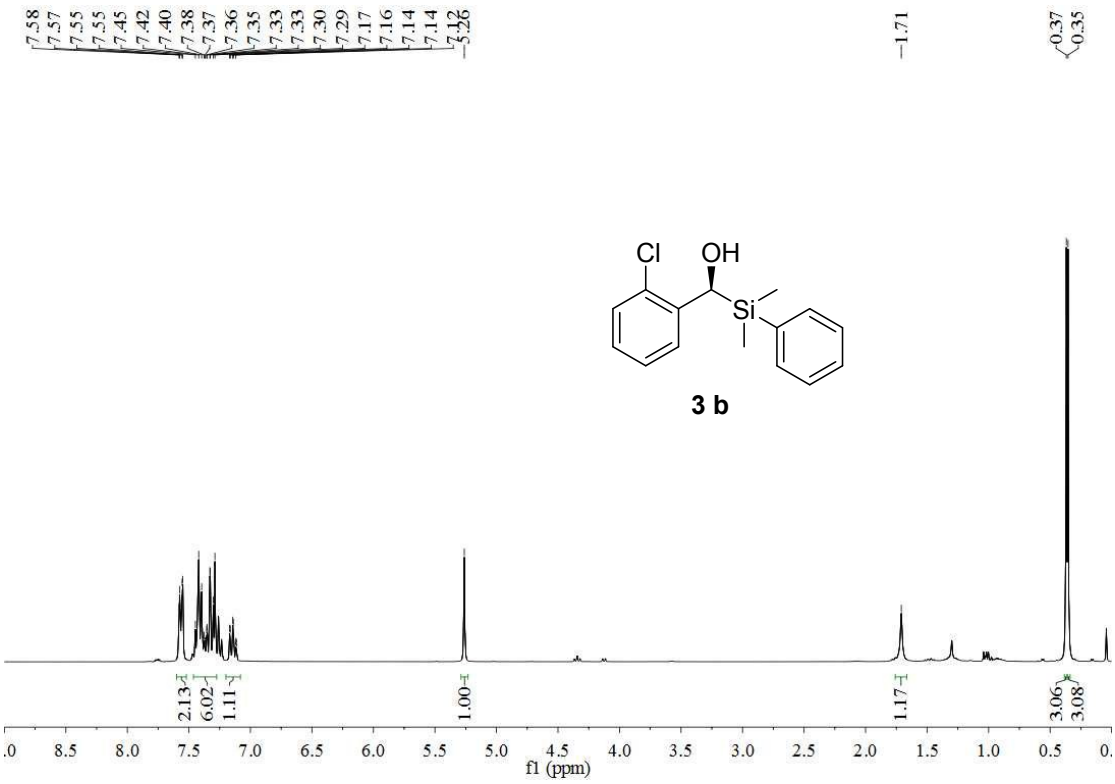
^{1}H NMR Spectrum of compound 3 d



^{13}C NMR Spectrum of compound **3 d**



^{1}H NMR Spectrum of compound **3 b**



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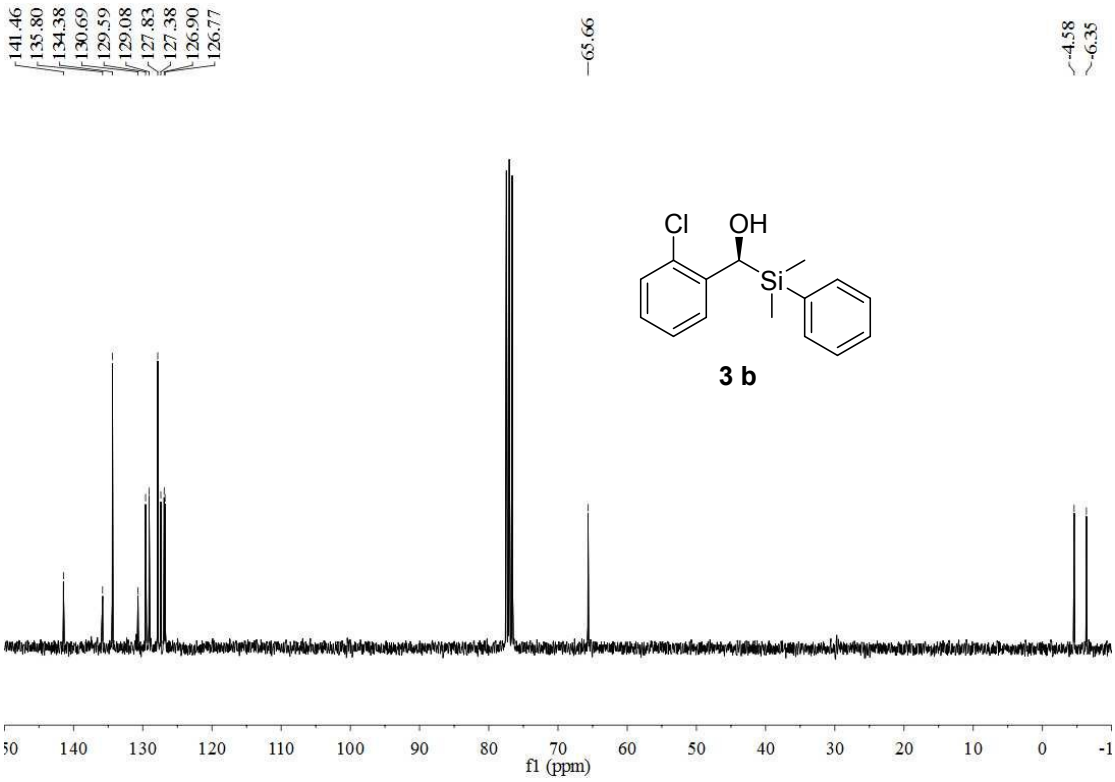
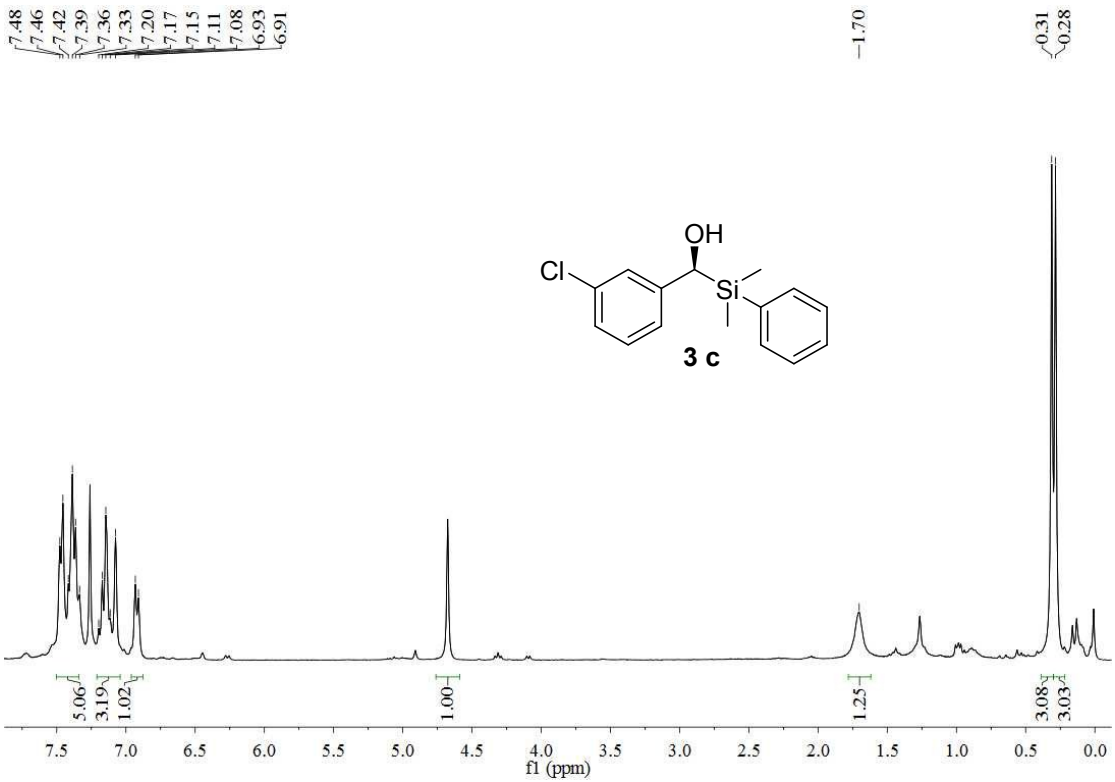
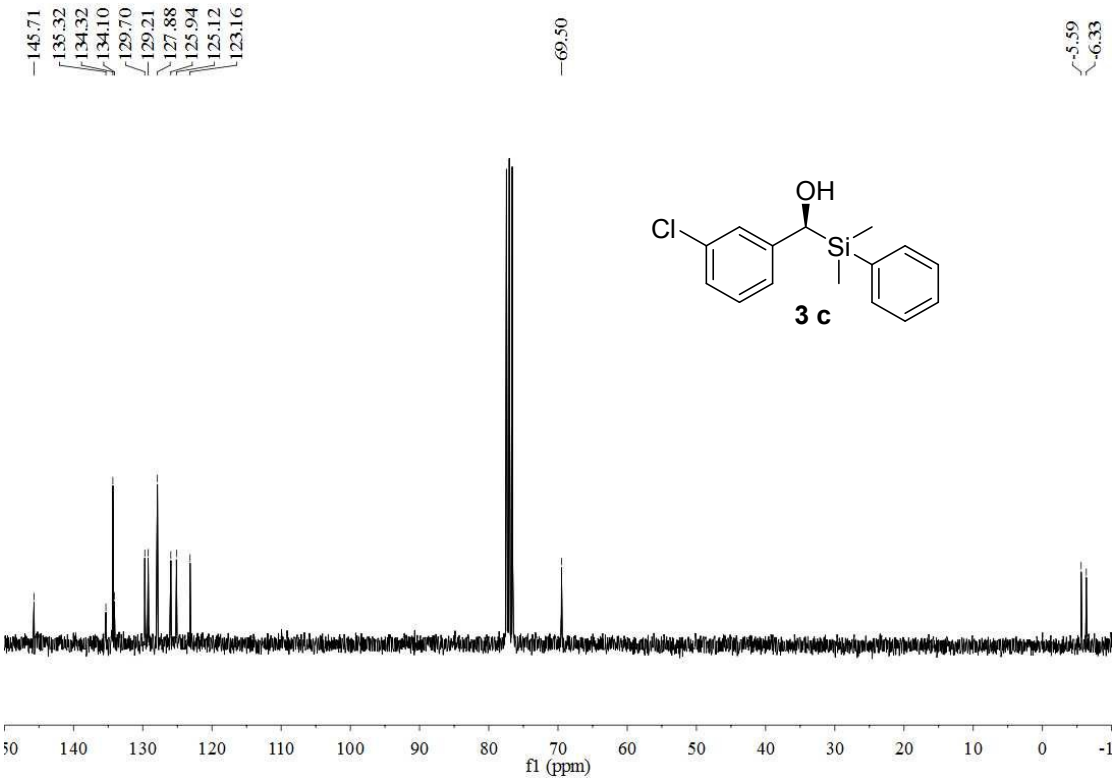


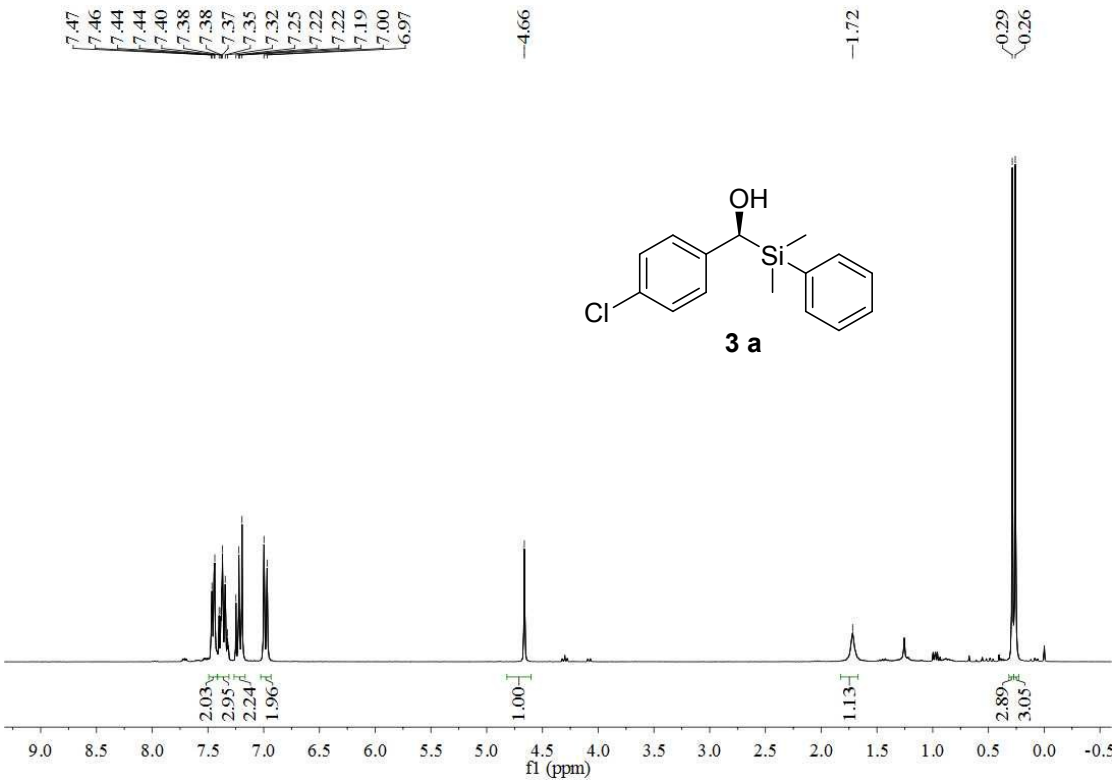
^{1}H NMR Spectrum of compound **3 c**



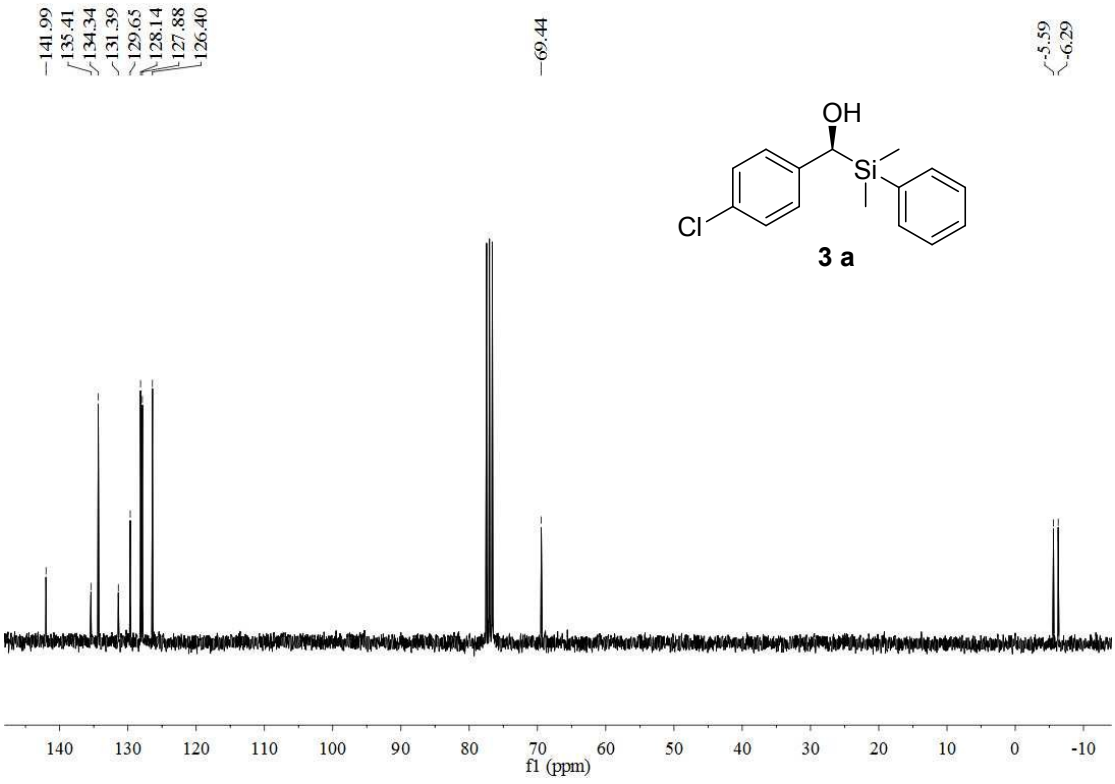
^{13}C NMR Spectrum of compound **3 c**



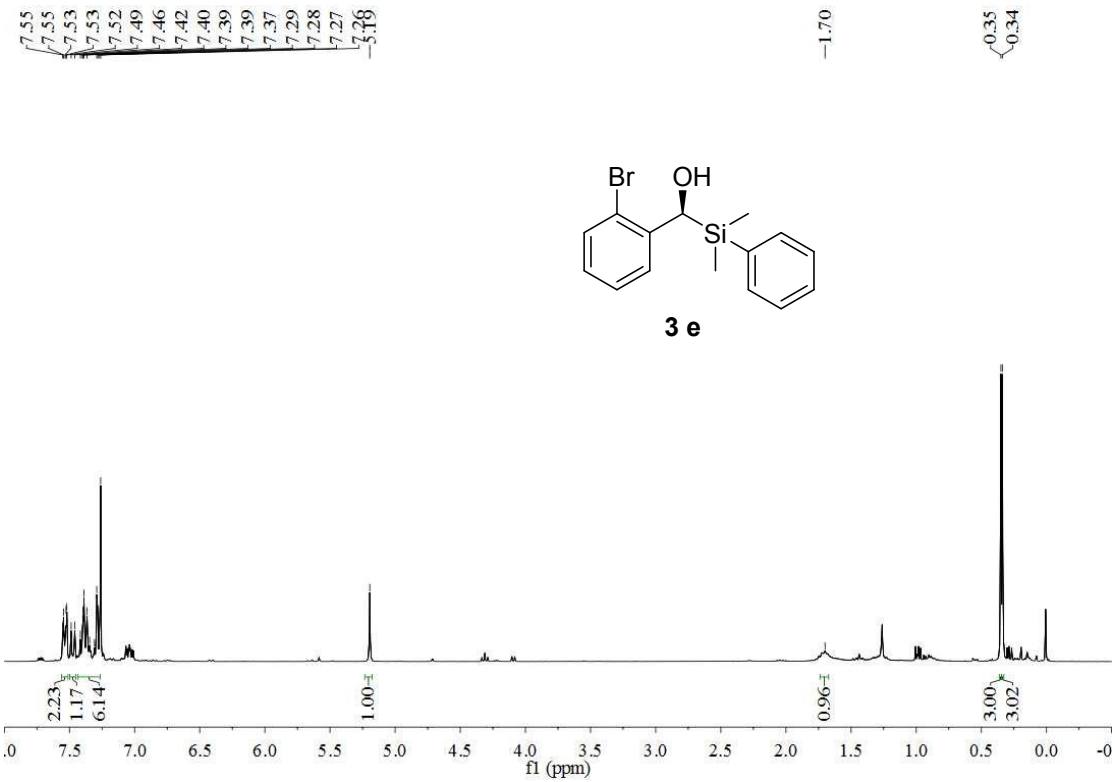
^{1}H NMR Spectrum of compound **3 a**



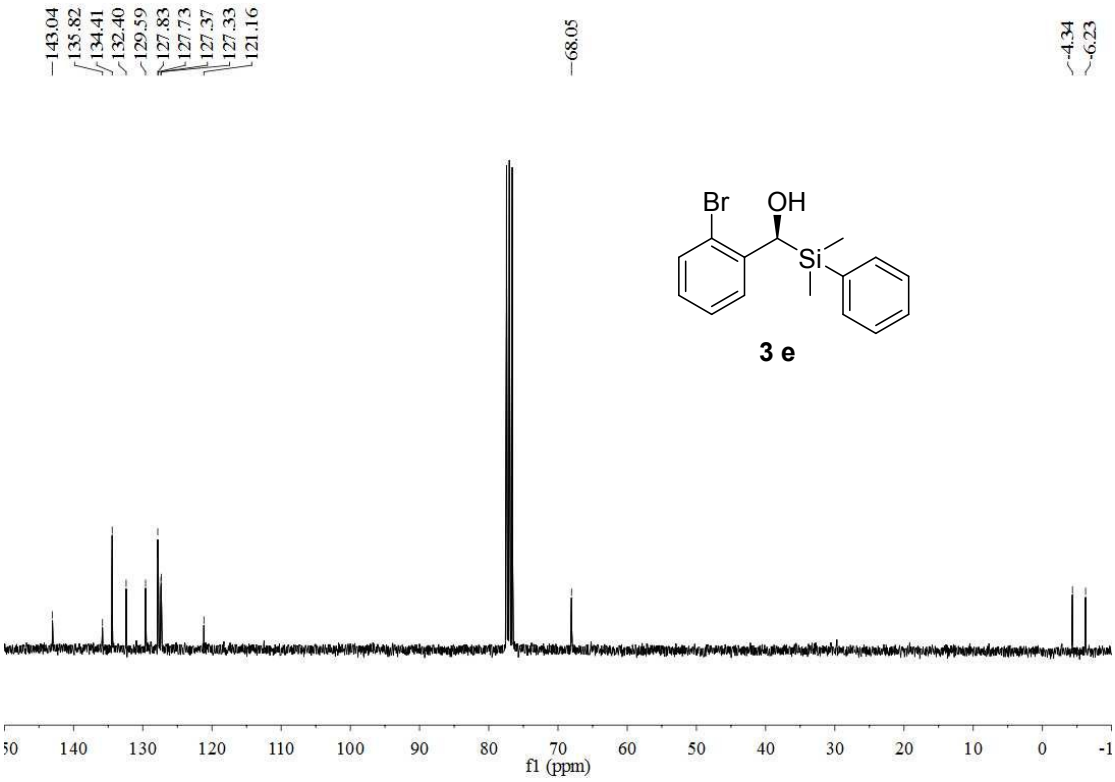
^{13}C NMR Spectrum of compound **3 a**



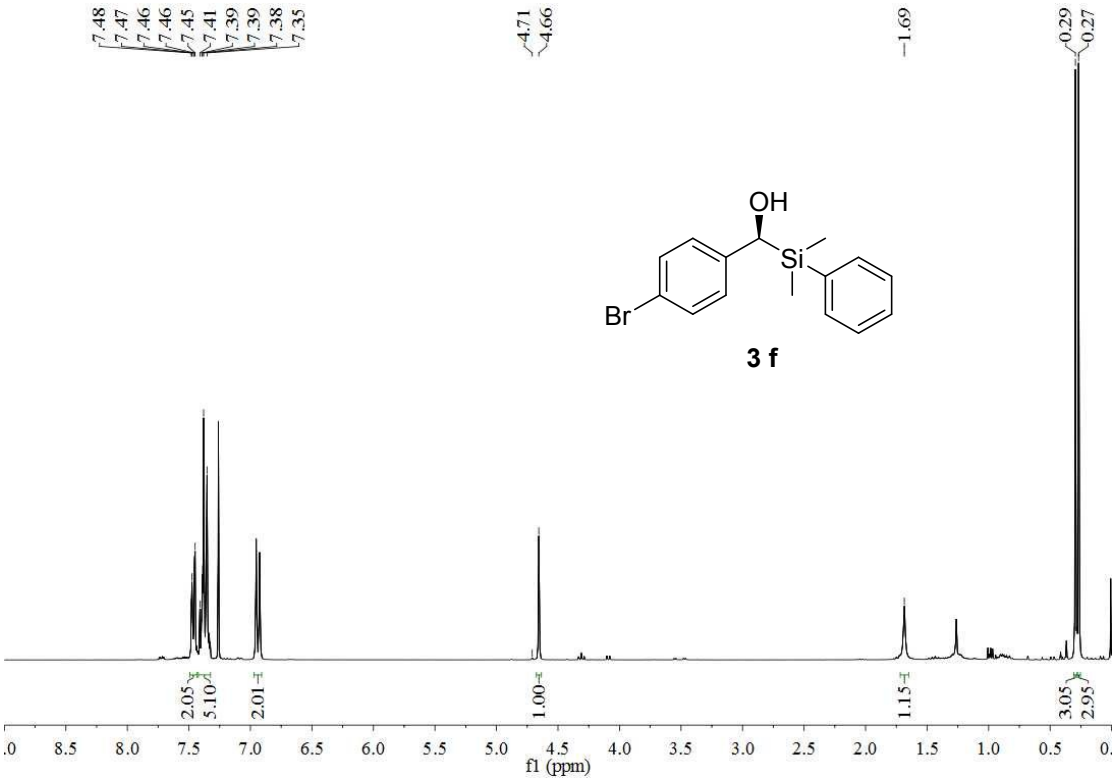
^{1}H NMR Spectrum of compound **3 e**



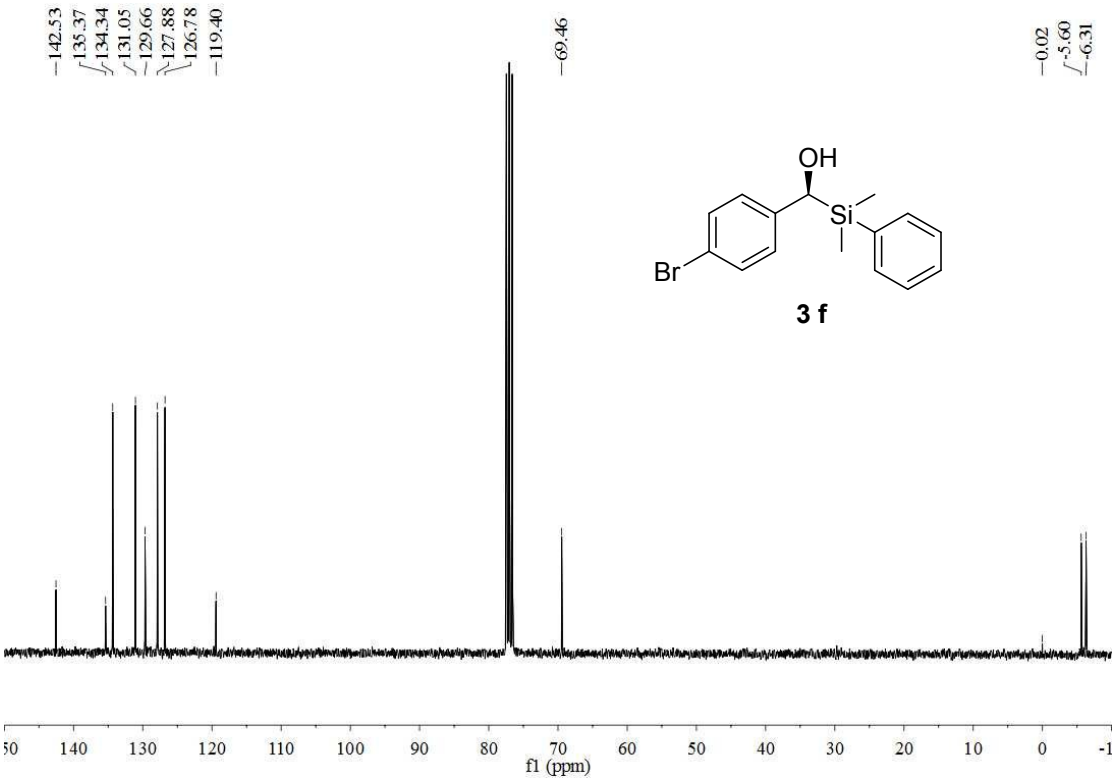
^{13}C NMR Spectrum of compound **3 e**



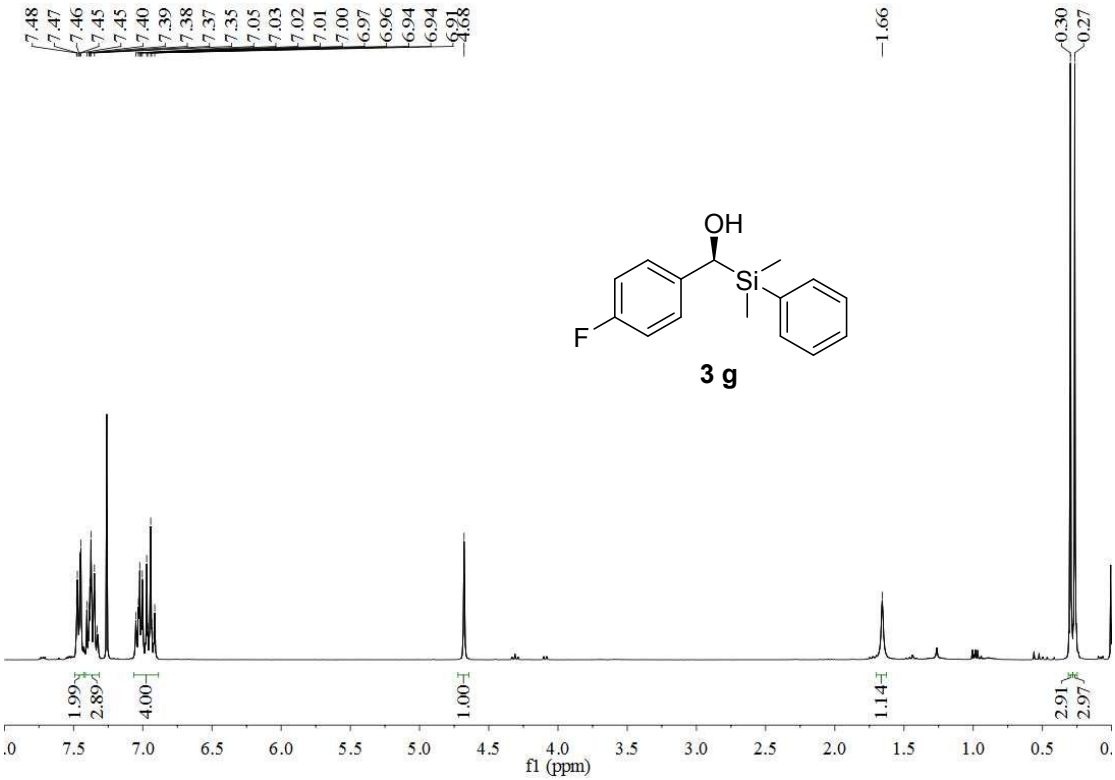
^{1}H NMR Spectrum of compound **3 f**



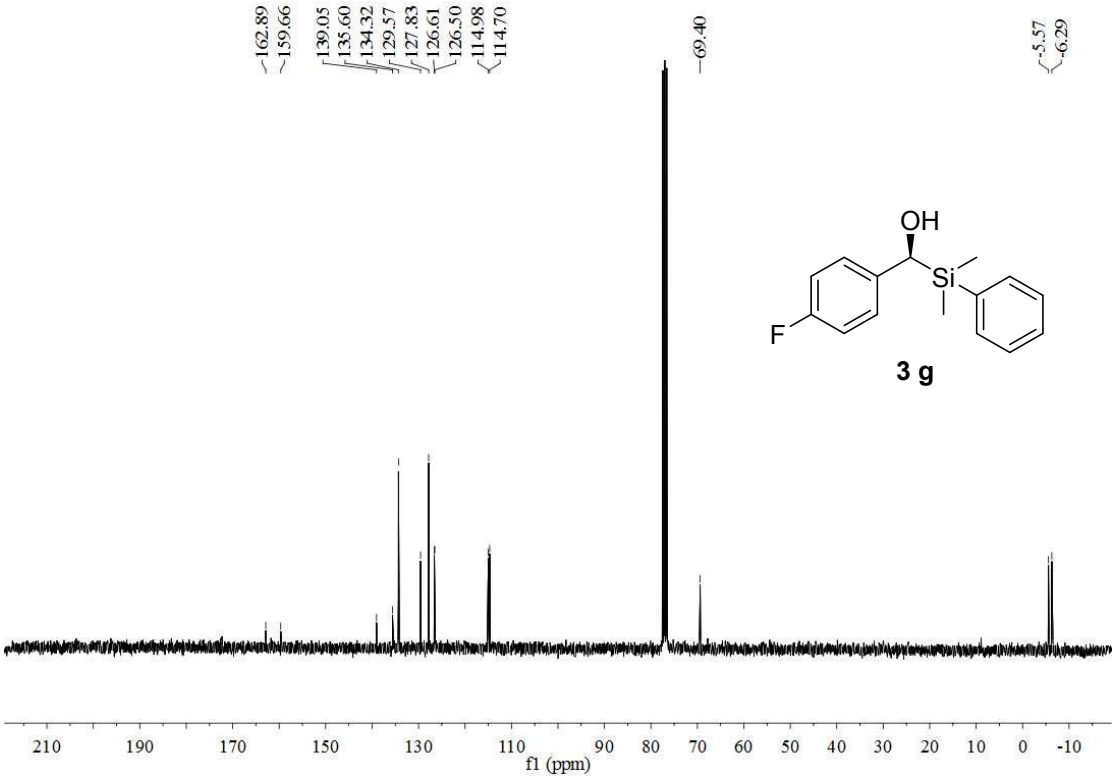
^{13}C NMR Spectrum of compound **3 f**



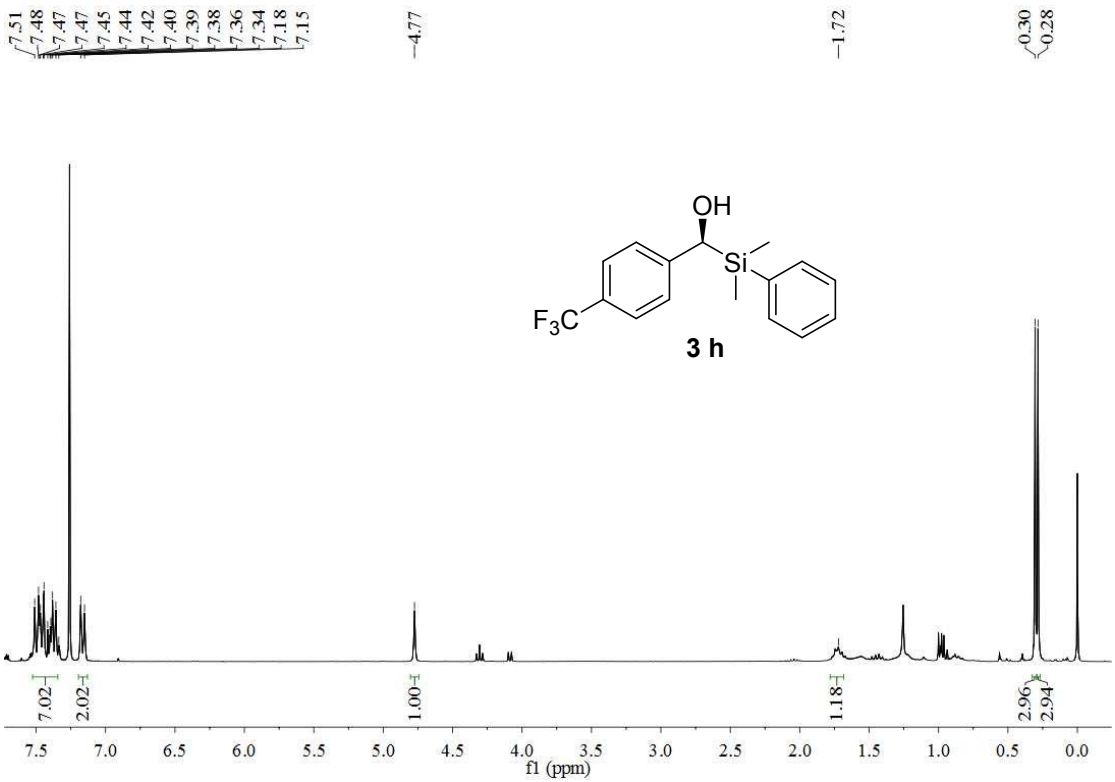
^{1}H NMR Spectrum of compound **3 g**



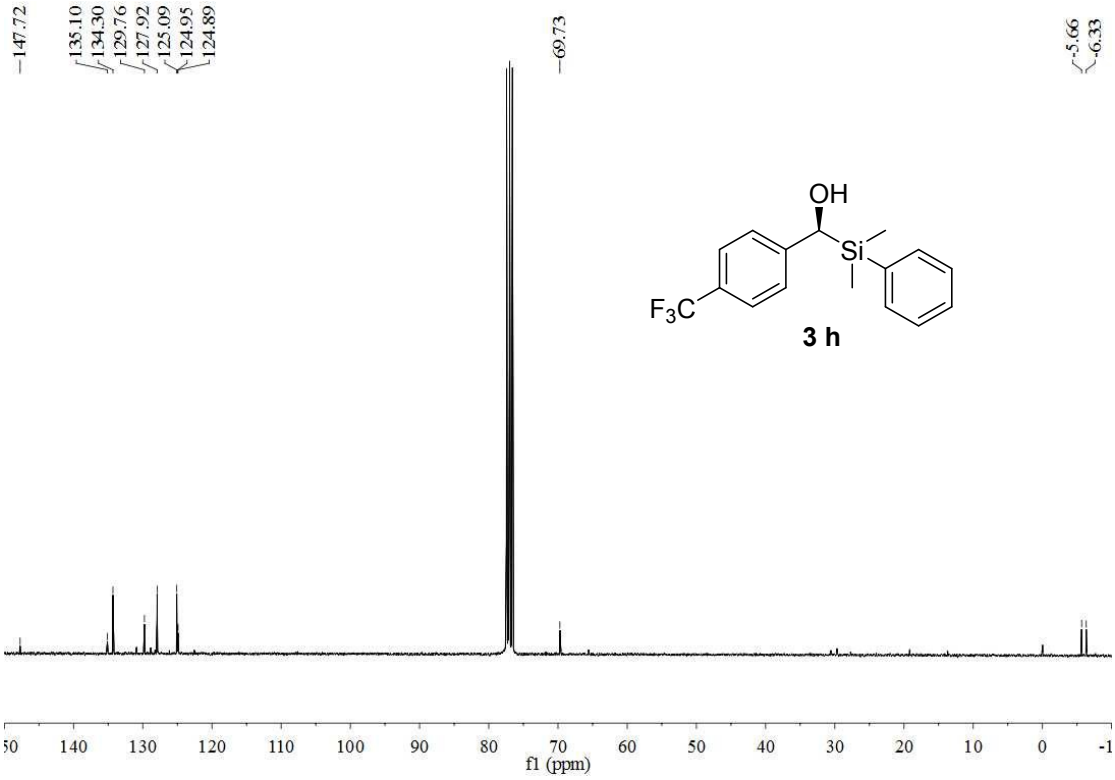
^{13}C NMR Spectrum of compound **3 g**



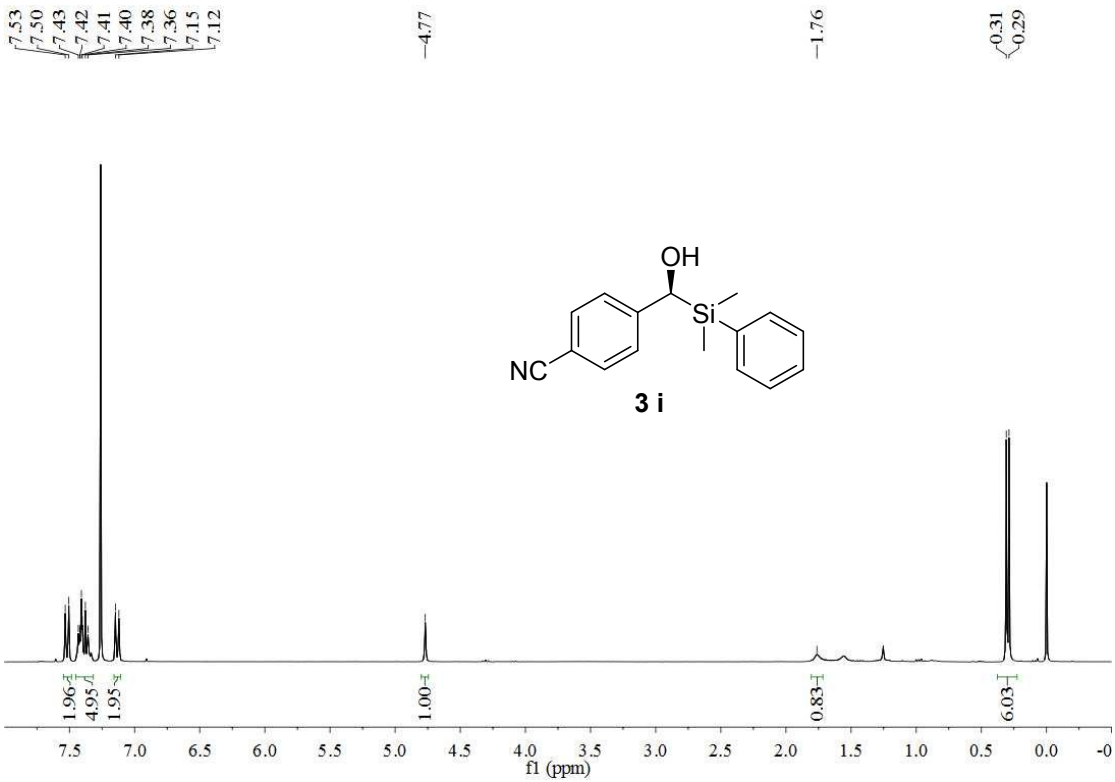
^{1}H NMR Spectrum of compound **3 h**



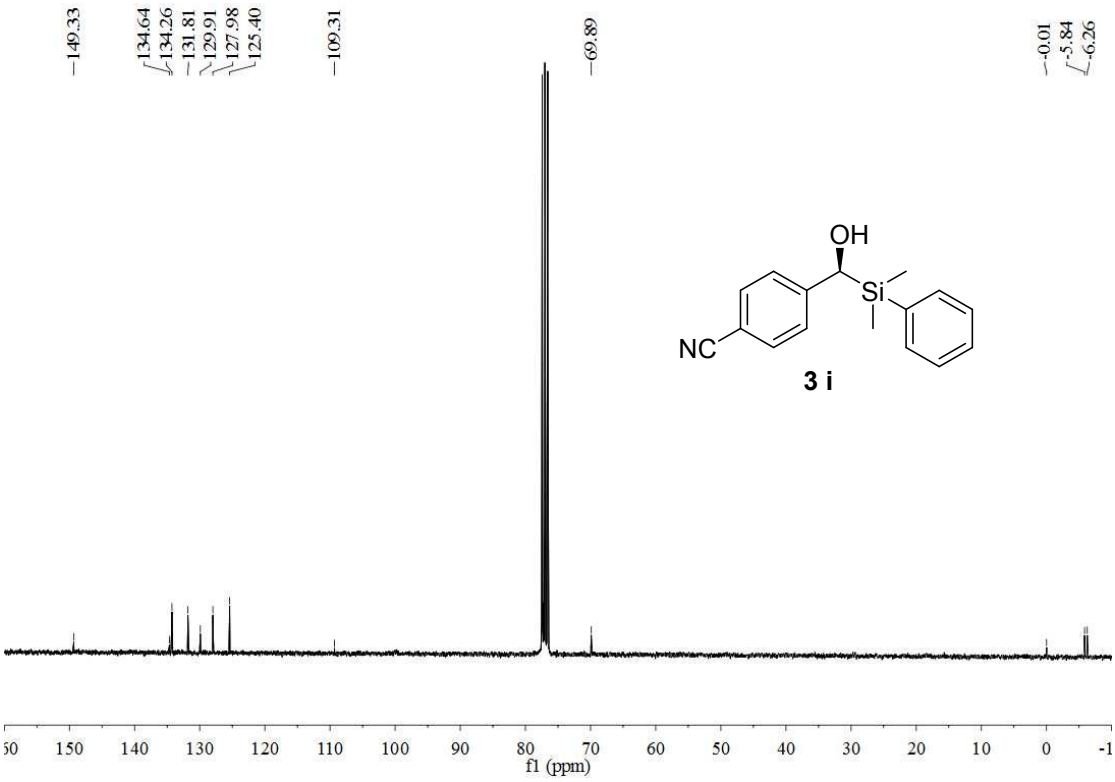
^{13}C NMR Spectrum of compound **3 h**



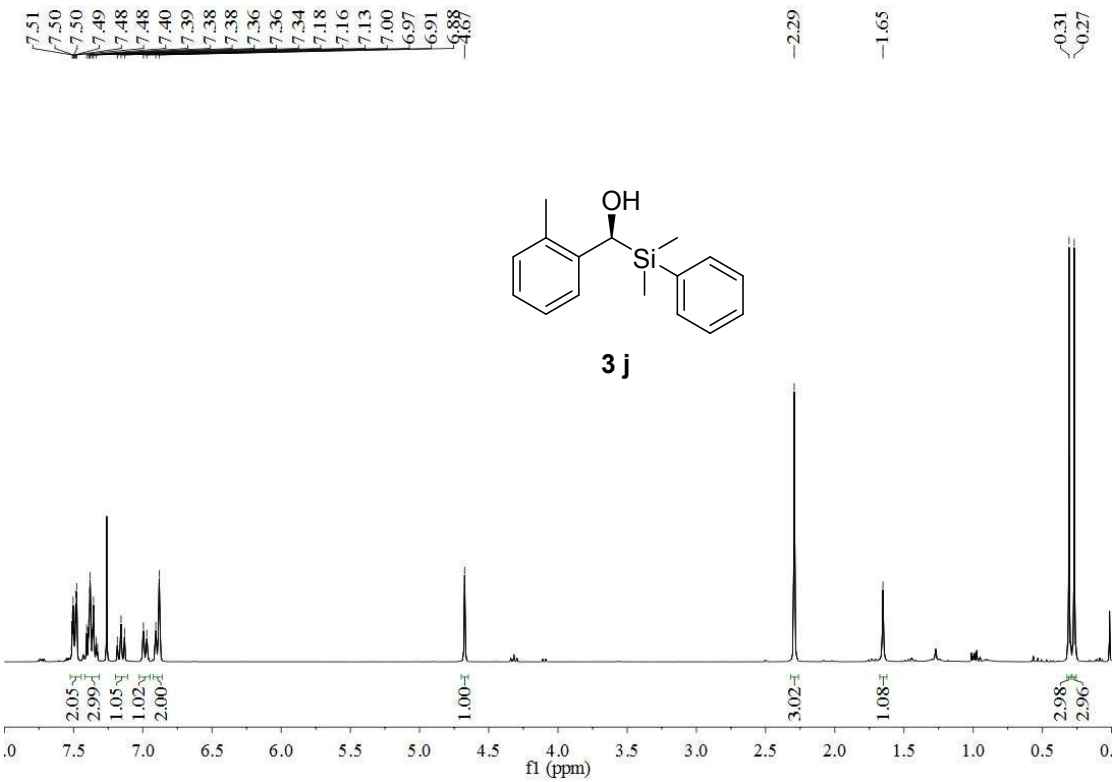
^{1}H NMR Spectrum of compound **3 i**



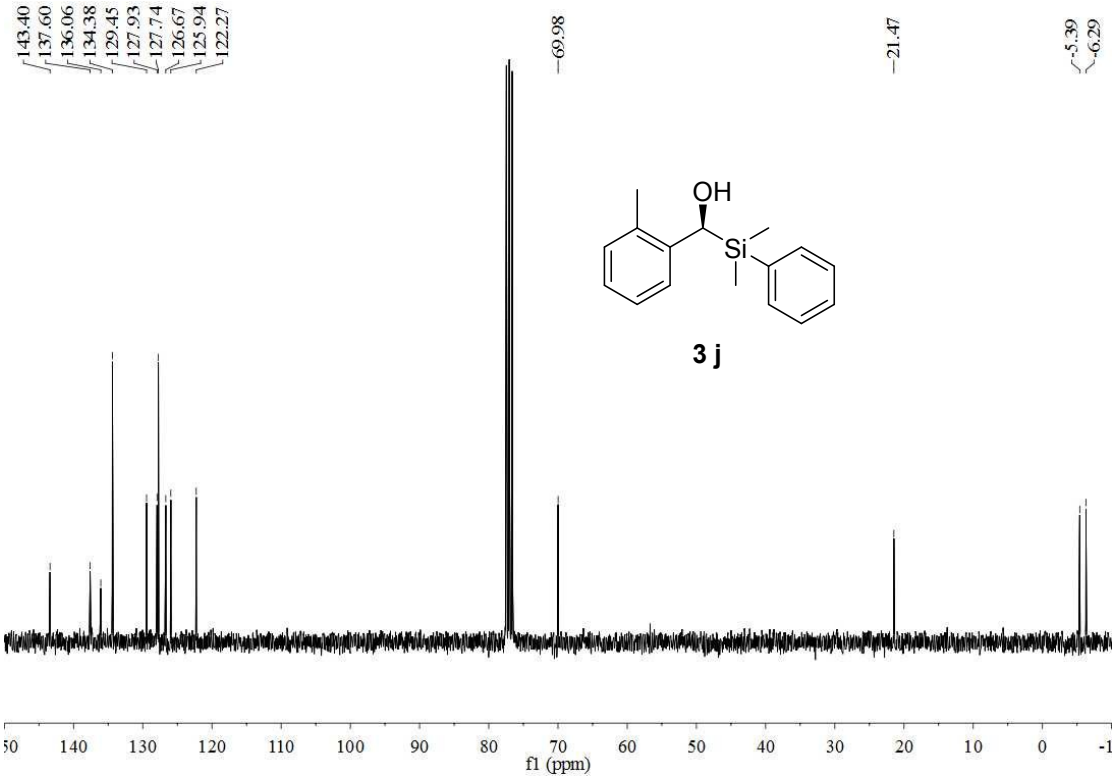
^{13}C NMR Spectrum of compound **3 i**



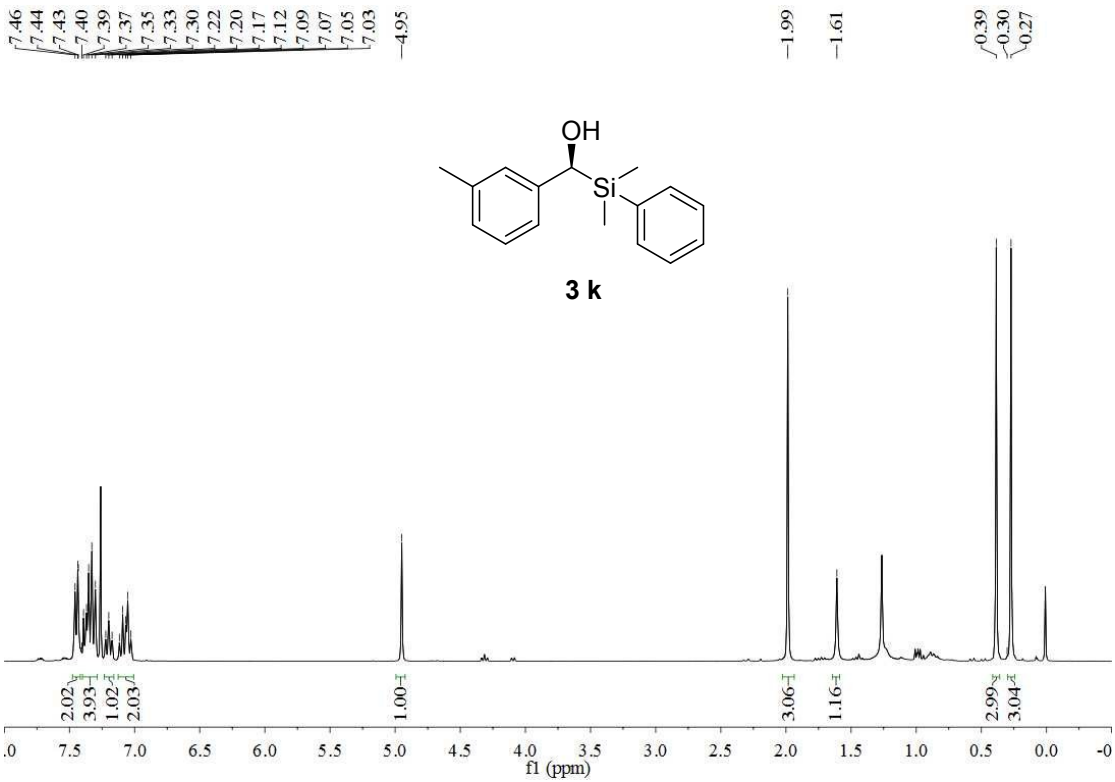
^{1}H NMR Spectrum of compound **3 j**



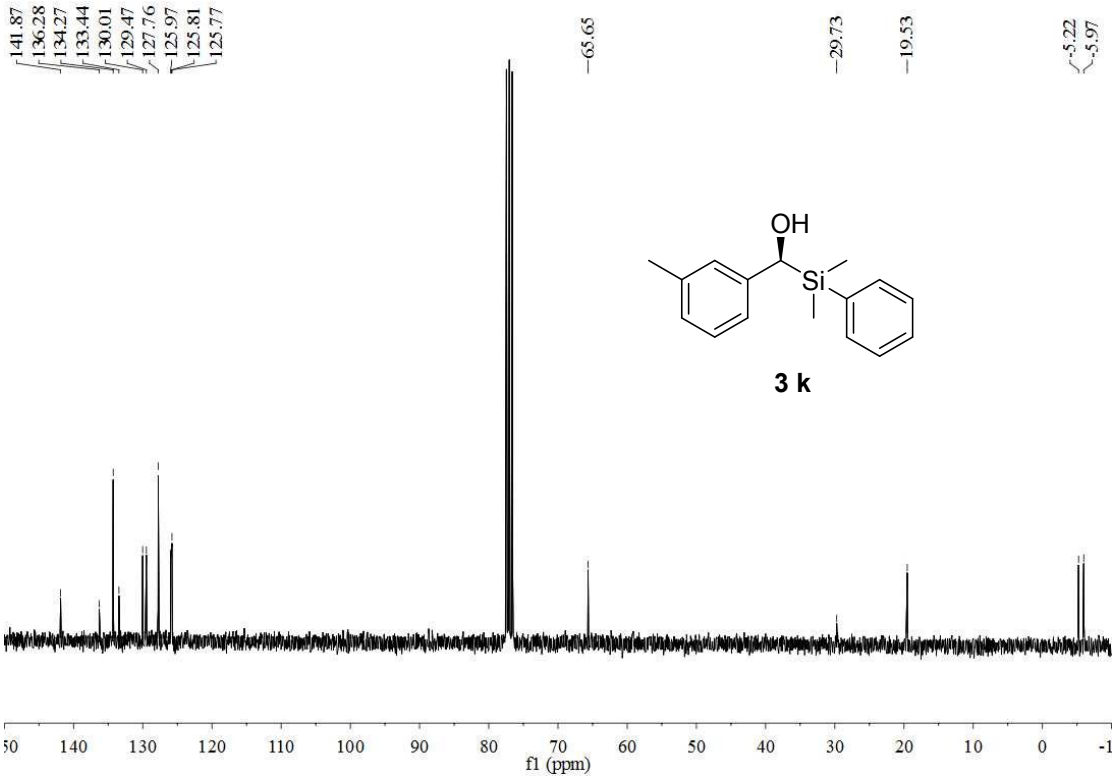
^{13}C NMR Spectrum of compound **3 j**



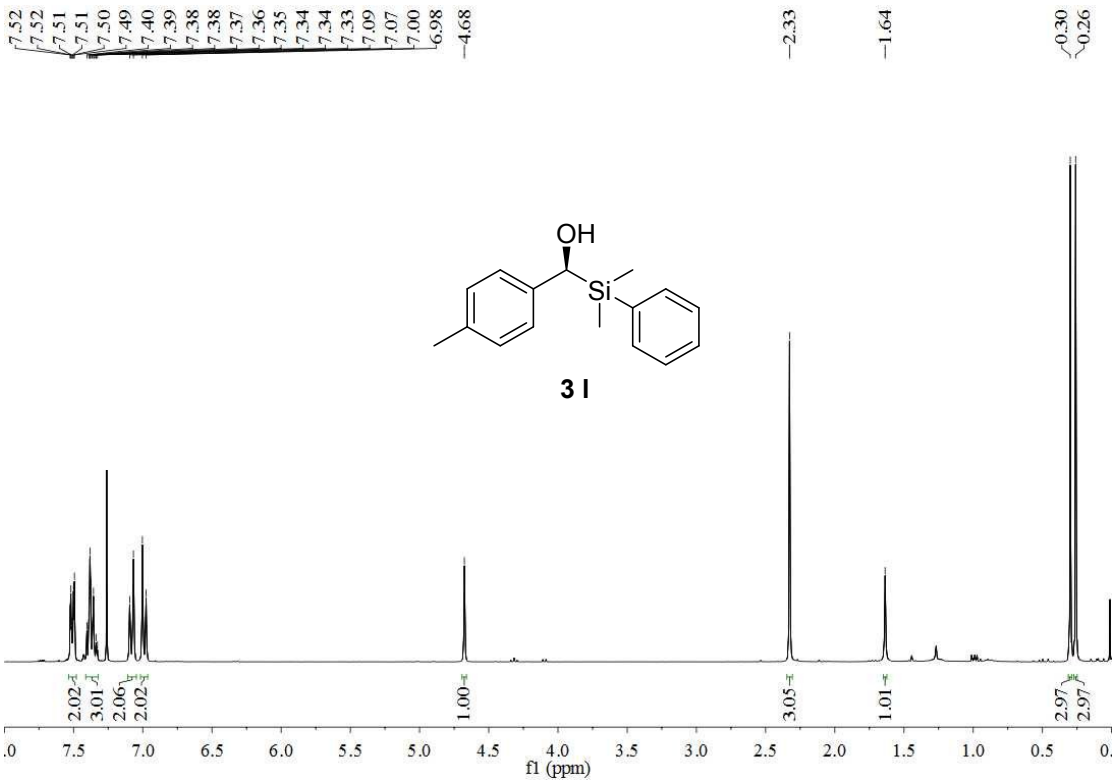
^{1}H NMR Spectrum of compound **3 k**



^{13}C NMR Spectrum of compound **3 k**

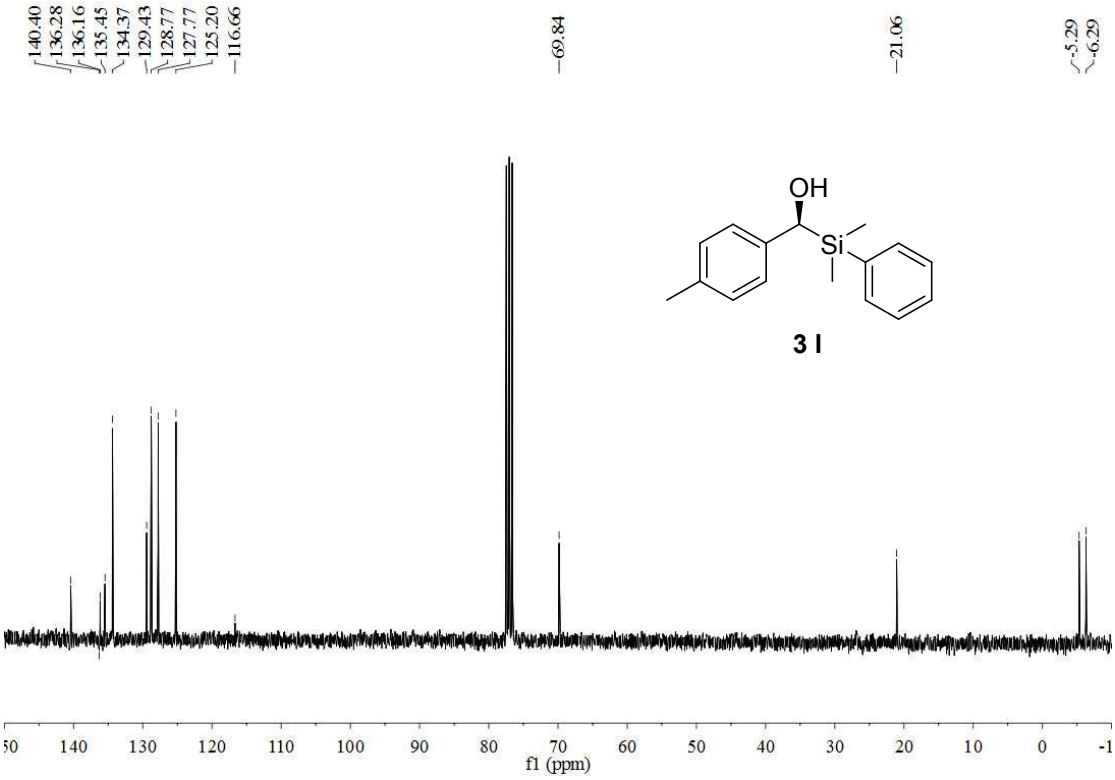


^{1}H NMR Spectrum of compound **3 l**



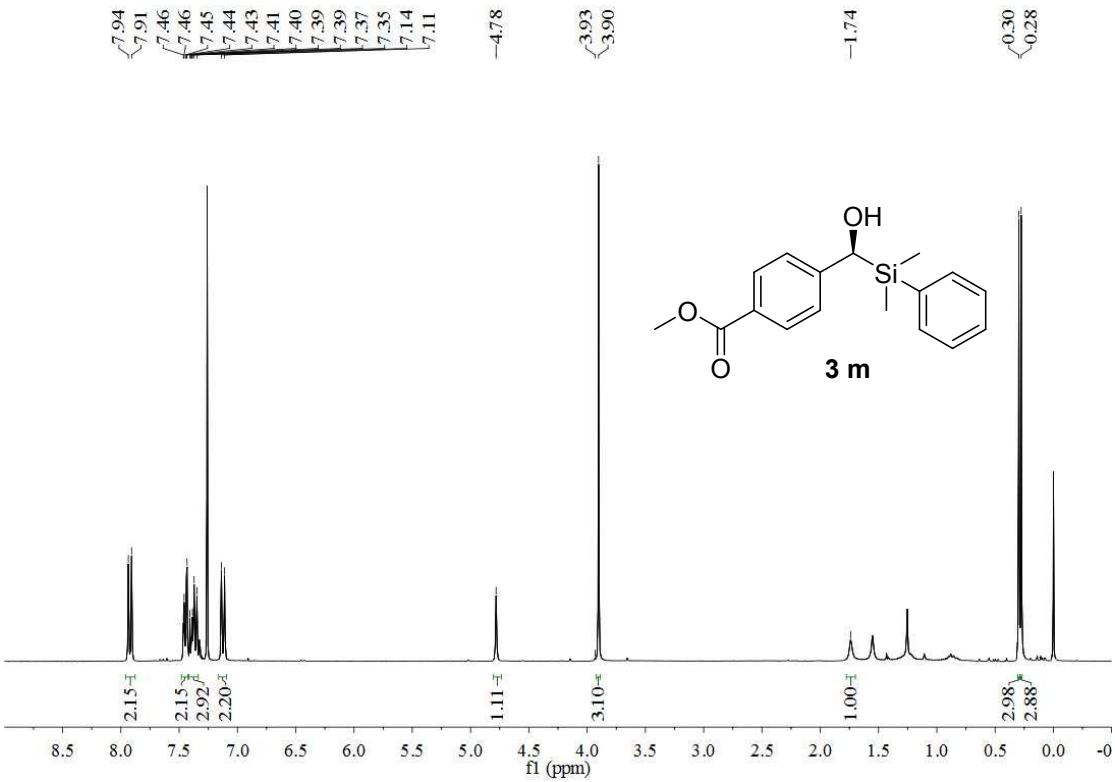
3 l

^{13}C NMR Spectrum of compound **3 l**

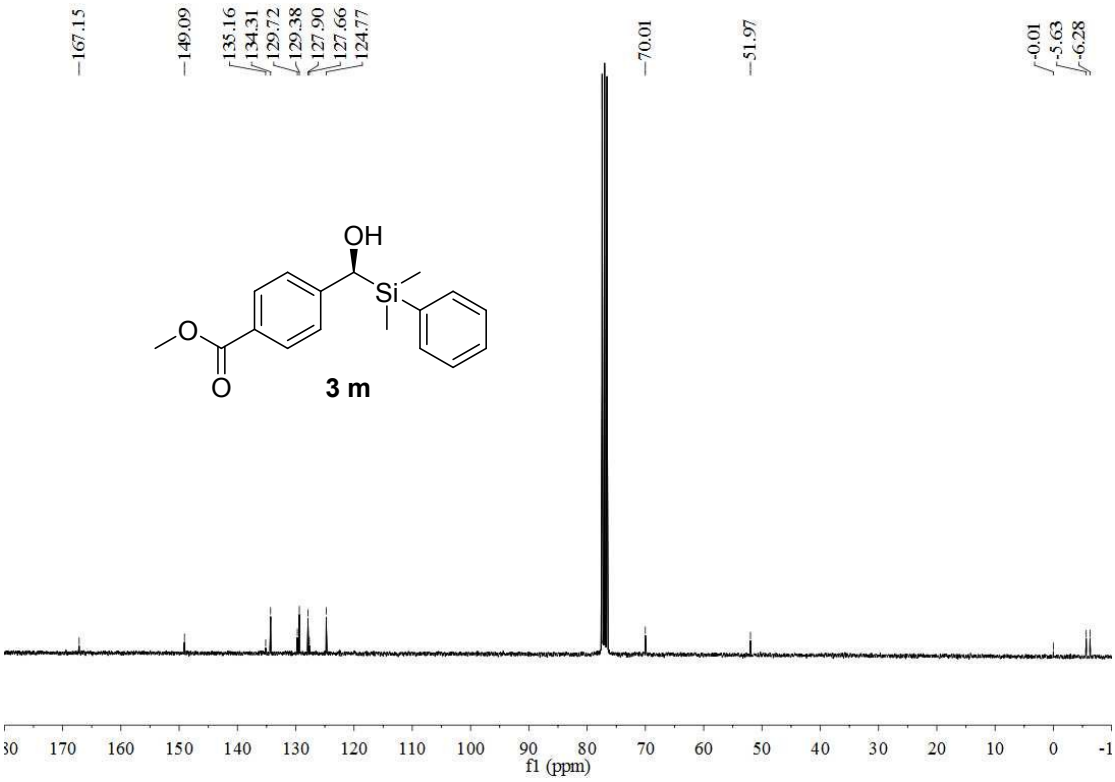


3 l

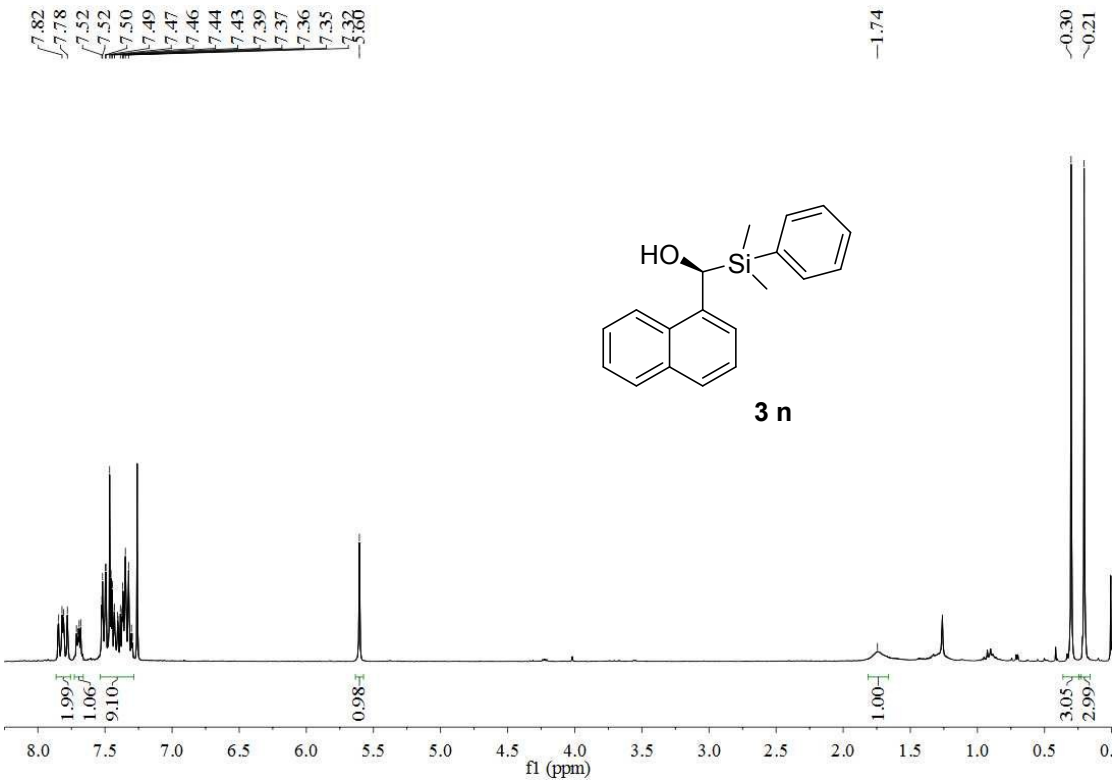
^{1}H NMR Spectrum of compound **3 m**



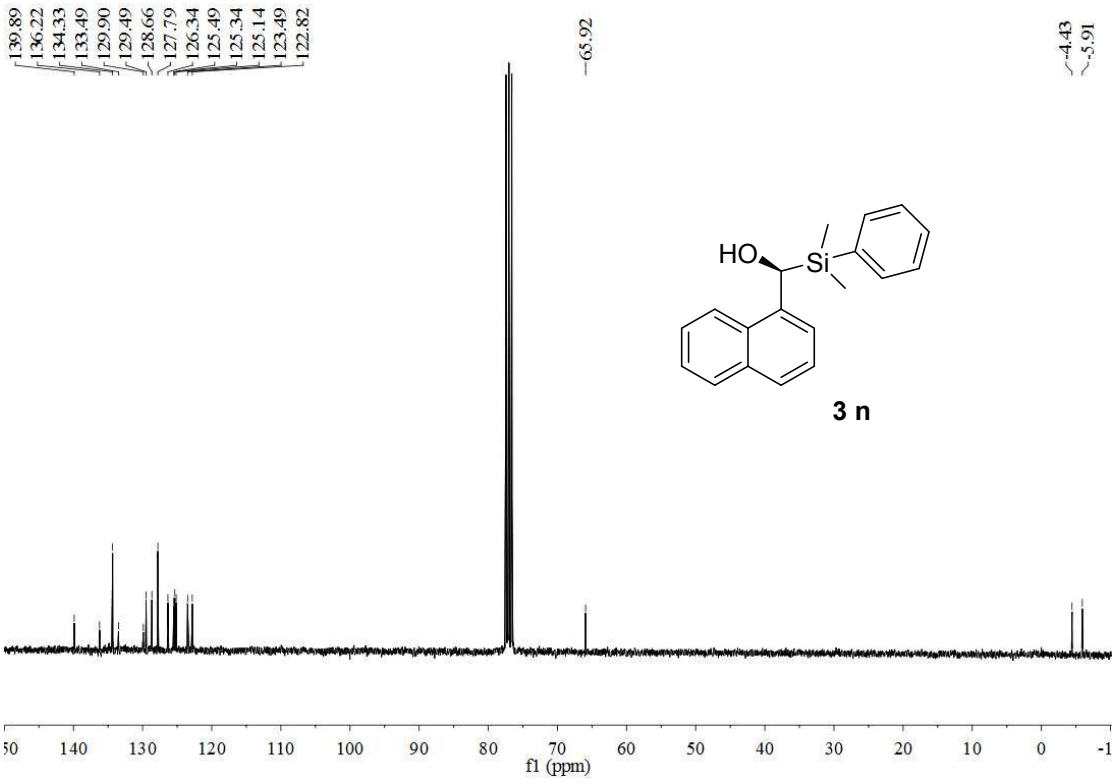
^{13}C NMR Spectrum of compound **3 m**



^{1}H NMR Spectrum of compound **3 n**

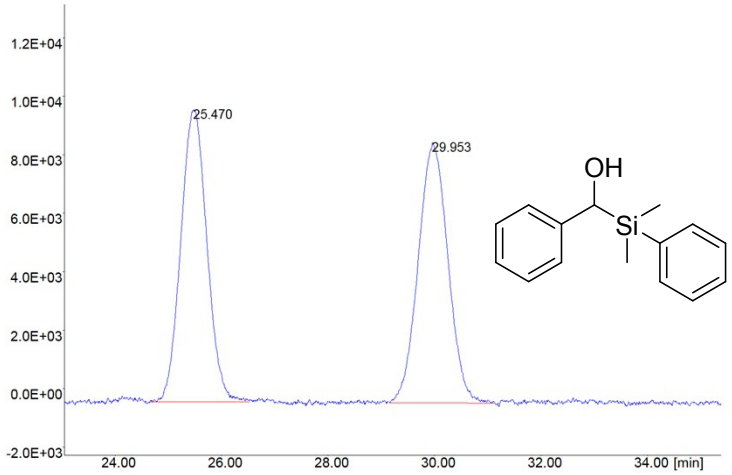


^{13}C NMR Spectrum of compound **3 n**



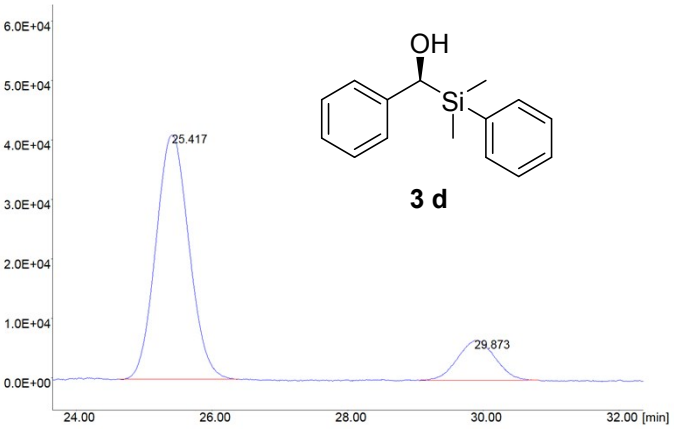
5, Copies of HPLC spectra

HPLC spectra of compound **3 d**



#	Name	RT	Height	Area	%Area
1		25.470	9999	337140.469	49.682
2		29.953	8905	341462.733	50.318

Total Area of Peak = 678603.202

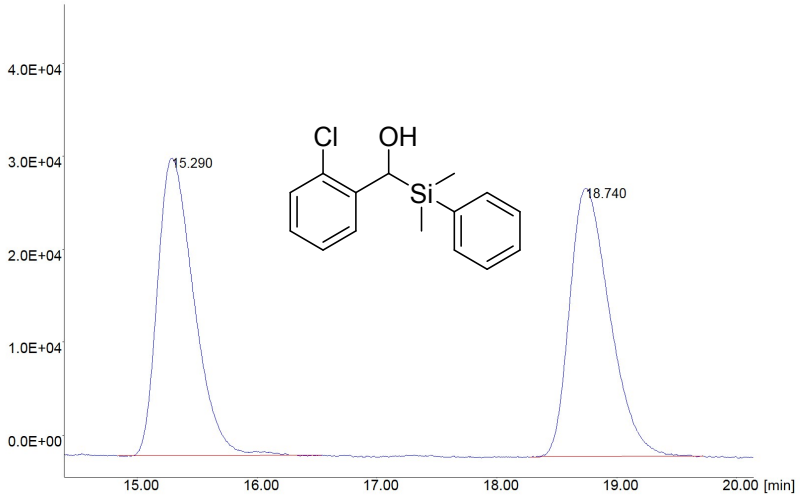


3 d

#	Name	RT	Height	Area	%Area
1		25.417	41080	1384069.200	84.460
2		29.873	6681	254649.314	15.540

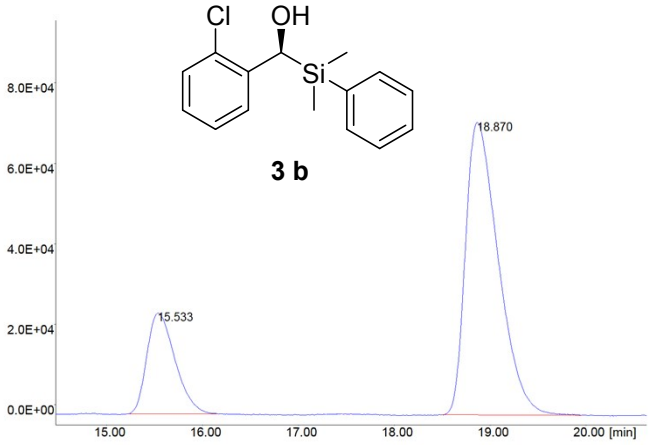
Total Area of Peak = 1638718.514

HPLC spectra of compound **3 b**



#	Name	RT	Height	Area	%Area
1		15.290	32018	675369.548	50.132
2		18.740	28874	671817.104	49.868

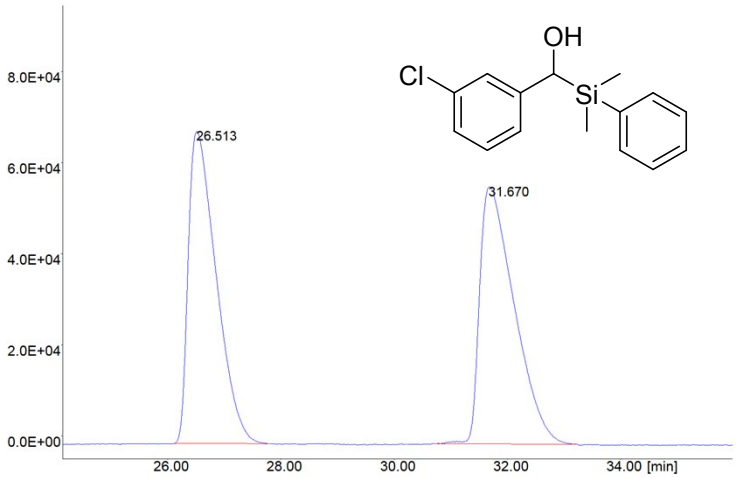
Total Area of Peak = 1347186.652



#	Name	RT	Height	Area	%Area
1		15.533	25029	511002.200	22.795
2		18.870	72619	1730758.406	77.205

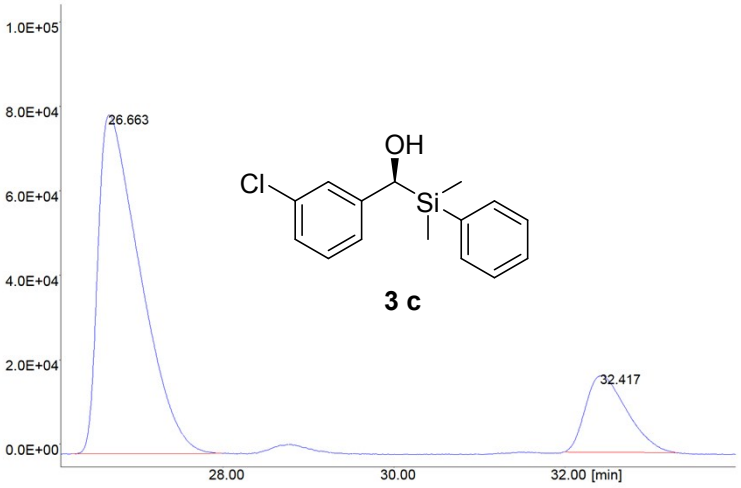
Total Area of Peak = 2241760.606

HPLC spectra of compound **3 c**



#	Name	RT	Height	Area	%Area
1		26.513	68558	2321606.505	49.461
2		31.670	56371	2372219.665	50.539

Total Area of Peak = 4693826.170

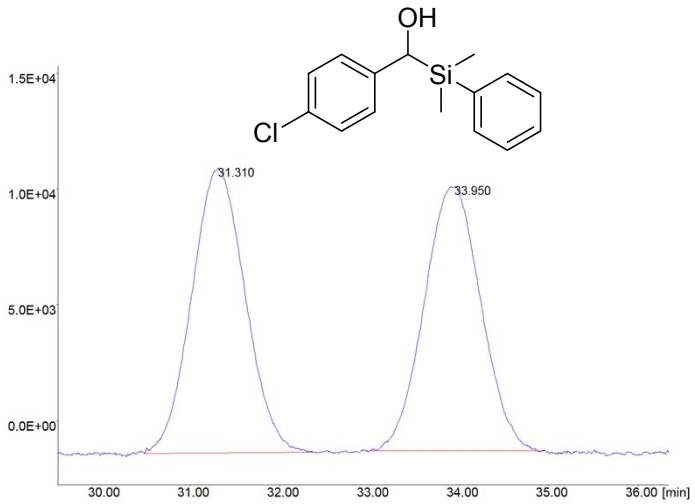


3 c

#	Name	RT	Height	Area	%Area
1		26.663	80193	2723989.455	81.804
2		32.417	18234	605889.180	18.196

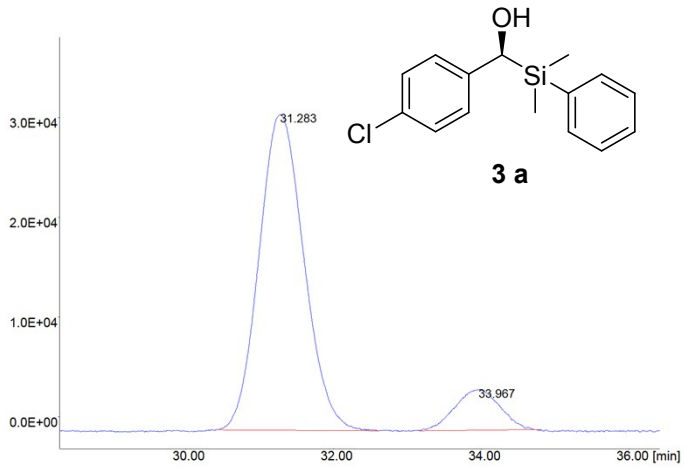
Total Area of Peak = 3329878.635

HPLC spectra of compound **3 a**



#	Name	RT	Height	Area	%Area
1		31.310	12298	508417.600	50.329
2		33.950	11428	501769.563	49.671

Total Area of Peak = 1010187.163

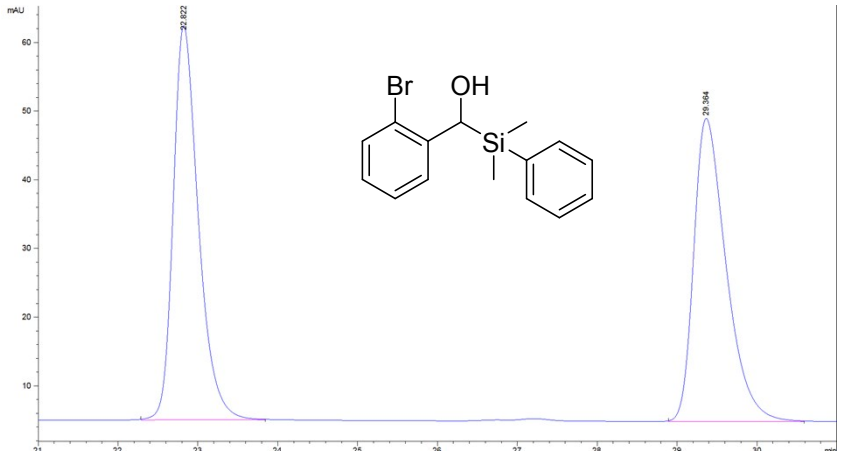


3 a

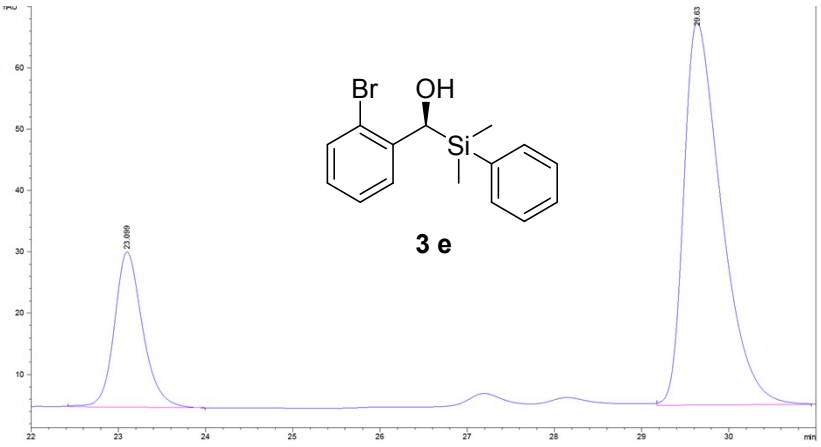
#	Name	RT	Height	Area	%Area
1		31.283	31654	1324805.726	88.524
2		33.967	4087	171741.738	11.476

Total Area of Peak = 1496547.464

HPLC spectra of compound **3 e**

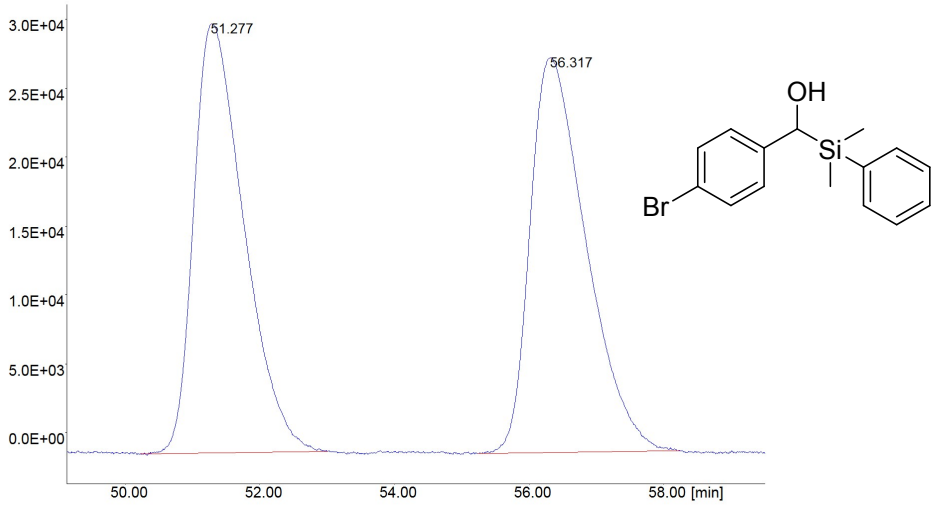


#Peak	RetTime	Type	Width	Area	Height	% Area
1	22.822	BB	0.3346	1259.07886	57.38102	50.3212
2	29.364	BB	0.4306	1243.00403	44.12172	49.6788
Totals :				2502.08289	101.50274	



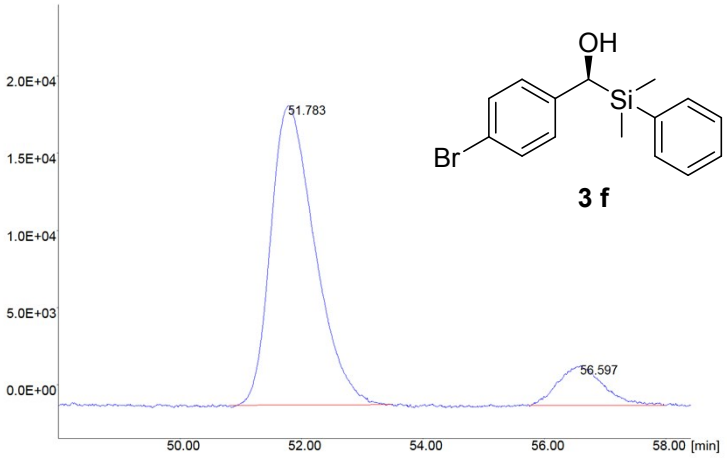
#Peak	RetTime	Type	Width	Area	Height	% Area
1	23.099	BB	0.3416	570.92706	25.32784	23.4573
2	29.636	BB	0.4527	1862.96973	62.47527	76.5427
Totals :				2433.89679	87.80311	

HPLC spectra of compound **3 f**



#	Name	RT	Height	Area	%Area
1		51.277	31147	1605859.682	49.324
2		56.317	28652	1649873.285	50.676

Total Area of Peak = 3255732.967

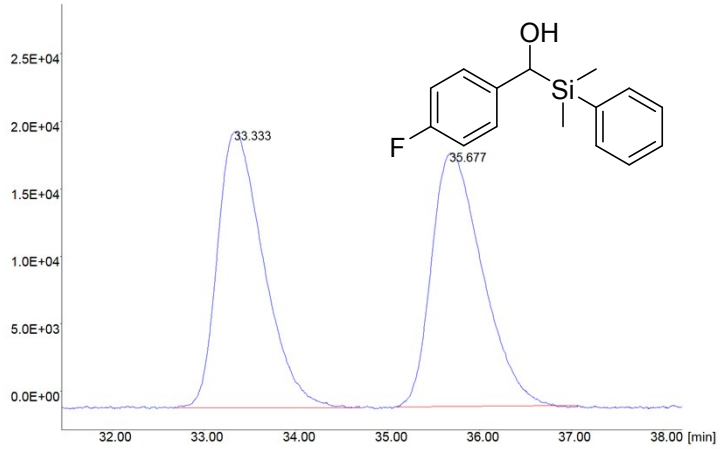


3 f

#	Name	RT	Height	Area	%Area
1		51.783	19362	972425.063	88.094
2		56.597	2557	131429.950	11.906

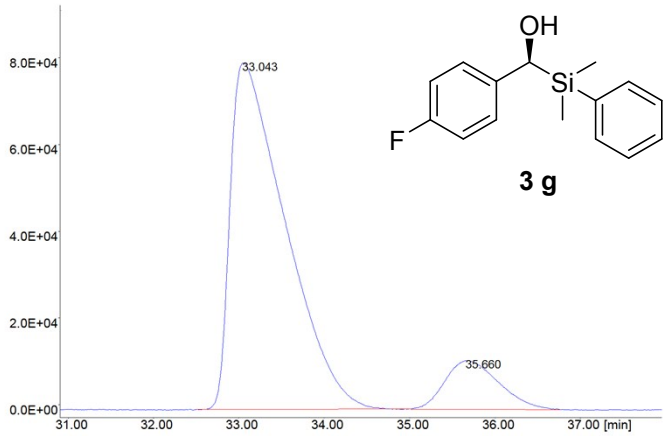
Total Area of Peak = 1103855.013

HPLC spectra of compound **3 g**



#	Name	RT	Height	Area	%Area
1		33.333	20429	709014.934	49.681
2		35.677	18766	718133.314	50.319

Total Area of Peak = 1427148.248

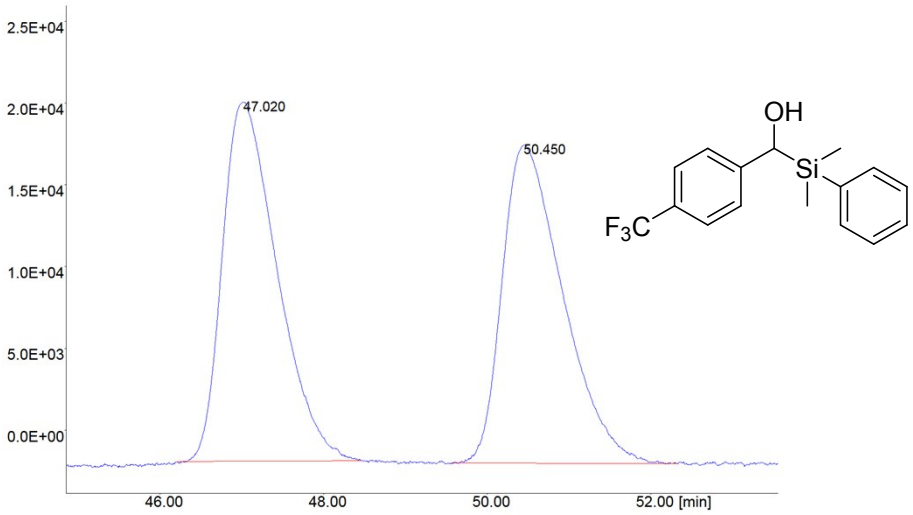


3 g

#	Name	RT	Height	Area	%Area
1		33.043	79884	3568488.604	87.947
2		35.660	11243	489038.120	12.053

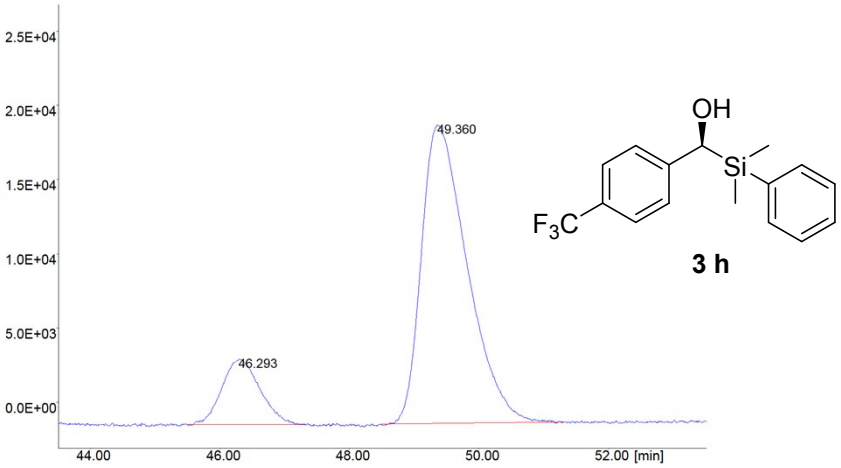
Total Area of Peak = 4057526.724

HPLC spectra of compound **3 h**



#	Name	RT	Height	Area	%Area
1		47.020	21969	1017293.573	50.399
2		50.450	19475	1001189.024	49.601

Total Area of Peak = 2018482.597

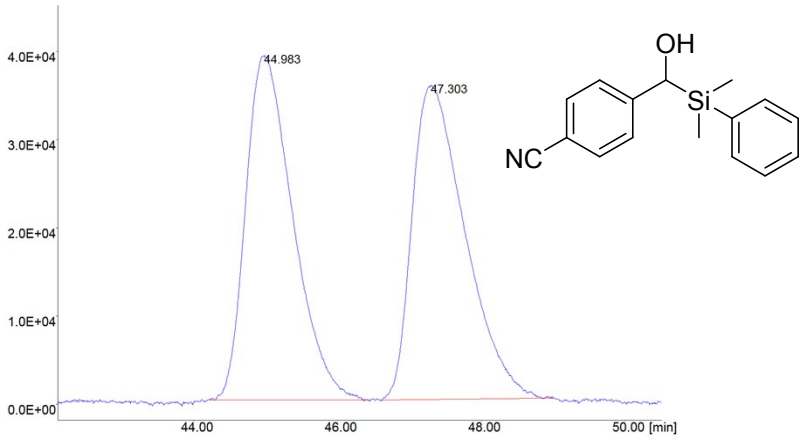


3 h

#	Name	RT	Height	Area	%Area
1		46.293	4417	179173.174	15.413
2		49.360	20106	983284.279	84.587

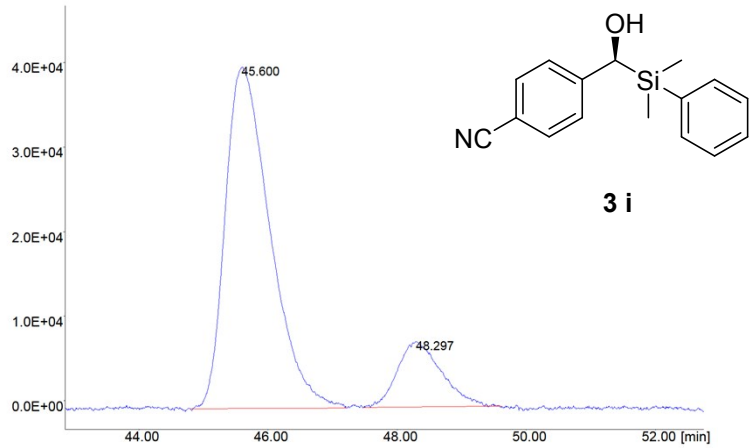
Total Area of Peak = 1162457.452

HPLC spectra of compound **3 i**



#	Name	RT	Height	Area	%Area
1		44.983	39103	1769989.794	49.387
2		47.303	35656	1813908.212	50.613

Total Area of Peak = 3583898.006

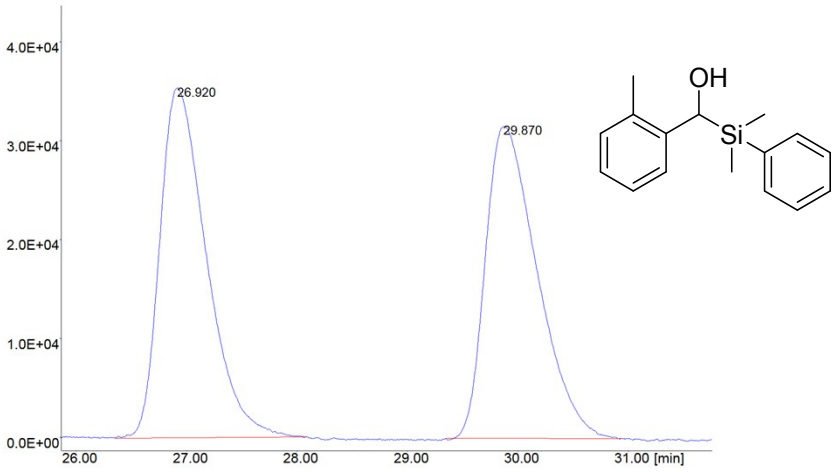


3 i

#	Name	RT	Height	Area	%Area
1		45.600	40380	1932097.107	84.139
2		48.297	7736	364217.137	15.861

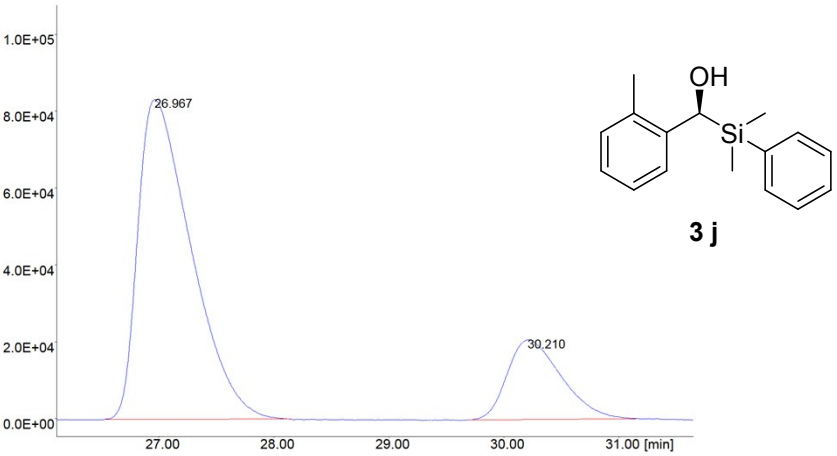
Total Area of Peak = 2296314.244

HPLC spectra of compound **3 j**



#	Name	RT	Height	Area	%Area
1		26.920	35393	1034458.777	50.148
2		29.870	31557	1028352.940	49.852

Total Area of Peak = 2062811.718

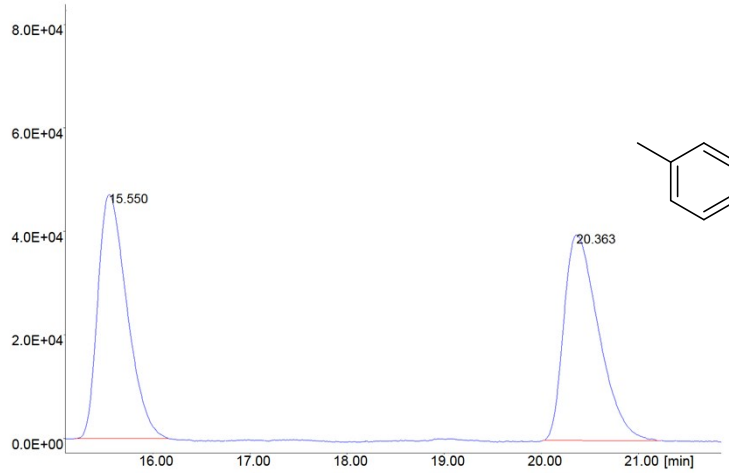


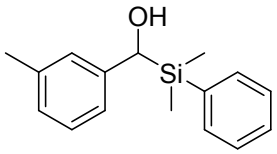
3 j

#	Name	RT	Height	Area	%Area
1		26.967	83223	2678465.787	79.876
2		30.210	20758	674806.318	20.124

Total Area of Peak = 3353272.105

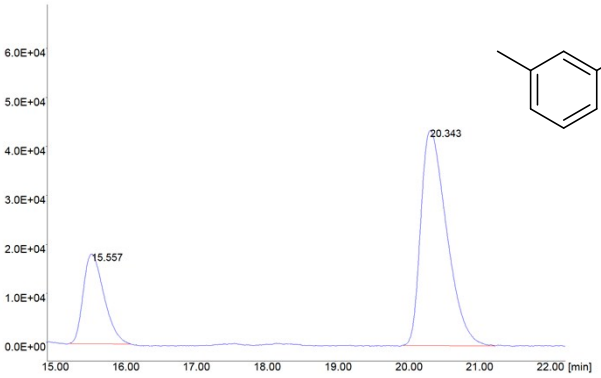
HPLC spectra of compound **3 k**

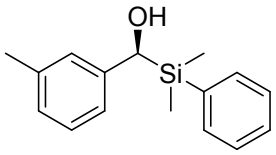




#	Name	RT	Height	Area	%Area
1		15.550	47174	973556.627	49.693
2		20.363	39752	985575.361	50.307

Total Area of Peak = 1959131.988



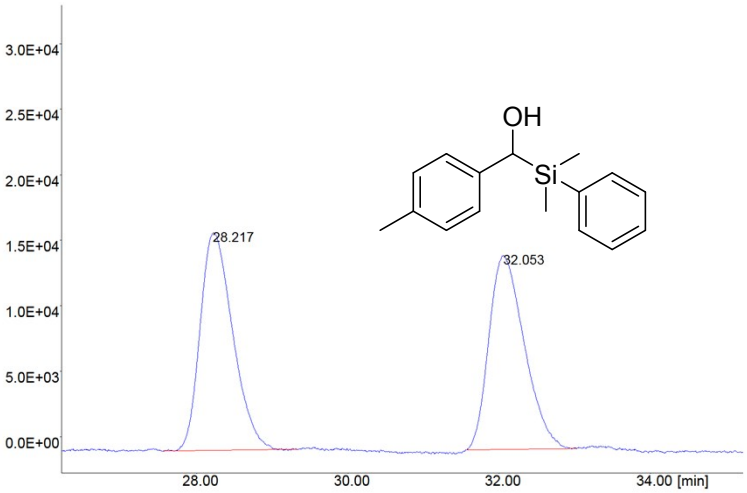


3 k

#	Name	RT	Height	Area	%Area
1		15.557	18336	369290.000	25.001
2		20.343	43939	1107834.879	74.999

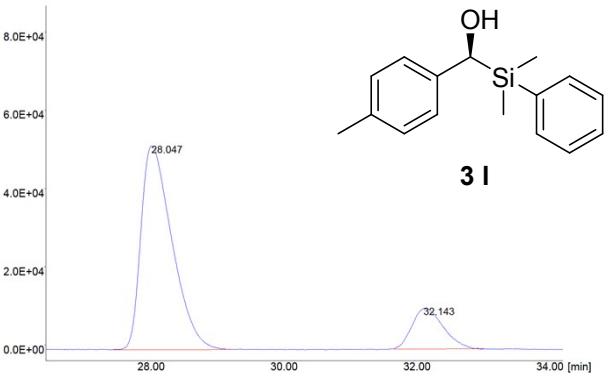
Total Area of Peak = 1477124.879

HPLC spectra of compound **3 l**



#	Name	RT	Height	Area	%Area
1		28.217	16607	494177.293	50.792
2		32.053	14816	478773.449	49.208

Total Area of Peak = 972950.742

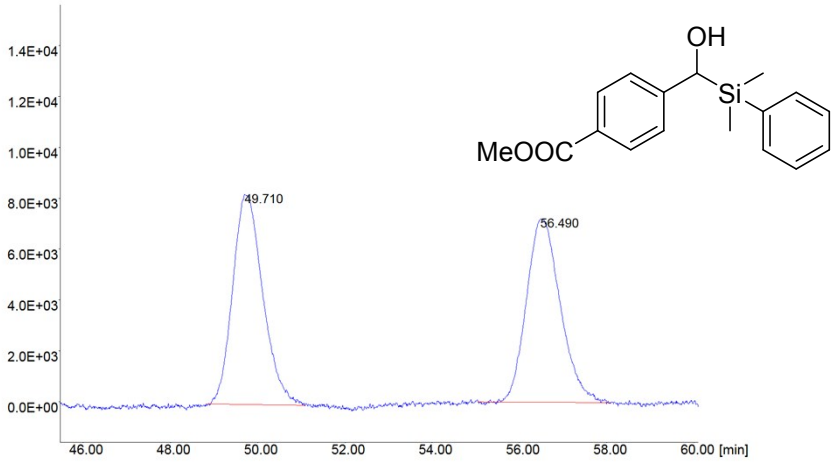


3 l

#	Name	RT	Height	Area	%Area
1		28.047	52020	1678308.331	83.311
2		32.143	10417	336191.949	16.689

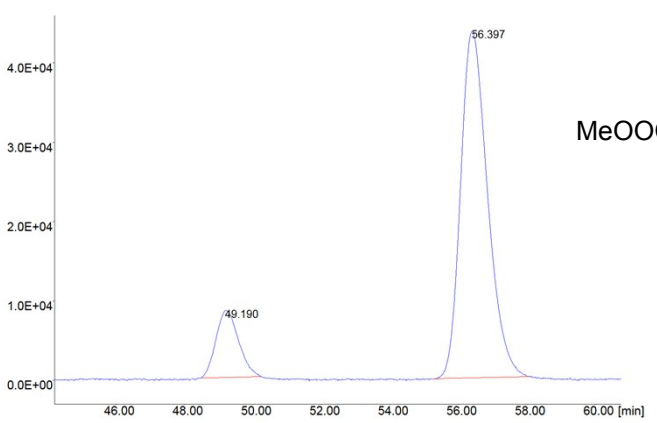
Total Area of Peak = 2014500.280

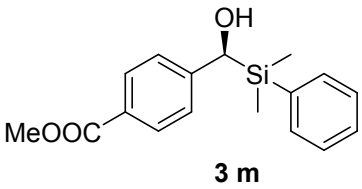
HPLC spectra of compound 3 m



#	Name	RT	Height	Area	%Area
1		49.710	8259	392525.540	50.438
2		56.490	7220	385705.827	49.562

Total Area of Peak = 778231.367



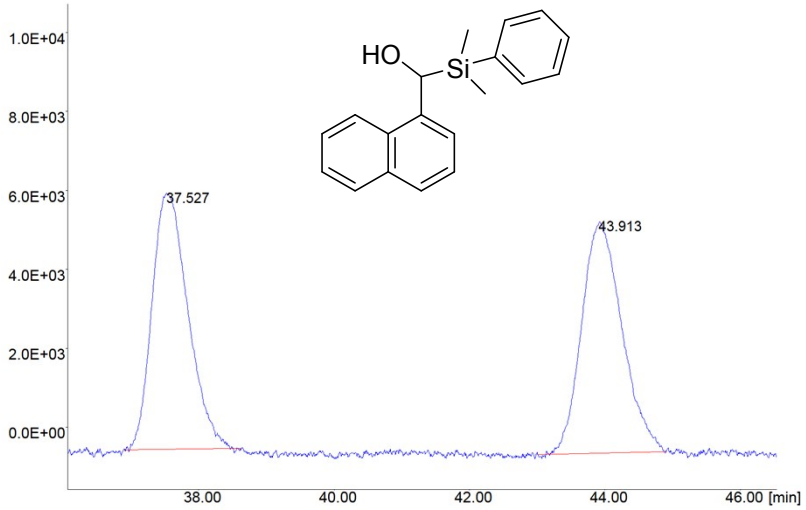


3 m

#	Name	RT	Height	Area	%Area
1		49.190	8458	382750.800	13.927
2		56.397	43774	2365519.332	86.073

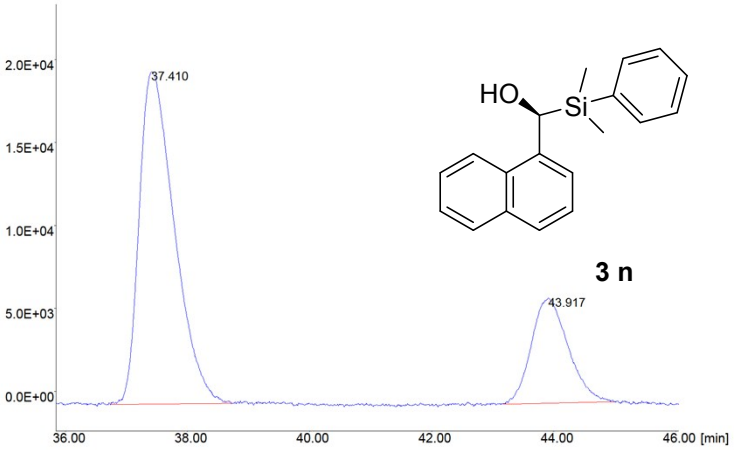
Total Area of Peak = 2748270.132

HPLC spectra of compound **3 n**



#	Name	RT	Height	Area	%Area
1		37.527	6494	237411.375	49.657
2		43.913	5868	240691.831	50.343

Total Area of Peak = 478103.206



3 n

#	Name	RT	Height	Area	%Area
1		37.410	20044	797246.300	75.072
2		43.917	6334	264730.947	24.928

Total Area of Peak = 1061977.247

6, CD spectra of the α-hydroxysilanes

The configurations of the other α-hydroxysilanes were assigned to *S* by comparison with **3d** on the basis of their CD spectra (***Figure 1***) measured in their dichloromethane solutions with uv-vis wavelength ranging from 220-300 nm.

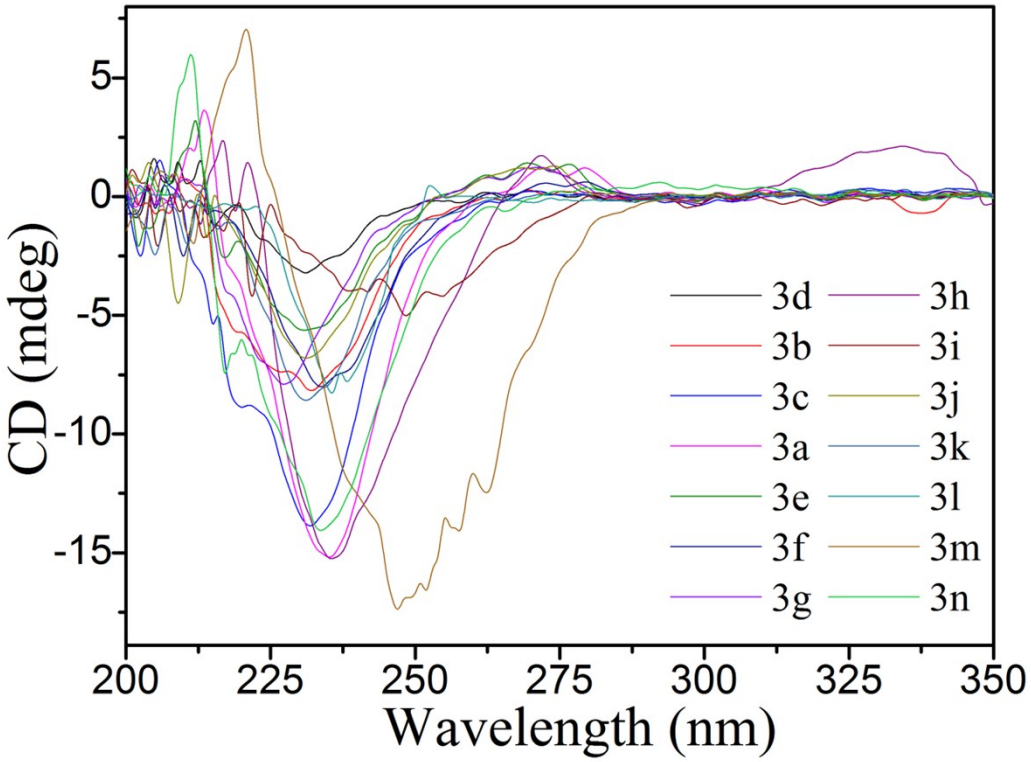


Figure 1. CD spectra of **3a-3n**