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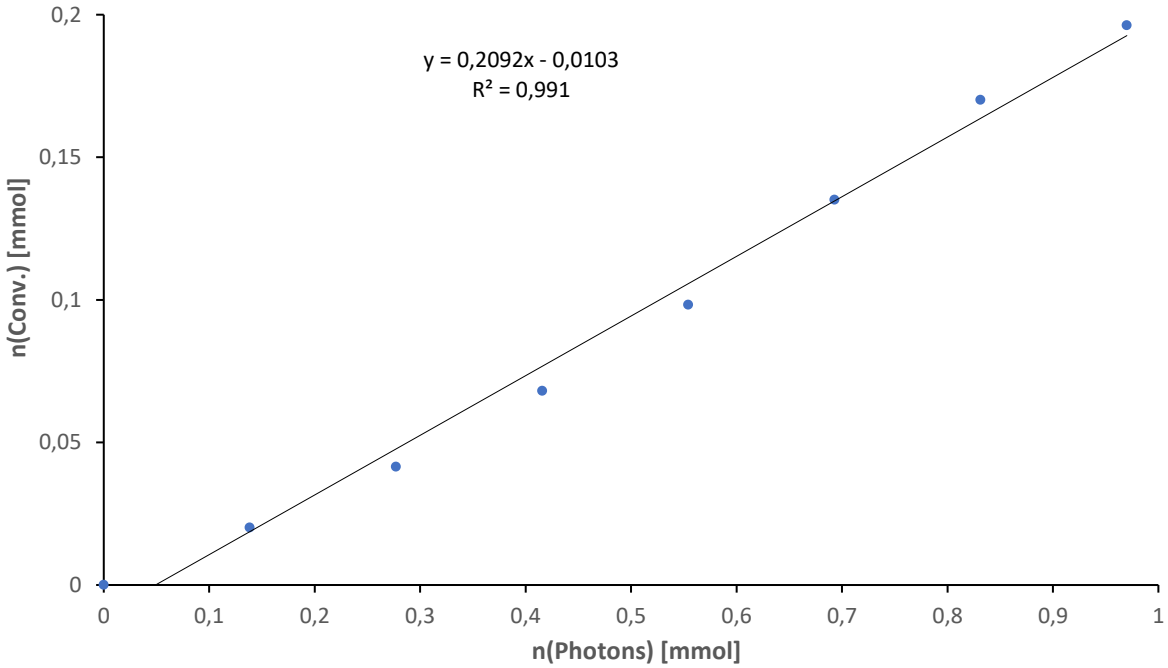


1. Instrumentation and General Information

Infrared Spectroscopy: Infrared (IR) spectra were measured on a *FTIR-4600LE Fourier-Transfrom Infrared Spectrometer* from Jasco or a *Digilab Varian 3100 FT-IR Excalibur Series*. The absorption signals are given via wavenumber (cm^{-1}).

NMR: ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR were recorded at 293 K using a Bruker Avance II 300, Agilent DD2 500 and an Agilent DD2 600 spectrometer. Chemical shifts (δ in ppm) were referenced to the solvent residual peak of $CDCl_3$ (δH = 7.26; δC = 77.16), C_6D_6 (δH = 7.16; δC = 128.06). Coupling constants (J) are quoted to the nearest 0.1 Hz. The multiplets of the observed signals were given as s (singlet), br (broad singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet) and combination of the above.

Mass Spectroscopy: High-resolution mass spectroscopy (HRMS) ESI and APCI (m/z) were measured on a Thermo Fisher Scientific LTQ XL Orbitrap,Thermo Fisher Scientific Orbitrap Velos Pro and Bruker Daltonics MicroTof. HRMS EI (m/z) spectra were measured on a Thermo Fischer Scientific Exactive GC Orbitrap GC-MS system. MassLinx 4.0 of Water-Micromass was used for data analysis.

Chromatography: *Merck silica gel 60 F254*-plates were used for analytical thin layer chromatography and detection was carried out using UV-light (λ=254 nm). Solvents for chromatography were purchased in technical grade and purified by ambient pressure distillation and diethyl ether (Et_2O) was distilled over ferrous sulfate heptahydrate. Column chromatography was carried out on *VWR* silica gel (40 – 63 μm).

Melting Points: Melting points were determined using a *Büchi M560* and are uncorrected.

Reagents and solvents: Tetrahydrofuran (THF) was dried by refluxing over sodium and freshly distilled over potassium prior to use. Et_2O dried by refluxing over Na/K-alloy and freshly distilled prior to use. Dichloromethane (DCM) was dried by refluxing over phosphorous pentoxide and was freshly distilled prior to use. Benzene (C_6H_6), Acetone, Methanol (MeOH) and dimethylformamide (DMF) were purchased in extra-dry grade from *Acros Organics* and stored over molecular sieves. Benzal bromide was purchased from *Sigma-Aldrich* and distilled under vacuum (0.05 mbar, 65 °C) and stored under argon at 4 °C. Diisopropyl amine was dried by refluxing over CaH_2 for 8 hours and subsequent distillation under argon and stored under Argon over molecular sieves. Otherwise noted all other reagents were purchased from *Sigma-Aldrich, TCI, Alfa Aesar, Acros Organics, BLD Pharm, ABCR or Fluorochem* and used without further purification. Silver trifluoromethanesulfonate was dried under high vaccum at 300°C for 30 minutes prior to use.

The compounds **5b**, **6b**,[1] **7b**-Me[2], **7b**-Bn[3], **7b**-PMB[4], **7b**-MOM[5], **7b**-THP[6] **7b**-TBDMS[7], **7b**-TIPS[8], **7b**-TBDPS[9], **7b**-Ac, **7b**-Bz, **7b**-Piv[8], **7p**, **7q**[10] have been synthetized according to the literature

Experimental procedures and glassware: Unless stated otherwise, all reactions were carried out in flame dried glassware (630 °C, high vacuum) and under argon atmosphere using *Schlenk* technique.

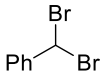
Gas Chromatography (GC-FID): Gas chromatography studies have been carried out on an *Agilent 8860 GC System* with a HP5 column (length: 30 m; diameter: 0.32 mm).

UV-Vis-Spectoscopy: UV/Vis-Spectra were measured on a *Jasco V770 spectrophotometer.*

2. Synthesis and Characterization

2.1 Protecting Reagent

Benzalbromide

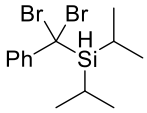


At ambient conditions benzylbromide (200 mmol, 24 ml, 1 eq.) was dissolved in DCM (p.a.) (100 ml) and bromine (210 mmol, 11 ml, 1.05 eq.) was added. The flask was connected to a washing bottle filled with Na_2CO_3 to trap evolving HBr. The solution was irradiated (350 nm) in a *Rayonet RPR-200* for 4 hours at room temperature. Then, the solution was washed with $Na_2S_2O_3$ (sat.) and the organic phase was evaporated. The residue was distilled (65 °C, 0.04 mbar) to obtain benzalbromide as a colorless liquid (49.7 g, 199 mmol, quant.). The analytical data are in accordance to the literature. [11]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.68 – 7.50 (m, 2H), 7.43 – 7.27 (m, 3H), 6.66 (s, 1H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 142.1, 130.0, 128.8, 126.6, 41.2.

(Dibromo(phenyl)methyl)diisopropylsilane 5a



The compound was prepared according to a procedure described in the literature.[12] In a flame dried 500 ml three-neck flask diisopropyl amine (60 mmol, 9.1 ml, 1.2 eq.) was dissolved in 100 ml of a THF/Et_2O (1:1) mixture and cooled to -78 °C. n-Butyllithium (55 mmol, 37.5 ml, 1.1 eq., 1.6 M in hexanes) was added dropwise and the resulting mixture was stirred for 30 minutes at this temperature. Then, the solution was cooled down to -90 °C (acetone/liquid nitrogen). Benzal bromide (distilled) (50 mmol, 8.3 ml, 1 eq.) was dissolved in 100 ml of a THF/Et_2O (1:1) mixture and transferred into an addition funnel with cooling jacket filled with dry ice and acetone. The benzal bromide solution was added dropwise over approximately 2.5 hours and the resulting mixture was stirred for an additional hour (Note: liquid nitrogen was constantly added to the cooling bath to ensure a sufficient cooling). Chlorodiisopropylsilane (65 mmol, 11 ml, 1.3 eq.) was then added dropwise and stirring continued for 60 minutes at -90 °C and afterwards the mixture was allowed to warm to room temperature by removing the cooling bath. Silica was added to quench the reaction and the mixture was filtered through a silica plug and washed with pentane. The solvents were evaporated and the residue was dissolved in pentane and filtered through silica and washed with pentane and evaporated again. Removal of impurities by distillation (70 °C, 0.08 mbar) gave the desired product as a colourless liquid (17.5 g, 48.1 mmol, 96%). The product can also be purified by column chromatography (pentane), albeit in decreased yield (10.6 g, 29.1 mmol, 58%).

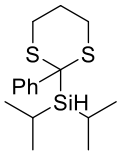
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90 – 7.75 (m, 2H), 7.36 (dd, J = 8.4, 6.6 Hz, 2H), 7.31 – 7.23 (m, 1H), 4.32 (t, J = 1.8 Hz, 1H), 1.46 – 1.24 (m, 2H), 1.10 (dd, J = 7.4, 6.3 Hz, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 143.2, 128.3, 128.2, 128.2, 61.2, 20.1, 19.0, 12.8.

FT-IR (neat) [cm^{-1}]: 3060, 2943, 2888, 2865, 2729, 2121, 1947, 1882, 1796, 1597, 1520, 1490, 1461, 1442, 1386, 1365, 1312, 1276, 1249, 1176, 1106, 1066, 1034, 1011, 918, 878, 857, 802, 783, 740, 690, 645, 613, 588

HRMS (EI): calculated for $[M-H]^+$: 360.9628, found: 360.9628.

Diisopropyl(2-phenyl-1,3-dithian-2-yl)silane



2-Phenyl-1,3-dithiane (588 mg, 3.00 mmol, 1.00 Äquiv.) was dissolved in THF (5 ml) and cooled to -30 °C. *n*-Butyllithium was added (3.6 mmol, 2.25 ml, 1.3 eq., 1.6 M in hexanes) was added dropwise. The solution was stirred for 2 hours and subsequently cooled to -78 °C. Chlorodiisopropylsilane (3.6 mmol, 614 µl, 1.3 eq.) was added dropwise and it was stirred for another hour. The reaction was quenched wit NH_4Cl (sat.) and as extracted with DCM. The combined organic phases were dried over $MgSO_4$, evaporated and the crude product was purified by column chromatography (pentane/EtOAc 100:5) to obtain the product as a white solid (636 mg, 2.05 mmol, 68%).

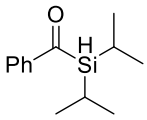
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.94 – 7.85 (m, 2H), 7.44 – 7.32 (m, 2H), 7.19 (ddt, J = 8.6, 7.6, 1.2 Hz, 1H), 3.91 (m, J = 3.6 Hz, 1H), 2.88 – 2.74 (m, 2H), 2.52 – 2.38 (m, 2H), 2.13 – 1.97 (m, 1H), 1.93 (dtt, J = 13.9, 4.1, 2.8 Hz, 1H), 0.09 (d, J = 3.6 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 141.3, 129.5, 128.4, 125.5, 46.4, 25.4, 25.1, 20.4, 19.2, 11.3

FT-IR (neat) [cm^{-1}]: 3058, 2941, 2891, 2864, 2114, 1591, 1478, 1461, 1441, 1421, 1387, 1336, 1273, 1248, 1155, 1078, 1033, 1011, 928, 914, 886, 852, 793, 752, 725, 698, 662, 647, 617, 586.

HRMS (EI): calculated for $[M]^+$: 310.1240, found: 310.1239.

Diisopropyl benzoyl silane 6a



From (dibromo(phenyl)methyl)diisopropylsilane:[1] Under ambient conditions, (dibromo(phenyl)methyl)diisopropylsilane (1 eq.) was dissolved in DCM (0.1 M, p.a.) and silver carbonate (1.2 eq.) was added. The resulting mixture was stirred for 6 hours at room temperature and was afterwards filtered through a frit. The solvent was evaporated at room temperature and the residue was dissolved in pentane and filtered through celite again. The resulting crude product can be purified by column chromatography (pentane/Et_2O 40:1) or distillation (0.05 mbar, 65 °C). The product was obtained as a bright yellow liquid (89%).

From diisopropyl(2-phenyl-1,3-dithian-2-yl)silane:[13] Under ambient conditions diisopropyl(2-phenyl-1,3-dithian-2-yl)silane (7.50 mmol, 2.33 g, 1.0 eq.) was dissolved in acetone (30 ml). A solution of chloroamine T (30.0 mmol, 8.46 g, 4.0 eq.) in methanol/water (60 ml, 80:20) was added. The mixture was stirred for 15 minutes at room temperature. Then, a 10% NaCl solution (20 ml) was added followed by a 0.5 N $NaHCO_3$ solution (20 ml). It was extracted with pentane and the combined organic phases were dried over $MgSO_4$ and the solvent was evaporated. The crude was purified by column chromatography (pentane/EtOAc 40:1) to obtain the product as a bright yellow liquid (409 mg, 1.86 mmol, 25 %).

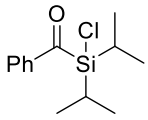
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 – 7.91 (m, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.43 (m, 2H), 4.41 (t, J = 3.3 Hz, 1H), 1.31 (dqd, J = 14.3, 7.2, 3.2 Hz, 2H), 1.10 (d, J = 7.4 Hz, 6H), 1.04 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.1, 143.1, 133.2, 128.8, 127.9, 77.6, 76.7, 18.71, 18.69, 10.5

FT-IR (neat) [cm^{-1}]: 3061, 2941, 289, 2864, 2728, 2111, 1718, 1611, 1590, 1577, 1462, 1447, 1386, 1366, 1311, 1274, 1249, 1211, 1711, 1105, 1070, 1009, 928, 882, 853, 781, 752, 727, 698, 690, 664, 616, 598

HRMS (EI): calculated for $[M-H]^+$: 219.1200, found: 219.1200.

(Chlorodiisopropylsilyl)(phenyl)methanone 1a



The compound was prepared according to a procedure described in the literature.[14] Diisopropyl benzoyl silane (**6a,** 1 eq.) was dissolved in DCM and cooled to 0 °C. TCCA (0.5 eq.) was added and stirring was continued at room temperature for 4.5 hours. The solvent was evaporated at 0 °C and the resulting slurry was distilled (100 °C, 0.06 mbar) to obtain the product as a bright yellow oil (quant.).

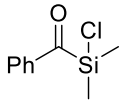
Note: For its use, **1a** was dissolved in DCM to obtain an approximately 0.2 M solution and was stored in a freezer. The concentration was determined by evaporation of a sample(0.5 ml) of the solution and back weighing of the flask.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.11 – 8.04 (m, 2H), 7.63 – 7.51 (m, 1H), 7.52 – 7.43 (m, 2H), 1.48 (hept, J = 7.3 Hz, 2H), 1.10 (dd, J = 13.2, 7.4 Hz, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 230.2, 141.7, 133.6, 128.8, 128.4, 17.3, 16.9, 14.3.

HRMS (EI): calculated for $[M-H]^+$: 253.0810, found: 253.0810.

(Chlorodimethylsilyl)(phenyl)methanone 1b



The compound was prepared according to a procedure described in the literature.[14] Dimethyl benzoyl silane[1] (1 eq.) was dissolved in DCM and cooled to 0 °C. TCCA (0.5 eq.) was added and stirring was continued at room temperature for 4.5 hours. The solvent was evaporated at 0 °C and the resulting slurry was distilled (80°C, 0.06 mbar) to obtain the product as a bright yellow oil (quant.).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.17 – 7.97 (m, 2H), 7.65 – 7.45 (m, 3H), 0.73 (s, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 227.6, 139.9, 133.8, 128.9, 128.5, 1.7.

2.2 Screening for Deprotection Conditions

8 (0.1 mmol, 35.5 mg, 1 eq.) and biphenyl (0.1 mmol, 35.5 mg, 1 eq.) as internal standard were dissolved in 1 ml of the corresponding solvent. The resulting solution was irradiated with a 456 nm 45 W Kessil LED for 15 minutes and stirring was continued for 24 h at room temperature. Samples were measured before irradiation and after 24 hours of stirring.

Substrate	**Solvent**	**Time**	**yield**
8a (1°)	Water*	24h	0%
8a (1°)	MeOH	4h	94%
8a (1°)	Acetone/MeOH (5:1)	16h	88%
8a (1°)	Acetone/MeOH (6:1)	16h	85%
8a (1°)	Acetone/MeOH (7:1)	16h	73%
8a (1°)	Acetone/MeOH (5:1)	24h	94%
8a (1°)	Acetone/MeOH (6:1)	24h	94%
8a (1°)	**Acetone/MeOH (7:1)**	**24h**	**94%**
8a (1°)	DCM/MeOH (7:1)	24h	92%
8a (1°)	Tolu/MeOH (7:1)	24h	92%
8a (1°)	THF/MeOH (7:1)	24h	89%
8a (1°)	Et_2O/MeOH (7:1)	24h	86%
8a (1°)	EtOAc/MeOH (7:1)	24h	62%
8a (1°)	ACN/MeOH (7:1)	24h	91%
8a (1°)	DMF/MeOH (7:1)	24h	0%
8a (1°)	DMSO/MeOH (7:1)	24h	0%
8b (2°)	**Acetone/MeOH (7:1)**	**24h**	**99%**
8c (3°)	Acetone/MeOH (7:1)	24h	0%
8c (3°)	Acetone/MeOH (4:1)	24h	0%
8c (3°)	**MeOH**	**24h**	**97%**

*When water was used as solvent, the reaction was extracted after 24 hours and the crude was analyzed by GC.

2.3 Stability Screening

8 (0.1 mmol, 1 eq.) and biphenyl (0.1 mmol, 35.5 mg, 1 eq.) as internal standard were dissolved in 1 ml of the corresponding solvent. It was stirred at 20 °C and the reaction temperature was kept at 20 °C using a circulating water system.

Substrate	solvent	Time	Conversion	Rec.
8a (1°)	Acetone/MeOH (4:1)	24h	54%	46%
8a (1°)	Acetone/MeOH (5:1)	24h	47%	53%
8a (1°)	Acetone/MeOH (6:1)	24h	38%	62%
8a (1°)	**Acetone/MeOH (7:1)**	**24h**	**4%**	**96%**
8a (1°)	Acetone/MeOH (7:1)	3d	12%	88%
8a (1°)	**Acetone/MeOH (7:1)**	**5d**	**46%**	**54%**
8a (1°)	Acetone/MeOH (7:1)	6d	60%	40%
8a (1°)	MeOH	8h	42%	58%
8a (1°)	**MeOH**	**12h**	**55%**	**45%**
8a (1°)	MeOH	24h	92%	8%
8a (1°)	Acetone/H_2O (9:1)	24h	22%	78%
8a (1°)	**Acetone/H_2O (9:1)**	**2d**	**48%**	**52%**
8b (2°)	Acetone/MeOH (7:1)	24h	5%	95%
8b (2°)	Acetone/MeOH (7:1)	7d	43%	57%
8b (2°)	**Acetone/MeOH (7:1)**	**8d**	**58%**	**42%**
8b (2°)	MeOH	8h	15%	85%
8b (2°)	**MeOH**	24h	**50%**	**50%**
8b (2°)	Acetone/H_2O (9:1)	24h	6%	94%
8b (2°)	**Acetone/H_2O (9:1)**	**6d**	**53%**	**47%**
8c (3°)	Acetone/H_2O (9:1)	1d	15%	85%
8c (3°)	**Acetone/H_2O (9:1)**	**6d**	**50%**	**50%**
8c (3°)	MeOH	24h	2%	98%
8c (3°)	MeOH	4d	37%	63%
8c (3°)	**MeOH**	**5d**	**53%**	**47%**
8c (3°)	MeOH	6d	69%	31%

Acid

8 (0.1 mmol, 1 eq.) and biphenyl (0.1 mmol, 35.5 mg, 1 eq.) as internal standard were dissolved in 0.5 ml of methanol. 0.5 ml of a 2% HCl solution in MeOH was added. Samples have been measured before addition of acid and after the corresponding time.

Substrate	time	Conversion	Rec.
8a (1°)	**2 min**	**99%**	**0%**
8b (2°)	**2 min**	**77%**	**23%**
8b (2°)	4 min	97%	3%
8c (3°)	2 h	25%	75%
8c (3°)	**4 h**	**48%**	**52%**
8c (3°)	6 h	62%	38%

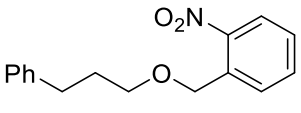
Base

8 (0.1 mmol, 1 eq.) and biphenyl (0.1 mmol, 35.5 mg, 1 eq.) as internal standard were dissolved in 0.5 ml of methanol. 0.5 ml of a 10% NaOH solution in MeOH was added. Samples have been measured before addition of base and after the corresponding time.

Substrate	**time**	**Conversion**	**Rec.**
8a (1°)	**2min**	**98%**	**2%**
8b (2°)	2 min	25%	75%
8b (2°)	**4 min**	**75%**	**25%**
8c (3°)	**12h**	**47%**	**53%**
8c (3°)	18h	62%	38%

2.4 Other Protecting Groups

1-Nitro-2-((3-phenylpropoxy)methyl)benzene 7a-oNBn



2-Nitrobenzyl bromide (3 mmol, 648 mg, 1 eq.) was dissolved in benzene (9 ml). Silveroxide (4.5 mmol, 972 mg, 1.5 eq.) and 4-phenyl-2-butanol (9 mmol, 1.22 ml, 3 eq.) were added. The mixture was stirred for 4 days and was then filtered through a pad of celite. After evaporation and purification by column chromatography the product was obtained as a colorless oil (546 mg, 2.01 mmol, 67%).

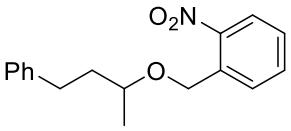
^{1}H-NMR (300 MHz, $CDCl_3$): δ =8.07 (dd, J = 8.2, 1.3 Hz, 1H), 7.80 (dq, J = 7.7, 1.1 Hz, 1H), 7.65 (td, J = 7.6, 1.3 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.35 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 4.88 (s, 2H), 3.60 (t, J = 6.3 Hz, 2H), 2.76 (t, 2H), 2.10 – 1.93 (m, 2H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 147.4, 141.9, 135.6, 133.7, 128.8, 128.6, 128.5, 128.0, 126.0, 124.8, 70.6, 69.5, 32.5, 31.4.

FT-IR (neat) [cm^{-1}]: 3061, 3026, 2924, 2859, 1948, 1612, 1577, 1522, 1496, 1476, 1452, 1408, 1338, 1305, 1196, 1146, 1108, 1074, 1031, 958, 925, 857, 789, 726, 698, 680, 612, 572, 521

HRMS (EI): calculated for $[M+Na]^+$: 294.1101, found: 294.1099

1-Nitro-2-(((4-phenylbutan-2-yl)oxy)methyl)benzene 7b-oNBn



2-Nitrobenzyl bromide (3 mmol, 648 mg, 1 eq.) was dissolved in benzene (9 ml). Silveroxide (4.5 mmol, 972 mg, 1.5 eq.) and 4-phenyl-2-butanol (9 mmol, 1.36 ml, 3 eq.) were added. The mixture was stirred for 4 days and was then filtered through a pad of celite. After evaporation and purification by column chromatography, the product was obtained as a colorless oil (338 mg, 1.19 mmol, 40%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.16 (dd, J = 8.2, 1.4 Hz, 1H), 7.95 (dd, J = 7.8, 1.4 Hz, 1H), 7.74 (td, J = 7.6, 1.3 Hz, 1H), 7.59 – 7.47 (m, 1H), 7.38 (dd, J = 7.8, 6.7 Hz, 2H), 7.30 (d, J = 7.3 Hz, 3H), 5.05 (d, J = 14.9 Hz, 1H), 4.92 (d, J = 14.9 Hz, 1H), 3.73 (dq, J = 12.3, 6.2 Hz, 1H), 2.85 (td, J = 9.6, 6.3 Hz, 2H), 2.17 – 1.83 (m, 2H), 1.38 (d, J = 6.1 Hz, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 147.4, 142.3, 135.9, 133.7, 129.0, 128.5, 127.9, 125.9, 124.7, 75.6, 67.1, 38.5, 31.9, 19.7. (one signal missing due to overlap of signals)

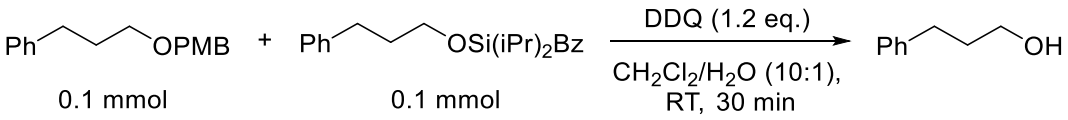
FT-IR (neat) [cm^{-1}]: 3062, 3026, 2968, 2925, 2862, 1608, 1577, 1523, 1496, 1452, 1342, 1304, 1194, 1134, 1095, 1068, 955, 928, 858, 789, 729, 698, 579

HRMS (EI): calculated for $[M+Na]^+$: 308.12571 , found: 308.12571

2.5 Orthogonality Towards Miscellaneous Protecting Groups

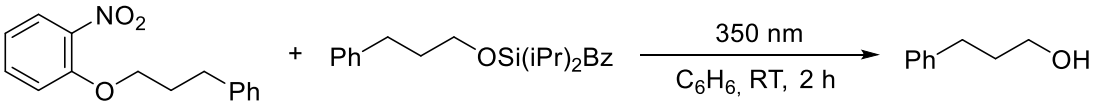
0.1 mmol of protected alcohol **7b-PG** were dissolved in 1 ml of an acetone/methanol mixture (7:1) conataining 0.1 mmol of biphenyl and 0.1 mmol of **8b**. The solution was irradiated with a 456 nm 45 W Kessil LED for 15 minutes and stirring was continued for 24 h at room temperature. Samples were measured before irradiation and after 24 hours of stirring.

Entry	7b-PG	Conversion **7b-PG**	Conversion **8b**
1	Me	0%	99%
2	Bn	0%	99%
3	PMB	1%	99%
4	MOM	1%	99%
5	THP	93%	99%
6	TBDMS	80%	99%
7	TIPS	34%	99%
8	TBDPS	1%	99%
9	Ac	1%	99%
10	Bz	0%	99%
11	Piv	1%	99%
12	oNB	2%	99%



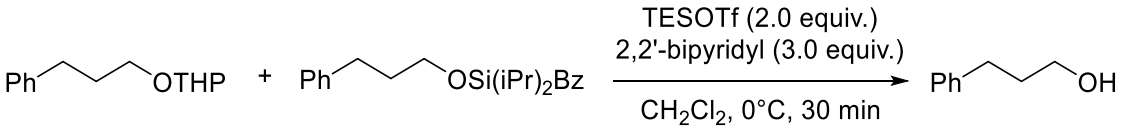
0.1 mmol 0.1 mmol

7a-PMB (0.1 mmol, 24.2 mg, 1eq.), biphenyl (0.1 mmol, 15.4 mg, 1 eq) as standard and **8a** (0.1 mmol, 35.4 mg, 1eq.) were dissolved in DCM (1 ml). Water (0.1 ml) and DDQ (0.12 mmol, 27.2 mg, 1.2 eq) were added and the resulting solution was stirred for 30 minutes. Samples have been measured before addition of DDQ and after 30 minutes of stirring. (Conversion(**7a-PMB**) = 99%; Conversion(**8a**) = 1%)[15]



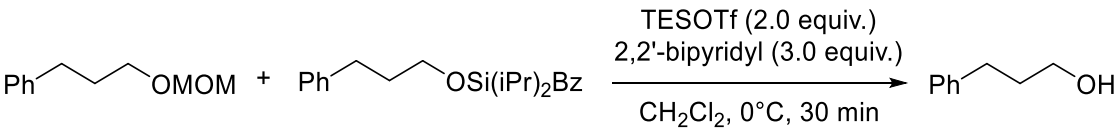
0.1 mmol 0.1 mmol

7a-oNBn (0.1 mmol, 27.1 mg, 1eq.), biphenyl (0.1 mmol, 15.4 mg, 1 eq) as standard and **8a** (0.1 mmol, 35.4 mg, 1eq.) were dissolved in benzene (4 ml). The solution was irradiated (350 nm) in a *Rayonet RPR-200* for 4 hours at room temperature. Samples have been measured before irradiation and after 6 hours. (Conversion(**7a-oNBn**) = 99%; Conversion(**8a**) = 2%)



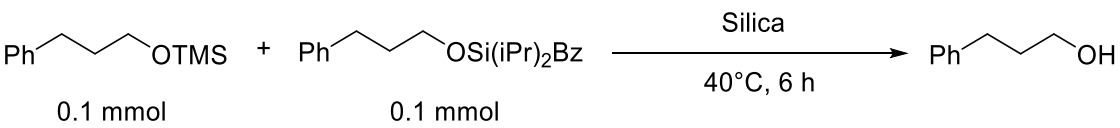
0.1 mmol 0.1 mmol

7a-THP (0.1 mmol, 27.1 mg, 1eq.), biphenyl (0.1 mmol, 15.4 mg, 1 eq) as standard and **8a** (0.1 mmol, 35.4 mg, 1 eq.) were dissolved in DCM (2 ml) at 0 °C. 2,2'-Bipyridine (0.3 mmol, 46.8 mg, 3 eq.) and TESOTf (0.2 mmol, 45 µl, 2 eq) were added. Samples have been measured before addition of 2,2'-bipyridine and TESOTf and after 6 hours of stirring. (Conversion(**7a-THP**) = 86%; Conversion(**8a**) = 1%)[16]



0.1 mmol 0.1 mmol

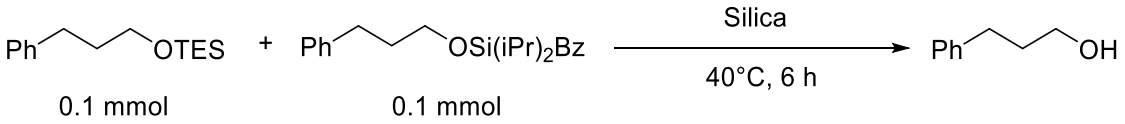
7a-MOM (0.1 mmol, 18.0 mg, 1eq.), biphenyl (0.1 mmol, 15.4 mg, 1 eq) as standard and **8a** (0.1 mmol, 35.4 mg, 1 eq.) were dissolved in DCM (2 ml) at 0 °C. 2,2'-Bipyridine (0.3 mmol, 46.8 mg, 3 eq.) and TESOTf (0.2 mmol, 45 µl, 2 eq) were added. Samples have been measured before addition of 2,2'-bipyridine and TESOTf and after 2 hours of stirring. (Conversion(**7a-MOM**) = 99%; Conversion(**8a**) = 0%)[16]



0.1 mmol 0.1 mmol

7a-TMS (0.1 mmol, 20.8 mg, 1eq.), biphenyl (0.1 mmol, 15.4 mg, 1 eq) as standard and **8a** (0.1 mmol, 35.4 mg, 1 eq.) were dissolved in Pentane (5 ml). Silica (1.00 g) was added and it was evaporated. After

the solvent was removed the flask was kept rotating in the water bath (40°C) of the rotavap at ambient pressure. Samples have been measured before addition of the silica and after 6 hours (Conversion(**7a-TMS**) = 91%; Conversion(**8a**) = 25%)



7a-TES (0.1 mmol, 25.0 mg, 1eq.), biphenyl (0.1 mmol, 15.4 mg, 1 eq) as standard and **8a** (0.1 mmol, 35.4 mg, 1 eq.) were dissolved in Pentane (5 ml). Silica (1.00 g) was added and it was evaporated. After the solvent was removed the flask was kept rotating in the water bath (50°C) of the rotavap at ambient pressure. Samples have been measured before addition of the silica and after 8 hours (Conversion(**7a-TMS**) = 55%; Conversion(**8a**) = 35%)

2.6 Scope

General procedure for the protection of alcohols (GP 1): To a solution of (chlorodiisopropylsilyl)(phenyl)methanone in DCM (appr. 0.2 M, 0.6 mmol, 1.2 eq.) the corresponding alcohol (0.5 mmol, 1 eq.) was added at room temperature. Imidazole (40.9 mg, 0.6 mmol, 1.2 eq.) was added subsequently and the resulting soution was stirred overnight. The mixture was washed with water, dried over Na_2SO_4 and evaporated. The resulting residue was purified by column chromatography.

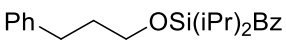
General procedure for the protection of alcohols (GP 2): To a solution of (chlorodiisopropylsilyl)(phenyl)methanone in DCM (appr. 0.2 M, 0.3 mmol, 1.5 eq.) the corresponding alcohol (0.2 mmol, 1 eq.) was added room temperature. Imidazole (40.9 mg, 0.24 mmol, 1.2 eq.) and silver trifluoromethanesulfonate (56.5 mg, 0.22 mmol, 1.1 eq.) were added subsequently and the resulting solution was stirred overnight. The mixture was filtered through celite, washed with water, dried over Na_2SO_4 and evaporated. The resulting residue was purified by column chromatography.

General procedure for the protection of alcohols (GP 3): A solution of (chlorodiisopropylsilyl)(phenyl)methanone in DCM (appr. 0.2 M, 0.6 mmol, 1.2 eq.) was evaporated at room temperature. DMF (3 ml) and the corresponding alcohol (0.5 mmol, 1 eq.) were added. Imidazole (40.9 mg, 0.6 mmol, 1.2 eq.) was added subsequently and it was stirred overnight. The mixture was washed with water, dried over Na_2SO_4 and evaporated. The resulting residue was purified by column chromatography.

General procedure for the deprotection of alcohols (GC yield, GP 4): 0.1 mmol of the protected alcohol was dissolved in 1 ml of a 0.1 M solution of biphenyl in the corresponding solvent. The solution was irradiated with a 456 nm 45 W Kessil LED for 15 minutes and stirring was continued for 24 h at room temperature. Samples were measured before irradiation and after 24 hours of stirring.

General procedure for the deprotection of alcohols (GP 5): 0.2 mmol of the protected alcohol was dissolved in 2 ml of an acetone/methanol mixture (7:1). The solution was irradiated with a 456 nm 45 W Kessil LED for 15 minutes and stirring was continued for 24 h at room temperature. DCM was added and the solution was washed with water. The solvent was evaporated and the alcohol was purified by column chromatography.

(Diisopropyl(3-phenylpropoxy)silyl)(phenyl)methanone 8a



Compound **8a** was prepared according to **GP1** using 3-phenylbutanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (176 mg, 0.496 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 99%).

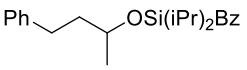
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.12 – 8.05 (m, 2H), 7.60 – 7.51 (m, 1H), 7.51 – 7.42 (m, 2H), 7.30 (dd, J = 7.8, 6.7 Hz, 2H), 7.21 (d, J = 7.2 Hz, 3H), 3.86 (t, J = 6.3 Hz, 2H), 2.77 (dd, J = 8.8, 6.8 Hz, 2H), 2.04 – 1.89 (m, 2H), 1.32 (hept, J = 7.3 Hz, 2H), 1.10 (d, J = 7.3 Hz, 6H), 1.07 (d, J = 7.3 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.2, 142.9, 142.0, 133.1, 128.7, 128.6, 128.5, 128.0, 126.0, 63.6, 34.5, 32.2, 17.6, 17.5, 12.4.

FT-IR (neat) [cm^{-1}]: 3061, 3027, 2944, 2866, 1608, 1590, 1575, 1525, 1496, 1447, 1386, 1364, 1341, 1304, 1213, 1173, 1094, 1040, 997, 965, 922, 881, 858, 785, 767, 743, 728, 691, 614, 505.

HRMS (ESI): calculated for $[M+Na]^+$: 377.1907, found: 377.1904.

(Diisopropyl((4-phenylbutan-2-yl)oxy)silyl)(phenyl)methanone 8b



Compound **8b** was prepared according to **GP1** using 4-phenyl-2-butanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (184 mg, 0.499 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 99%).

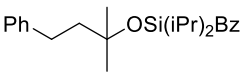
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.23 – 7.98 (m, 2H), 7.60 – 7.39 (m, 3H), 7.30 – 7.22 (m, 2H), 7.22 – 7.10 (m, 3H), 4.18 (h, J = 6.0 Hz, 1H), 2.78 – 2.63 (m, 2H), 1.99 – 1.77 (m, 2H), 1.37 – 1.23 (m, 5H), 1.08 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.3, 142.8, 142.3, 132.9, 128.5, 128.4, 128.3, 125.9, 77.6, 76.7, 70.0, 41.6, 31.9, 23.6, 17.8, 17.7, 17.62, 17.60, 13.0, 12.9.

FT-IR (neat) [cm^{-1}]: 3061, 3027, 2944, 2866, 1700, 1608, 1590, 1575, 1496, 1447, 1378, 1304, 1212, 1173, 1157, 1132, 1088, 1059, 1025, 996, 920, 882, 820, 767, 747, 691, 613, 592

HRMS (ESI): calculated for $[M+Na]^+$: 391.2064, found: 391.2058.

(Diisopropyl((2-methyl-4-phenylbutan-2-yl)oxy)silyl)(phenyl)methanone 8c



Compound **8c** was prepared according to **GP2** using 2-methyl-4-phenyl-2-butanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (150 mg, 0.392 mmol, 78%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 0%; acetone/methanol 4:1: 0%; methanol: 97%).

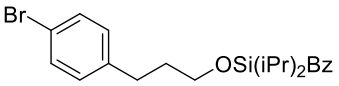
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.15 – 8.06 (m, 2H), 7.59 – 7.40 (m, 3H), 7.36 – 7.25 (m, 2H), 7.26 – 7.13 (m, 3H), 2.85 – 2.68 (m, 2H), 1.97 – 1.85 (m, 2H), 1.40 (s, 6H), 1.38 – 1.25 (m, 3H), 1.14 (d, J = 7.4 Hz, 6H), 1.12 (d, J = 7.4 Hz, 6H), .

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.7, 142.9, 142.7, 132.7, 128.5, 128.4, 128.1, 125.9, 75.6, 47.0, 31.1, 30.0, 18.0, 17.8, 14.0.

FT-IR (neat) [cm^{-1}]: 3062, 3027, 2945, 2866, 1610, 1590, 1575, 1496, 1462, 1384, 1366, 1303, 1235, 1209, 1172, 1128, 1073, 1047, 999, 921, 882, 802, 767, 747, 693, 612, 593, 511.

HRMS (ESI): calculated for $[M+Na]^+$: 405.2220, found: 405.2220.

((3-(4-Bromophenyl)propoxy)diisopropylsilyl)(phenyl)methanone 8d



Compound **8d** was prepared according to **GP1** using 3-(4-bromophenyl)propan-1-ol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (214 mg, 0.494 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 56%; acetone/methanol 4:1: 85%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.11 – 8.03 (m, 2H), 7.61 – 7.36 (m, 5H), 7.14 – 7.04 (m, 2H), 3.85 (t, J = 6.2 Hz, 2H), 2.79 – 2.68 (m, 2H), 2.01 – 1.87 (m, 2H), 1.34 (hept, J = 7.3 Hz, 2H), 1.11 (d, J = 7.3 Hz, 6H), 1.07 (d, J = 7.3 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.0, 142.9, 140.9, 133.1, 131.5, 130.3, 128.7, 128.0, 119.7, 63.4, 34.3, 31.6, 17.6, 17.5, 12.4.

FT-IR (neat) [cm^{-1}]: 3061, 2944, 2866, 1897, 1609, 1589, 1574, 1488, 1462, 1446, 1386, 1304, 1213, 1173, 1092, 1071, 1026, 1011, 967, 922, 881, 832, 808, 789, 766, 729, 690, 613, 597.

HRMS (ESI): calculated for $[M+Na]^+$: 457.0992, found: 457.0988.

((Icosyloxy)diisopropylsilyl)(phenyl)methanone 8e

Compound **8e** was prepared according to **GP1** using 1-icosanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (257 mg, 0.497 mmol, 99%).

Deprotection was carried out according to **GP5** (acetone/methanol 7:1: 99%).

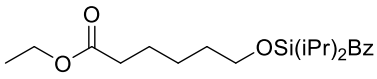
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.14 – 8.00 (m, 2H), 7.60 – 7.40 (m, 3H), 3.82 (t, J = 6.5 Hz, 2H), 1.75 – 1.56 (m, 2H), 1.26 (s, 36H), 1.09 (d, J = 7.4 Hz, 6H), 1.06 (d, J = 7.4 Hz, 6H), 0.92 – 0.83 (m, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.3, 143.0, 133.0, 128.6, 128.1, 64.5, 32.9, 32.1, 29.9, 29.8, 29.8, 29.6, 29.5, 26.0, 22.8, 17.6, 17.5, 14.3, 12.4.

FT-IR (neat) [cm^{-1}]: 2922, 2852, 2372, 2347, 1610, 1591, 1576, 1551, 1463, 1387, 1214, 1173, 1094, 997, 922, 882, 767, 721, 691, 671, 660, 615.

HRMS (ESI): calculated for $[M+H]^+$: 517.44353, found: 517.44351.

Ethyl 6-((benzoyldiisopropylsilyl)oxy)hexanoate 8f



Compound **8f** was prepared according to **GP1** using ethyl 6-hydroxyhexanoate as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 10:1) as a yellow oil (188 mg, 0.496 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 0%; acetone/methanol 4:1: 97%).

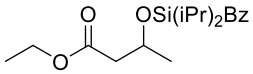
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.12 – 7.99 (m, 2H), 7.65 – 7.39 (m, 3H), 4.12 (q, J = 7.1 Hz, 2H), 3.82 (t, J = 6.4 Hz, 2H), 2.31 (t, J = 7.5 Hz, 2H), 1.79 – 1.56 (m, 4H), 1.54 – 1.37 (m, 2H), 1.37 – 1.17 (m, 5H), 1.08 (d, J = 7.4 Hz, 6H), 1.05 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.0, 173.7, 142.8, 133.0, 128.6, 127.9, 64.1, 60.2, 34.4, 32.4, 25.5, 24.8, 17.5, 17.4, 14.3, 12.3.

FT-IR (neat) [cm^{-1}]: 2943, 2867, 1736, 1609, 1590, 1575, 1463, 1447, 1372, 1302, 1212, 1173, 1159, 1092, 1034, 998, 921, 882, 799, 767, 724, 691, 614, 598.

HRMS (ESI): calculated for $[M+H]^+$: 401.2119, found: 401.2119.

Ethyl 3-((benzoyldiisopropylsilyl)oxy)butanoate 8g



Compound **8g** was prepared according to **GP1** using ethyl 3-hydroxybutyrate as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 10:1) as a yellow oil (172 mg, 0.491 mmol, 98%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 93%.)

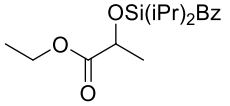
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.03 (dt, J = 6.9, 1.6 Hz, 2H), 7.65 – 7.31 (m, 3H), 4.57 (dt, J = 7.1, 5.8 Hz, 1H), 4.00 (qd, J = 7.1, 3.2 Hz, 2H), 2.63 (dd, J = 15.0, 7.1 Hz, 1H), 2.46 (dd, J = 15.0, 5.6 Hz, 1H), 1.28 (m, 5H), 1.17 (t, J = 7.2 Hz, 3H), 1.06 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.4, 170.8, 142.1, 132.5, 128.0, 127.7, 66.9, 60.1, 44.3, 23.6, 17.2, 17.0, 13.8, 12.3.

FT-IR (neat) [cm^{-1}]: 2947, 2868, 1736, 1609, 1590, 1575, 1463, 1447, 1378, 1302, 1245, 1212, 1184, 1138, 1081, 1030, 1009, 997, 934, 924 882, 853, 767, 735, 720, 691, 614 594.

HRMS (ESI): calculated for $[M+Na]^+$: 373.1806, found: 373.1806.

Ethyl 2-((benzoyldiisopropylsilyl)oxy)propanoate 8h



Compound **8h** was prepared according to **GP1** using ethyl lactate as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 10:1) as a yellow oil (147 mg, 0.437 mmol, 87%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 95%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.06 (dt, J = 6.9, 1.6 Hz, 2H), 7.59 – 7.34 (m, 3H), 4.59 (q, J = 6.7 Hz, 1H), 4.11 (m, 2H), 1.49 (d, J = 6.8 Hz, 3H), 1.39 – 1.25 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H), 1.06 (d, J = 7.5 Hz, 6H), 1.03 (d, J = 7.5 Hz, 6H).

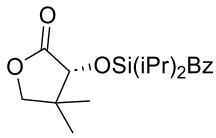
^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.1, 173.5, 142.4, 132.9, 128.5, 128.0, 69.4, 60.9, 21.5, 17.4,

17.2, 14.1, 12.72.

FT-IR (neat) [cm^{-1}]: 2947, 2895, 2868, 1750, 1742, 1609, 1590, 1575, 1463, 1447, 1372, 1304, 1274, 1212, 1172, 1136, 1106, 1061, 1020, 1004, 976, 921, 882, 860, 767, 745, 691, 614.

HRMS (ESI): calculated for $[M+Na]^+$: 359.1649, found: 359.1649.

(R)-3-((Benzoyldiisopropylsilyl)oxy)-5,5-dimethyldihydrofuran-2(3H)-one 8i



Compound **8i** was prepared according to **GP1** using D-pantolactone as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 3:1) as a yellow oil (173 mg, 0.497 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 25%; methanol: 54%; methanol (40 °C): 92%)).

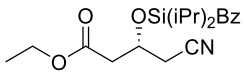
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.99 – 7.89 (m, 2H), 7.58 – 7.40 (m, 3H), 4.58 (s, 1H), 4.03 – 3.89 (m, 2H), 1.45 (hept, J = 7.4 Hz, 2H), 1.21 (s, 3H), 1.16 – 1.04 (m, 15H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.0, 175.4, 142.3, 133.1, 128.6, 127.9, 77.7, 75.8, 41.6, 23.1, 19.5, 17.6, 17.52, 17.49, 17.4, 13.4, 13.3.

FT-IR (neat) [cm^{-1}]: 3063, 2949, 2895, 2968, 1794, 1770, 1609, 1591, 1575, 1467, 1448, 1386, 1368, 1350, 1298, 1270, 1203, 1172, 1125, 1073, 1010, 993, 940, 920, 882, 849, 845, 806, 767, 690, 638, 615, 556.

HRMS (ESI): calculated for $[M+Na]^+$: 371.1649, found: 371.1649.

Ethyl (R)-3-((benzoyldiisopropylsilyl)oxy)-4-cyanobutanoate 8j



Compound **8j** was prepared according to **GP1** using ethyl-(R)-(-)-4-cyano-3-hydroxybutyrate as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 2:1) as a yellow oil (187 mg, 0.499 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 0%; acetone/methanol 4:1: 0%; methanol: 0%; methanol (70 °C): 84%).

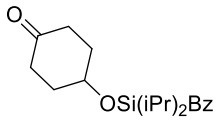
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 – 7.86 (m, 2H), 7.65 – 7.39 (m, 3H), 4.73 (dtd, J = 6.9, 5.5, 4.2 Hz, 1H), 4.07 (qt, J = 7.1, 3.7 Hz, 2H), 3.00 – 2.65 (m, 4H), 1.35 (m 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.13 – 1.04 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.2, 170.2, 142.1, 133.4, 128.9, 127.8, 117.1, 66.5, 61.0, 41.2, 26.2, 17.6, 17.5, 17.4, 14.2, 13.4, 13.3.

FT-IR (neat) [cm^{-1}]: 2946, 2868, 2251, 1731, 1609, 1590, 1574, 1463, 1446, 1380, 1315, 1269, 1212, 1173, 1101, 1025, 1000, 970, 921, 881, 845, 768, 737, 690, 613.

HRMS (ESI): calculated for $[M+H]^+$: 376.19386, found 376.19384.

4-((Benzoyldiisopropylsilyl)oxy)cyclohexan-1-one 8k



Compound **8k** was prepared according to **GP1** using 4-hydroxycyclohexanone as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow oil (158 mg, 0.474 mmol, 95%).

Deprotection was carried out according to **GP4.** (acetone/methanol 7:1: 62%; acetone/methanol 4:1: 64%; methanol: 61%)

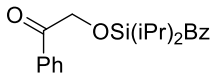
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.07 – 7.93 (m, 2H), 7.60 – 7.40 (m, 3H), 4.45 (tt, J = 5.6, 2.9 Hz, 1H), 2.68 (ddd, J = 15.5, 10.4, 5.8 Hz, 2H), 2.30 (dt, J = 14.7, 5.9 Hz, 2H), 2.21 – 2.06 (m, 2H), 2.06 – 1.92 (m, 2H), 1.47 – 1.20 (m, 3H), 1.11 (d, J = 7.4 Hz, 6H), 1.09 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.7, 211.0, 142.6, 133.2, 128.7, 127.8, 68.1, 37.1, 34.2, 17.7, 17.6, 13.1.

FT-IR (neat) [cm^{-1}]: 2945, 2867, 2372, 2347, 1716, 1609, 1590, 1575, 1551, 1462, 1446, 1364, 1306, 1245, 1214, 1172, 1096, 1040, 1011, 982, 935, 882, 849, 821, 768, 750, 690, 672, 661, 616, 566**.**

HRMS (ESI): calculated for $[M+Na]^+$: 355.16999, found: 355.16973.

2-((Benzoyldiisopropylsilyl)oxy)-1-phenylethan-1-one 8l



Compound **8l** was prepared according to **GP1** using 2-hydroxyacetophenone as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 10:1) as a yellow oil (128 mg, 0.361 mmol, 72%).

Deprotection was carried out according to **GP4.** (acetone/methanol 7:1: 35%; methanol: 47%)

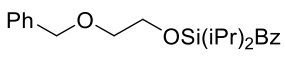
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.18 – 8.04 (m, 2H), 7.97 – 7.86 (m, 2H), 7.69 – 7.37 (m, 6H), 5.20 (s, 2H), 1.40 (hept, J = 7.4 Hz, 2H), 1.13 (d, J = 7.4 Hz, 6H), 1.08 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.2, 196.4, 142.5, 134.6, 133.7, 133.1, 128.8, 128.7, 128.0, 127.8, 68.0, 17.6, 12.8.

FT-IR (neat) [cm^{-1}]: 3062, 2925, 2866, 1699, 1607, 1589, 1574, 1463, 1447, 1386, 1368, 1286, 1214, 1156, 1096, 1072, 976, 921, 882, 825, 768, 753, 688, 613.

HRMS (ESI): calculated for $[M+Na]^+$: 377.1543, found: 377.1543.

((2-(Benzyloxy)ethoxy)diisopropylsilyl)(phenyl)methanone 8m



Compound **8m** was prepared according to **GP1** using 2-(benzyloxy)ethanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 20:1) as a yellow oil (175 mg, 0.472 mmol, 94%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 90%; acetone/methanol 4:1: 92%).

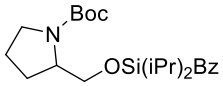
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.24 – 8.00 (m, 2H), 7.61 – 7.48 (m, 1H), 7.48 – 7.27 (m, 7H), 4.57 (s, 2H), 4.03 (dd, J = 5.6, 4.5 Hz, 2H), 3.67 (dd, J = 5.6, 4.5 Hz, 2H), 1.34 (hept, J = 7.3 Hz, 2H), 1.11 (d, J = 7.4 Hz, 6H), 1.08 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.8, 142.8, 138.4, 133.0, 128.6, 128.5, 128.1, 127.7, 73.4, 71.5, 63.9, 17.4, 12.3.

FT-IR (neat) [cm^{-1}]: 3062, 3031, 2943, 2866, 1608, 1589, 1574, 1496, 1447, 1384, 1359, 1305, 1245, 1213, 1173, 1134, 1092, 1042, 1026, 997, 956, 881, 845, 801, 768, 734, 691, 613, 598

HRMS (ESI): calculated for $[M+Na]^+$: 393.1856, found 393.1856.

tert-Butyl 2-(((benzoyldiisopropylsilyl)oxy)methyl)pyrrolidine-1-carboxylate 8n



Compound **8n** was prepared according to **GP1** using N-(*tert*-butoxycarbonyl)-D-prolinol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow oil (209 mg, 0.499 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 99%).

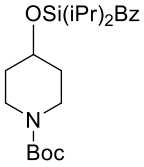
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.06 – 8.00 (m, 2H), 7.56 – 7.50 (m, 1H), 7.50 – 7.44 (m, 2H), 4.09 – 3.68 (m, 3H), 3.40 (m, 2H), 2.22 – 1.75 (m, 4H), 1.43 (m, 9H), 1.32 (hept, J = 7.5 Hz, 2H), 1.11 – 1.03 (m, 12H).

^{13}C-NMR (151 MHz, $CDCl_3$): δ = 234.9, 234.6, 154.7, 154.6, 142.9, 142.8, 133.1, 133.0, 128.7, 128.6, 128.1, 128.0, 79.5, 79.2, 64.9, 64.4, 58.4, 47.4, 46.9, 28.7, 28.5, 27.8, 24.2, 23.1, 17.53, 17.48, 12.3 (Signal split-up due to rotamers).

FT-IR (neat) [cm^{-1}]: 3062, 2945, 2867, 1692, 1609, 1590, 1575, 1461, 1447, 1390, 1365, 1342, 1307, 1285, 1248, 1214, 1168, 1095, 1028, 997, 937, 910, 882, 829, 801, 768, 731, 691, 614, 551, 533.

HRMS (ESI): calculated for $[M+Na]^+$: 442.23841, found 442.23740

tert-Butyl 4-((benzoyldiisopropylsilyl)oxy)piperidine-1-carboxylate 8o



Compound **8o** was prepared according to **GP1** using 1-(*tert*-butoxycarbonyl)-4-hydroxypiperidine as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow oil (204 mg, 0.485 mmol, 97%).

Deprotection was carried out according to **GP4** (acetone/methanol 4:1: 0%; methanol: 70%).

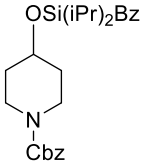
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.07 – 7.98 (m, 2H), 7.60 – 7.40 (m, 3H), 4.15 (tt, J = 7.6, 3.6 Hz, 1H), 3.73 (ddd, J = 13.5, 7.1, 3.9 Hz, 2H), 3.21 (ddd, J = 13.5, 8.3, 3.6 Hz, 2H), 1.82 (m 2H), 1.63 (m, 2H), 1.46 (s, 9H), 1.38 – 1.24 (m, 2H), 1.12 – 0.96 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.0, 155.0, 142.6, 133.1, 128.6, 128.0, 79.6, 69.4, 40.9, 34.5, 28.6, 17.64, 17.55, 12.9.

FT-IR (neat) [cm^{-1}]: 2945, 2866, 1693, 1610, 1589, 1574, 1458, 1421, 1365, 1317, 1273, 1234, 1171, 1093, 1041, 999, 933, 877, 804, 768, 690, 615.

HRMS (ESI): calculated for $[M+Na]^+$: 442.23841, found 442.23804.

Benzyl 4-((benzoyldiisopropylsilyl)oxy)piperidine-1-carboxylate 8p



Compound **8p** was prepared according to **GP1** using 1-(benzyloxycarbonyl)-4-hydroxypiperidine as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow oil (206 mg, 0.454 mmol, 91%).

Deprotection was carried out according to **GP5** (methanol: 99%).

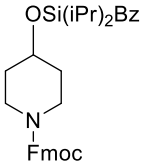
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.06 – 7.97 (m, 2H), 7.60 – 7.41 (m, 3H), 7.40 – 7.28 (m, 5H), 5.13 (d, J = 1.0 Hz, 2H), 4.19 (tt, J = 7.2, 3.5 Hz, 1H), 3.79 (ddd, J = 12.1, 7.4, 3.9 Hz, 2H), 3.34 (ddd, J = 13.6, 7.9, 3.8 Hz, 2H), 1.83 (s, 2H), 1.66 (s, 3H), 1.32 (hept, J = 7.4 Hz, 2H), 1.08 (t, J = 7.4 Hz, 6H), .1.06 (t, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.9, 155.4, 142.6, 137.0, 133.1, 128.6, 128.1, 128.00, 127.97, 69.0, 67.2, 41.0, 34.4, 17.65, 17.55, 12.9 (one signal missing due to overlap of signals).

FT-IR (neat) [cm^{-1}]: 2941 ,2927, 2866, 1699, 1610, 1589, 1574, 1429, 1365, 1315, 1273, 1225, 1173, 1090, 1041, 999, 924, 881, 845, 806, 766, 737, 692, 613.

HRMS (ESI): calculated for $[M+Na]^+$: 476.22276, found: 476.22294.

(9H-Fluoren-9-yl)methyl 4-((benzoyldiisopropylsilyl)oxy)piperidine-1-carboxylate 8q



Compound **8q** was prepared according to **GP1** using (9H-fluoren-9-yl)methyl 4-hydroxypiperidine-1-carboxylate as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow oil (240mg, 0.443 mmol, 89%).

Deprotection was carried out according to **GP5.** (methanol: 99%)

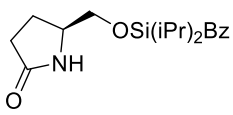
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.08 – 7.99 (m, 2H), 7.81 – 7.73 (m, 2H), 7.63 – 7.53 (m, 3H), 7.52 – 7.44 (m, 2H), 7.44 – 7.36 (m, 2H), 7.32 (td, J = 7.4, 1.2 Hz, 2H), 5.29 (d, J = 0.8 Hz, 1H), 4.44 (d, J = 6.8 Hz, 2H), 4.31 – 4.13 (m, 2H), 3.76 (s, 2H), 3.32 (ddd, J = 12.2, 7.7, 3.6 Hz, 2H), 1.82 (s, 2H), 1.65 (s, 3H), 1.42 – 1.25 (m, 2H), 1.33 (hept, J = 7.1 Hz, 2H), 1.10 (d, J = 7.1 Hz, 6H), 1.08 (d, J = 7.1 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.9, 155.3, 144.2, 142.6, 141.5, 133.2, 128.6, 128.0, 127.8, 127.2, 125.1, 120.1, 69.0, 67.4, 47.5, 41.0, 34.3, 17.7, 17.6, 13.0.

FT-IR (neat) [cm^{-1}]: 3064, 2945, 2866, 1697, 1610, 1574, 1446, 1362, 1315, 1271, 1223, 1173, 1088, 1039, 930, 881, 847, 804, 760, 739, 690, 617.

HRMS (ESI): calculated for $[M+Na]^+$: 564.25406, found 564.25367.

(S)-5-(((Benzoyldiisopropylsilyl)oxy)methyl)pyrrolidin-2-one 8r



Compound **8r** was prepared according to **GP1** using (S)-(+)-5-hydroxymethyl-2-pyrrolidinone as the alcohol. The product was obtained via column chromatography (DCM/MeOH 30:1) as a yellow oil (166 mg, 0.497 mmol, 99%).

Deprotection was carried out according to **GP5.** (methanol: 22.2 mg, 0.193 mmol, 96%)

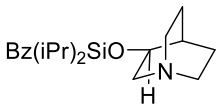
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.91 (dd, J = 8.1, 1.6 Hz, 2H), 7.57 – 7.40 (m, 3H), 6.53 (s, 1H), 3.85 (m, 2H), 3.77 – 3.64 (m, 1H), 2.42 – 2.27 (m, 2H), 2.27 – 2.11 (m, 1H), 1.92 – 1.74 (m, 1H), 1.29 (hept, J = 7.4 Hz, 2H), 1.06 (d, J = 7.4 Hz, 6H), 1.02 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.3, 178.4, 142.3, 133.3, 128.8, 127.6, 77.6, 76.7, 67.6, 55.7, 29.9, 22.8, 17.55, 17.53, 17.39, 17.37, 12.6, 12.5.

FT-IR (neat) [cm^{-1}]: 3209, 2944, 2892, 2866, 1693, 1608, 1589, 1575, 1462, 1446, 1423, 1387, 1368, 1303 1216, 1173, 1110 1073, 1027, 997, 921, 882, 865, 768, 730, 691, 616.

HRMS (ESI): calculated for $[M+Na]^+$: 356.1652, found: 356.1663.

(Diisopropyl(((1R,3S,4R)-quinuclidin-3-yl)oxy)silyl)(phenyl)methanone 8s



Compound **8s** was prepared according to **GP3** using (±)-3-quinuclidinol as the alcohol. The product was obtained via column chromatography (toluene/MeOH 10:1) as a yellow oil (140 mg, 0.405 mmol, 81%).

Deprotection was carried out according to **GP4** (methanol (70 °C): 0%).

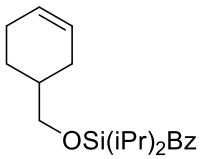
^{1}H-NMR (300 MHz, $CDCl_3$): δ =8.04 (d, J = 7.1 Hz, 2H), 7.61 – 7.40 (m, 3H), 4.04 (dt, J = 7.7, 3.3 Hz, 1H), 3.16 (ddd, J = 14.0, 8.0, 2.3 Hz, 1H), 3.05 – 2.90 (m, 1H), 2.76 (tddd, J = 25.5, 10.7, 5.0, 2.3 Hz, 4H), 2.19 – 1.98 (m, 1H), 1.91 (q, J = 3.3 Hz, 1H), 1.66 (ddt, J = 14.0, 9.2, 4.4 Hz, 1H), 1.49 – 1.22 (m, 4H), 1.12 – 0.96 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ =235.1, 142.7, 133.1, 128.6, 128.0, 70.5, 59.2, 47.7, 46.5, 28.7, 24.8, 19.3, 17.62, 17.60, 17.5, 17.4, 12.8.

FT-IR (neat) [cm^{-1}]: 3061, 2940, 2805, 1608, 1590, 1574, 1462, 1447, 1383, 1321, 1214 1173, 1112, 1079, 1051, 996, 986, 950, 921, 881, 805, 787, 766, 689, 611, 576.

HRMS (ESI): calculated for $[M+H]^+$: 346.2197, found: 346.2197.

((Cyclohex-3-en-1-ylmethoxy)diisopropylsilyl)(phenyl)methanone 8t



Compound **8t** was prepared according to **GP1** using 3-cyclohexene-1-methanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (145 mg, 0.439 mmol, 88%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 82%; acetone/methanol 4:1: 99%).

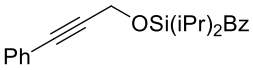
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.17 – 7.98 (m, 2H), 7.62 – 7.40 (m, 3H), 5.70 (d, J = 2.4 Hz, 2H), 3.73 (d, J = 6.0 Hz, 2H), 2.29 – 2.01 (m, 3H), 2.01 – 1.73 (m, 3H), 1.49 – 1.23 (m, 3H), 1.10 (d, J = 7.3 Hz, 6H), 1.06 (d, J = 7.3 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.2, 142.9, 133.1, 128.7, 128.1, 127.2, 126.2, 69.1, 36.6, 28.3, 25.5, 24.9, 17.6, 17.5, 12.4, 12.4.

FT-IR (neat) [cm^{-1}]: 3023, 2922, 2866, 1651, 1609, 1590, 1575, 1462, 1447, 1386, 1304, 1214, 1173, 1117, 1068, 997, 922, 882, 816, 789, 767, 732, 691, 656, 616.

HRMS (ESI): calculated for $[M+H]^+$: 331.20878, found 331.20860.

(Diisopropyl((3-phenylprop-2-yn-1-yl)oxy)silyl)(phenyl)methanone 8u



Compound **8u** was prepared according to **GP1** using 3-phenyl-2-propyn-1-ol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (159 mg, 0.454 mmol, 91%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 44%; methanol: 76%; methanol (40 °C): 69%).

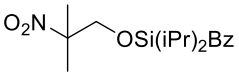
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.17 – 8.05 (m, 2H), 7.59 – 7.41 (m, 3H), 7.36 – 7.27 (m, 5H), 4.75 (s, 2H), 1.42 (hept, J = 14.2 Hz, 2H), 1.14 (dd, J = 13.8, 7.4 Hz, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.7, 143.1, 133.6, 132.1, 129.1, 129.0, 128.8, 128.6, 123.0, 87.4, 86.6, 53.8, 18.0, 17.9, 12.9.

FT-IR (neat) [cm^{-1}]: 2925, 2866, 1699, 1663, 1608, 1589, 1574, 1490, 1463, 1446, 1370, 1314, 1284, 1259, 1214, 1173, 1069, 1026, 998, 966, 920, 882, 768, 756, 713, 689, 616.

HRMS (ESI): calculated for $[M+Na]^+$: 373.1594, found 373.1594.

(Diisopropyl(2-methyl-2-nitropropoxy)silyl)(phenyl)methanone 8v



Compound **8v** was prepared according to **GP1** using 2-Methyl-2-nitro-1-propanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 10:1) as a yellow oil (167 mg, 0.496 mmol, 99%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 31%; Methanol: 75%; Methanol (40 °C): 90%).

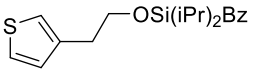
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 – 7.86 (m, 2H), 7.63 – 7.41 (m, 3H), 4.16 (s, 2H), 1.63 (s, 6H), 1.39 – 1.23 (m, 2H), 1.07 (d, J = 7.4 Hz, 6H), 1.04 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.2, 142.5, 133.4, 128.9, 127.9, 88.6, 70.3, 22.8, 17.5, 17.3, 12.6.

FT-IR (neat) [cm^{-1}]: 3064, 2946, 2868, 1608, 1590, 1575, 1542, 1463, 1447, 1405, 1371, 1348, 1295, 1215, 1172, 1100, 1025, 997, 922, 881, 864, 831, 799, 768, 728, 690, 616, 561

HRMS (ESI): calculated for $[M+Na]^+$: 360.1602, found: 360.1595.

(Diisopropyl(2-(thiophen-2-yl)ethoxy)silyl)(phenyl)methanone 5w



Compound **5w** was prepared according to **GP1** using 3-thiopheneethanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow oil (166 mg, 0.478 mmol, 96%).

Deprotection was carried out according to **GP4** (acetone/methanol 7:1: 78%; acetone/methanol 4:1: 88%; Methanol: 99%).

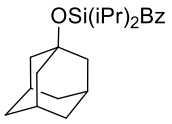
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.62 – 7.51 (m, 1H), 7.50 – 7.42 (m, 2H), 7.35 – 7.26 (m, 1H), 7.11 – 6.99 (m, 2H), 4.07 (t, J = 6.7 Hz, 2H), 3.02 (t, J = 6.7 Hz, 2H), 1.34 (hept, J = 7.3 Hz, 2H), 1.11 (d, J = 7.3 Hz, 6H), 1.08 (d, J = 7.3 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.0, 142.8, 139.1, 133.1, 128.7, 128.7, 128.0, 125.4, 121.7, 64.8, 33.8, 17.6, 17.4, 12.3.

FT-IR (neat) [cm^{-1}]: 2943, 2866, 1610, 1574, 1462, 1385, 1306, 1213, 1173, 1090, 1041, 997, 922, 881, 839, 768, 688, 613.

HRMS (ESI): calculated for $[M+H]^+$: 347.14955, found 347.14954.

((((3s,5s,7s)-Adamantan-1-yl)oxy)diisopropylsilyl)(phenyl)methanone 8x



Compound **8x** was prepared according to **GP2** using 1-adamantanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (135 mg, 0.365 mmol, 73%).

Deprotection was carried out according to **GP4** (Acetone/Methanol 7:1: 84%; Acetone/Methanol 4:1: 99%).

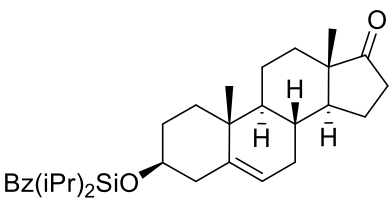
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.15 (dt, J = 6.8, 1.6 Hz, 2H), 7.56 – 7.38 (m, 3H), 2.17 – 2.09 (m, 3H), 1.87 (d, J = 3.2 Hz, 6H), 1.69 – 1.52 (m, 6H), 1.30 (hept, J = 7.3 Hz, 2H), 1.08 (d, J = 7.3 Hz, 6H), 1.05 (d, J = 7.3 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.7, 142.9, 132.6, 128.3, 128.2, 73.0, 46.2, 36.2, 31.2, 31.1, 17.7, 17.7, 13.8.

FT-IR (neat) [cm^{-1}]: 2910, 2854, 1643, 1612, 1591, 1574, 1452, 1354, 1302, 1211, 1169, 1120, 1090, 1020, 962, 924, 881, 825, 766, 690, 615, 507.

HRMS (ESI): calculated for $[M+Na]^+$: 393.22203, found 393.22182.

(3S,8R,9S,10R,13S,14S)-3-((Benzoyldiisopropylsilyl)oxy)-10,13-dimethyl-1,2,3,4,7,8,9,10,11,12,13,14,15,16-tetradecahydro-17H-cyclopenta[a]phenanthren-17-one 8y



Compound **8y** was prepared according to **GP1** using dehydroepiandrosterone as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a yellow solid (250 mg, 0.493 mmol, 99%).

Melting point: 144-146 °C.

Deprotection was carried out according to **GP5** (Acetone/Methanol 7:1: 99%).

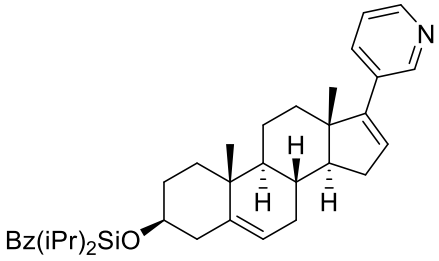
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.14 – 8.05 (m, 2H), 7.59 – 7.40 (m, 3H), 5.38 – 5.30 (m, 1H), 3.76 (tt, J = 10.5, 5.1 Hz, 1H), 2.53 – 2.28 (m, 3H), 2.19 – 2.00 (m, 2H), 2.00 – 1.78 (m, 4H), 1.76 – 1.39 (m, 6H), 1.39 – 1.19 (m, 5H), 1.12 – 1.01 (m, 15H), 0.88 (s, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.2, 221.2, 142.8, 141.3, 132.9, 128.5, 128.2, 121.1, 73.9, 51.9, 50.3, 47.7, 42.9, 37.3, 36.8, 36.0, 32.3, 31.6, 31.5, 30.9, 22.0, 20.5, 19.6, 17.6, 17.5, 17.5, 13.7, 12.7.

FT-IR (neat) [cm^{-1}]: 3061, 2928, 2865, 1739, 1644, 1609, 1590, 1574, 1463, 1408, 1372, 1304, 1267, 1245, 1215, 1173, 1087, 1058, 1031, 999, 959, 931, 884, 863, 846, 832, 799, 768, 736, 691, 633, 615.

HRMS (ESI): calculated for $[M+Na]^+$: 529.31084, found 529.31048.

((((3S,8R,9S,10R,13S,14S)-10,13-Dimethyl-17-(pyridin-3-yl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)diisopropylsilyl)(phenyl)methanone 8z



Compound **8z** was prepared according to **GP1** using abiraterone as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 2:1) as a yellow oil (261 mg, 0.460 mmol, 92%).

Melting point: 98-100°C.

Deprotection was carried out according to **GP5** (acetone/methanol 7:1: 0%)

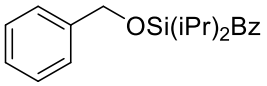
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.61 (d, J = 1.4 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 8.16 – 8.02 (m, 2H), 7.63 (dt, J = 7.9, 2.0 Hz, 1H), 7.58 – 7.40 (m, 3H), 7.20 (ddd, J = 7.9, 4.8, 0.9 Hz, 1H), 5.98 (dd, J = 3.3, 1.8 Hz, 1H), 5.45 – 5.22 (m, 1H), 3.76 (tt, J = 10.4, 4.8 Hz, 1H), 3.46 (q, J = 7.0 Hz, 1H), 2.46 – 2.18 (m, 3H), 2.13 – 1.98 (m, 3H), 1.94 – 1.39 (m, 9H), 1.41 – 1.21 (m, 3H), 1.20 (t, J = 7.0 Hz, 1H), 1.12 – 1.01 (m, 18H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.2, 151.8, 148.0, 147.9, 142.8, 141.4, 133.8, 133.0, 132.9, 129.3, 128.5, 128.2, 123.1, 121.5, 74.0, 66.0, 57.6, 50.4, 47.4, 43.0, 37.3, 36.8, 35.3, 32.3, 31.9, 31.6, 30.5, 21.0, 19.5, 17.6, 17.54, 17.53, 16.7, 15.4, 12.7.

FT-IR (neat) [cm^{-1}]: 2930, 2864, 1608, 1590, 1574, 1462, 1409, 1372, 1302, 1213, 1173, 1085, 1023, 997, 961, 922, 883, 862, 842, 827, 795, 768, 738, 710, 691, 648, 616.

HRMS (ESI): calculated for $[M+H]^+$: 568.36053, found 568.36079.

((Benzyloxy)diisopropylsilyl)(phenyl)methanone 8ae



Compound **8ae** was prepared according to **GP1** using benzyl alcohol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (163 mg, 0.498 mmol, 99%).

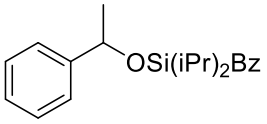
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.11 – 8.01 (m, 2H), 7.58 – 7.48 (m, 1H), 7.48 – 7.23 (m, 7H), 4.96 (s, 2H), 1.38 (hept, J = 7.4 Hz, 2H), 1.13 (d, J = 7.4 Hz, 6H), 1.10 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.91, 142.86, 140.52, 133.15, 128.74, 128.49, 128.03, 127.39, 126.34, 66.17, 17.69, 17.53, 12.55.

FT-IR (neat) [cm^{-1}]: 3063, 3032, 2945, 2866, 1608, 1589, 1575, 1526, 1496, 1461, 1379, 1305, 1213, 1173, 1092, 1066, 1027, 997, 921, 882, 809, 768, 731, 692, 617, 577.

HRMS (ESI): calculated for $[M+Na]^+$: 349.15943, found 349.15909.

(Diisopropyl(1-phenylethoxy)silyl)(phenyl)methanone 8af



Compound **8af** was prepared according to **GP1** using (+/-)-1-phenylethanol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (164 mg, 0.481 mmol, 96%).

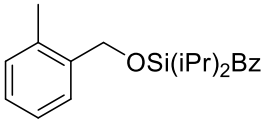
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.01 – 7.92 (m, 2H), 7.48 – 7.37 (m, 1H), 7.36 – 7.13 (m, 7H), 5.03 (q, J = 6.3 Hz, 1H), 1.46 (d, J = 6.3 Hz, 3H), 1.20 (hept, J = 7.3 Hz, 2H), 1.02 – 0.83 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.1, 146.0, 142.8, 132.9, 128.5, 128.4, 128.2, 127.4, 125.6, 72.8, 27.6, 17.6, 17.5, 17.3, 12.8, 12.7.

FT-IR (neat) [cm^{-1}]: 3063, 3031, 2945, 2891, 2867, 1608, 1590, 1575, 1493, 1462, 1447, 1385, 1369, 1303, 1283, 1211, 1173, 1086, 1032, 999, 959, 922, 882, 789, 767, 692, 616, 587, 541.

HRMS (ESI): calculated for $[M+Na]^+$: 363.17508, found 363.17490.

(Diisopropyl((2-methylbenzyl)oxy)silyl)(phenyl)methanone 8ag



Compound **8ag** was prepared according to **GP1** using 2-methylbenzyl alcohol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (167 mg, 0.490 mmol, 98%).

Deprotection was carried out according to **GP4** (Acetone/Methanol 7:1: 99%).

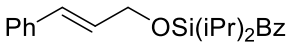
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.11 – 8.02 (m, 2H), 7.58 – 7.37 (m, 4H), 7.22 (ddd, J = 14.2, 8.5, 4.7 Hz, 3H), 4.94 (s, 2H), 2.30 (s, 3H), 1.42 (hept, J = 7.4 Hz, 2H), 1.15 (d, J = 7.4 Hz, 6H), 1.12 (d, J = 7.4 Hz, 6H).

z**^{13}C-NMR (76 MHz, $CDCl_3$):** δ = 234.9, 142.9, 138.3, 135.3, 133.1, 130.1, 128.7, 128.0, 127.4, 126.8, 126.0, 64.5, 18.7, 17.7, 17.6, 12.6.

FT-IR (neat) [cm^{-1}]: 3065, 3021, 2945, 2889, 2866, 1608, 1590, 1575, 1462, 1446, 1386, 1215, 1173, 1121, 1068, 998, 922, 882, 812, 767, 742, 690, 618, 591, 546, 518.

HRMS (ESI): calculated for $[M+Na]^+$: 363.17508, found 363.17481.

((Cinnamyloxy)diisopropylsilyl)(phenyl)methanone 8ah



Compound **8ah** was prepared according to **GP1** using cinnamyl alcohol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 2:1) as a yellow oil (161 mg, 0.456 mmol, 91%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.10 – 8.01 (m, 2H), 7.57 – 7.38 (m, 3H), 7.38 – 7.15 (m, 5H), 6.63 (dt, J = 15.8, 1.8 Hz, 1H), 6.30 (dt, J = 15.8, 5.1 Hz, 1H), 4.52 (dd, J = 5.1, 1.7 Hz, 2H), 1.34 (hept, J = 7.4 Hz, 2H), 1.11 (d, J = 7.4 Hz, 6H), 1.07 (d, J = 7.4 Hz, 6H).

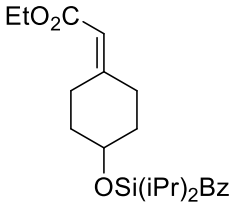
^{13}C-NMR (76 MHz, $CDCl_3$): δ = 234.9, 142.8, 137.0, 133.2, 130.4, 128.74, 128.71, 128.2, 128.1, 127.7, 126.6, 77.6, 76.7, 65.1, 17.7, 17.5, 12.5.

FT-IR (neat) [cm^{-1}]: 3060, 3026, 2945, 2866, 1608, 1589, 1574, 1495, 1462, 1447, 1380, 1303, 1213, 1173, 1114, 1071, 1054, 998, 964, 922, 882, 851, 767, 733, 690, 613, 519.

HRMS (ESI): calculated for $[M+Na]^+$: 375.17508, found 375.17440.

2.7 Additional Transformations

Ethyl 2-(4-((benzoyldiisopropylsilyl)oxy)cyclohexylidene)acetate 8aa (1390/1401)



8k (66.6 mg, 0.2 mmol, 1 eq.) and ethyl triphenylphosphoranylideneacetate (83.5 mg, 0.4 mmol, 2 eq.) were dissolved in toluene (2 ml) and refluxed for 24 hours. The solvent was evaporated and the residue was purified by column chromatography (pentane/Et_2O 10:1) to give **8aa** as a yellow liquid (71%, 0.142 mmol, 57.2 mg).[17]

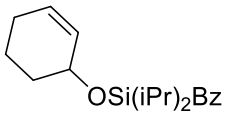
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.12 – 7.98 (m, 2H), 7.59 – 7.36 (m, 3H), 5.75 – 5.59 (m, 1H), 4.23 (tt, J = 6.9, 3.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.16 (ddd, J = 13.5, 8.2, 4.7 Hz, 1H), 2.78 (dddd, J = 14.1, 8.4, 4.6, 1.1 Hz, 1H), 2.50 (ddd, J = 13.2, 8.1, 4.7 Hz, 1H), 2.14 (dddd, J = 13.3, 12.2, 6.1, 3.2 Hz, 1H), 1.98 – 1.69 (m, 4H), 1.40 – 1.24 (m, 5H), 1.09 (d, J = 7.3 Hz, 6H), 1.06 (d, J = 7.3 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.1, 166.8, 161.3, 142.7, 133.0, 128.5, 128.0, 114.0, 70.1, 59.7, 36.2, 35.4, 33.7, 25.4, 17.6, 17.5, 14.4, 12.9.

FT-IR (neat) [cm^{-1}]: 3064, 2941, 2866, 1709, 1649, 1610, 1589, 1574, 1446, 1369, 1306, 1261, 1213, 1167, 1149, 1090, 1039, 1016, 995, 922, 879, 814, 768, 735, 690, 615, 571.

HRMS (ESI): calculated for $[M+Na]^+$: 425.21186, found 425.21236.

((Cyclohex-2-en-1-yloxy)diisopropylsilyl)(phenyl)methanone 8ab



Compound **8ab** was prepared according to **GP1** using 2-cyclohexen-1-ol as the alcohol. The product was obtained via column chromatography (pentane/Et_2O 40:1) as a yellow oil (136 mg, 0.429 mmol, 86%).

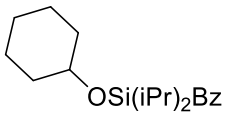
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.16 – 8.06 (m, 2H), 7.58 – 7.39 (m, 3H), 5.86 – 5.70 (m, 2H), 4.49 (td, J = 4.5, 2.4 Hz, 1H), 2.15 – 1.66 (m, 5H), 1.65 – 1.51 (m, 1H), 1.32 (hept, J = 7.1 Hz, 2H), 1.13 – 1.03 (m, 12H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 235.3, 142.8, 132.9, 130.3, 130.1, 128.5, 128.3, 77.6, 76.7, 67.8, 32.5, 25.1, 19.4, 17.7, 17.6, 17.5, 12.9, 12.8.

FT-IR (neat) [cm^{-1}]: 3062, 3028, 2942, 2891, 2866, 1650, 1609, 1590, 1574, 1462, 1446, 1389, 1316, 1213, 1173, 1160, 1136, 1067, 1017, 997, 921, 881, 833, 795, 767, 724, 689, 613, 552.

HRMS (ESI): calculated for $[M+Na]^+$: 339.17508, found 339.17497.

((Cyclohexyloxy)diisopropylsilyl)(phenyl)methanone 8ac



8ab (63.4 mg, 0.2 mmol, 1 eq.) was dissolved in EtOAc (3 ml). Pd/C (5% on charcoal) (10.9 mg, 5 µmol, 2.5 mol%) was added and the mixture was freezed with liquid nitrogen and evaporated to remove the argon atmosphere. The atmosphere was back filled with hydrogen and the mixture was warmed to room temperature by a water bath. The reaction mixture was stirred for 1 hour at room temperature and the mixture was filtered through celite subsequently. The solvent was evaporated to give the product as a yellow liquid without further purification (63.6 mg, 0.199 mmol, 99%).[18]

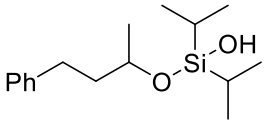
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.13 (dd, J = 8.2, 1.5 Hz, 2H), 7.59 – 7.39 (m, 3H), 3.98 – 3.86 (m, 1H), 1.93 – 1.83 (m, 2H), 1.82 – 1.69 (m, 2H), 1.55 – 1.40 (m, 3H), 1.37 – 1.23 (m, 5H), 1.09 (d, J = 7.4 Hz, 6H), 1.06 (d, J = 7.4 Hz, 6H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ =235.4, 142.9, 132.9, 128.4, 128.3, 72.4, 36.0, 25.7, 24.1, 17.6, 17.5, 12.8.

FT-IR (neat) [cm^{-1}]: 2931, 2865, 2347, 1719, 1609, 1590, 1575, 1551, 1462, 1447, 1370, 1214, 1173, 1088, 1045, 1016, 997, 923, 882, 859, 820, 767, 691, 671, 661, 644, 617, 582.

HRMS (ESI): calculated for $[M+Na]^+$: 341.19073, found 341.189561401.

Diisopropyl((4-phenylbutan-2-yl)oxy)silanol 4a



8b (55.4 mg, 0.15 mmol) was dissolved in EtOAc (2 ml) and MeOH (0.15 ml) at room temperature. The solution was irradiated for 15 minutes and the mixture was evaporated. Purification by column chromatography (pentane/Et_2O 5:1) gave diisopropyl((4-phenylbutan-2-yl)oxy)silanol as a colorless liquid (35.6 mg, 0.127 mmol, 85%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35 – 7.24 (m, 2H), 7.24 – 7.12 (m, 3H), 4.08 (dt, J = 12.5, 6.2 Hz, 1H), 2.70 (qdd, J = 13.8, 9.9, 6.3 Hz, 2H), 1.94 (s, 1H), 1.93 – 1.68 (m, 3H), 1.26 (d, J = 6.1 Hz, 3H), 1.11 – 0.87 (m, 14H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 142.7, 128.5, 125.8, 68.1, 41.5, 32.1, 23.9, 17.4, 17.4, 17.3, 12.9, 12.7.

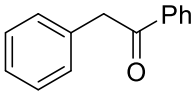
FT-IR (neat) [cm^{-1}]: 3026, 2931, 2864, 1666, 1604, 1495, 1460, 1377, 1250, 1132, 1090, 1059, 1030, 999, 883, 833, 744, 696, 586, 525.

HRMS (ESI): calculated for $[M+Na]^+$: 303.17508, found 303.17431.

2.8 Benzoylation

General procedure (GP6): The corresponding acylsilane (0.2 mmol) was dissolved in dry acetonitrile (2 ml) and the solution was irradiated for 30 minutes with a 456 nm 45 W Kessil LED. 8 N HCl was added and stirring was continued for approximately 10 minutes. The resulting mixture was extracted with DCM and the compound was purified by column chromatography.

1,2-Diphenylethan-1-one 9a

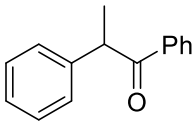


Compound **9a** was prepared according to **GP6** using **8ae** as the starting material. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a colorless solid (39.1 mg, 0.199 mmol, 99%). The spectroscopic data were in accordance to the literature. [19]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.51 – 7.40 (m, 1H), 7.39 – 7.31 (m, 2H), 7.29 – 7.09 (m, 5H), 4.18 (s, 2H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 197.7, 136.7, 134.7, 133.2, 129.6, 128.8, 128.73, 128.71, 127.0, 45.6.

1,2-Diphenylpropan-1-one 9b

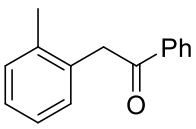


Compound **9b** was prepared according to **GP6** using **8af** as the starting material. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a colorless solid (35.5 mg, 0.169 mmol, 85%). The spectroscopic data were in accordance to the literature.[20]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.02 – 7.92 (m, 2H), 7.52 – 7.44 (m, 1H), 7.42 – 7.34 (m, 2H), 7.30 (m, 4H), 7.20 (m, 1H), 4.70 (q, J = 6.9 Hz, 1H), 1.55 (d, J = 6.9 Hz, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 200.4, 141.6, 136.6, 132.9, 129.1, 128.9, 128.6, 127.9, 127.0, 48.0, 19.6.

1-Phenyl-2-(o-tolyl)ethan-1-one 9c

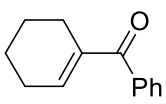


Compound **9c** was prepared according to **GP6** using **8ag** as the starting material. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a colorless oil (40.4 mg, 0.192 mmol, 96%). The spectroscopic data were in accordance to the literature.[21]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.04 – 7.94 (m, 2H), 7.59 – 7.48 (m, 1H), 7.43 (m, 2H), 7.22 – 7.03 (m, 4H), 4.26 (s, 2H), 2.23 (s, 3H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 197.6, 137.0, 137.0, 133.6, 133.2, 130.5, 130.4, 128.8, 128.4, 127.3, 126.2, 43.6, 19.9.

Cyclohex-1-en-1-yl(phenyl)methanone 9d

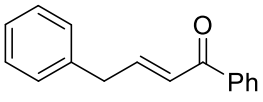


Compound **9d** was prepared according to GPX using **8ab** as the starting material. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a colorless oil (32.2 mg, 0.173 mmol, 91%). The spectroscopic data were in accordance to the literature.[22]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.67 – 7.54 (m, 2H), 7.54 – 7.44 (m, 1H), 7.44 – 7.32 (m, 2H), 6.57 (tt, J = 3.9, 1.7 Hz, 1H), 2.41 (m, 2H), 2.26 (m, 2H), 1.80 – 1.59 (m, 4H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 198.3, 144.1, 138.8, 131.3, 129.2, 128.1, 26.2, 24.1, 22.1, 21.8.

(E)-1,4-diphenylbut-2-en-1-one 9e



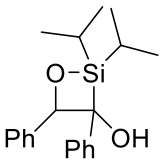
Compound **9e** was prepared according to **GP6** using **8ah** as the starting material. The product was obtained via column chromatography (pentane/Et_2O 5:1) as a colorless oil (30.7 mg, 0.139 mmol, 70%). The spectroscopic data were in accordance to the literature.[23]

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.13 – 7.99 (m, 2H), 7.63 – 7.55 (m, 1H), 7.53 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.31 (m, 2H), 7.26 – 7.19 (m, 1H), 6.63 – 6.41 (m, 2H), 4.00 – 3.88 (m, 2H).

^{13}C-NMR (76 MHz, $CDCl_3$): δ = 198.1, 137.1, 136.7, 133.7, 133.3, 128.8, 128.6, 128.4, 127.6, 126.4, 122.7, 42.8.

2.8.1 NMR-Studies

2,2-Diisopropyl-3,4-diphenyl-1,2-oxasiletan-3-ol 10



8ae (50 µmol, 16.3 mg) was dissolved in dry acetonitrile-*d3* (1 ml). The solution was transferred into a flame dried NMR-tube under argon atmosphere. The tube was sealed by flame and irradiated with a 456 nm 45 W Kessil LED until the yellow colour completely vanished (approx. 1 hour). NMR-spectra were measured immediately after irradiation.

^{1}H-NMR (600 MHz, CD_3CN): δ = 7.69 – 7.64 (m, 2H), 7.53 – 7.45 (m, 4H), 7.45 – 7.41 (m, 2H), 7.41 – 7.37 (m, 1H), 7.37 – 7.32 (m, 1H), 7.31 – 7.25 (m, 4H), 7.23 – 7.18 (m, 3H), 7.16 – 7.11 (m, 2H), 7.08 – 7.02 (m, 1H), 6.29 (s, 1H), 5.97 (s, 1H), 3.99 (s, 1H), 2.42 (s, 1H), 1.78 (hept, J = 7.6 Hz, 1H), 1.68 (hept, J = 7.5 Hz, 1H), 1.43 (m, 8H), 1.36 (d, J = 3.0 Hz, 3H), 1.35 (d, J = 2.9 Hz, 3H), 1.15 (d, J = 7.6 Hz, 3H), 1.07 (d, J = 7.5 Hz, 3H), 0.95 (d, J = 7.6 Hz, 3H), 0.85 (d, J = 7.6 Hz, 3H) (1:1 mixture of diastereomers).

^{13}C-NMR (151 MHz, CD_3CN): δ = 144.9, 143.2, 141.6, 140.2, 129.3, 129.0, 128.5, 128.2, 128.0, 127.3, 127.2, 126.9, 126.5, 126.3, 125.8, 125.7, 118.3, 91.2, 86.7, 84.5, 83.2, 17.60, 17.59, 17.1, 16.8, 16.8, 16.6, 16.40, 16.38, 14.7, 14.5, 14.4, 14.2 (1:1 mixture of diastereomers).

^{29}Si NMR (119 MHz, CD_3CN): δ = 35.15, 33.07 (1:1 mixture of diastereomers).

2.9 Determination of Quantum yield

2.9.1 Determiation of Photonflux

The quantum yield was determined according to procedures described in the literature.[24]

A 0.2 M sulfuric acid solution was prepared by placing 1.96 g H_2SO_4 (0.2 mmol) into a 100 ml measuring flask and filling up to the mark with distilled water.

Solution (1): potassium ferrioxalate (737 mg, 1.50 mmol) was placed in a 10.0 ml measuring flask and flask was filled to the mark with 0.2 M aqueous H_2SO_4

Solution (2): NaOAc (3.08 g, 37.5 mmol) and 1,10-phenanthroline (1.35 g, 7.5 mmol) were placed in a 25.0 ml measuring flask and it was filled up to the mark with 0.2 M H_2SO_4.

Next in five Schlenk tubes 1 ml of solution (1) were placed, and the tubes were sealed. The tubes were irradiated for different times (0, 10, 20, 30 and 40 seconds) in a distance of 9 cm to the 456 nm-LED (35 W). After irradiation first 3.0 ml of 0.2 M sulfuric acid and subsequently 4.0 ml of solution (2) were added. The resulting mixtures were stirred for 40 minutes in the dark. Afterwards a sample (25 µl) of the resulting solution was placed in a 5 ml measuring flask and it was filled up to the mark with 0.2 M sulfuric acid. The absorbance of the resulting solutions was measured in a cuvette (l = 1 cm). The procedure was carried out for each sample.

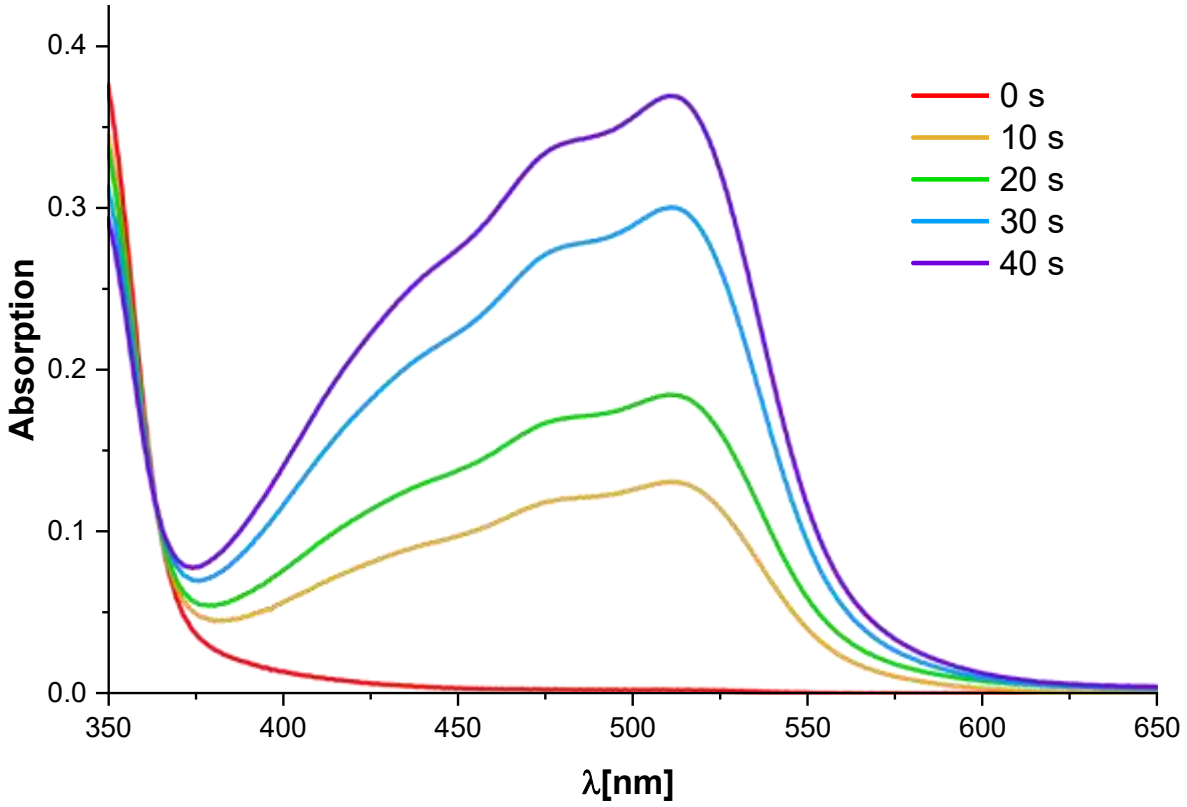


Figure S1: Absorption spectra oft he described soulutions after different irradiation times.

The amount of formed Fe^{2+} was calculated as follows:

$$n(Fe^{2+})[mol] = \frac{V_1 \cdot V_2 \cdot \Delta A(510\ nm)}{V_3 \cdot l \cdot \varepsilon(510\ nm)} \cdot 10^{-3} \text{ with } V_3 = \frac{V_{sample}}{DF} \text{ with } DF = \frac{V_{dilution}}{V_{irradiation}}$$

With V_1 being the irradiated volume (1.0 ml), V_2 the volume after complexation (5.0 ml), $\Delta A(510\ nm)$ the absorbance difference between the irradiated sample and the unirradiated sample (0 s) at 510 nm. V_3 is the volume of the irradiated aliquot, which is calculated by the volume of the taken sample

(V_{sample} = 0.025 ml) divided by the dilution factor (DF) of the irradiated solution. DF is the diluted volume ($V_{dilution}$ = 8.0 ml) divided by the irradiated Volume ($V_{irradiation}$ = 1.0 ml). l is the length of the cuvette (1 cm) and $\varepsilon(510\ nm)$ is the extinction coefficient at 510 nm (11100 $Lmol^{-1}cm^{-1}$).

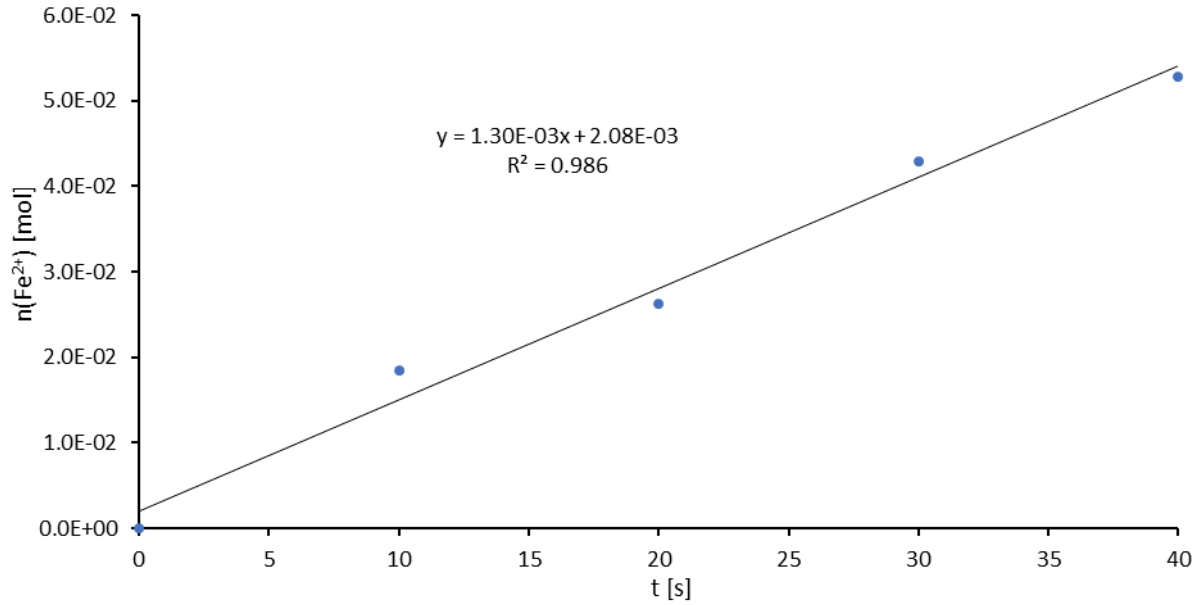


***Figure S2**:* Fe^{2+}-amount of formed plotted against the time.

By determination of the slope the photon flux can be calculated as follows:

$$flux\ \left[\frac{mol}{s}\right] = \frac{dn(Fe)/dt}{\Phi_{Fe(456\ nm)} \cdot f} \text{ with } f = 1 - 10^{-A(456\ nm)}$$

$dn(Fe)/dt$ is the slope of the previous plot. $\Phi_{Fe(456\ nm)}$ is the quantum yield for the ferrioxalate actinometer (appr. 0.845, reported for λ = 457.9 nm)[25] and f is the fraction of light absorbed by the ferrioxalate actinometer at 456 nm. Since the absorption of the ferrioxalate solution at 456 nm $A(456\ nm)$ was determined to be larger than 3, f was approximated to 1. The flux was therefore determined to be **1.54*10^{-6} mol/s.**

2.9.2Determination of quantum yield

0.2 mmol (70.9 mg) of **8a** was dissolved in 2.0 ml of a 0.1 M solution of biphenyl in an Acetone/Methanol mixture. The solution was irradiated with a 456 nm 45 W Kessil LED. Samples were taken before irradiation and in intervals of 90 seconds and the conversion was determined by GC. By plotting the converted amount of **8a** against the photon flux. The quantum yield was determined to be $\Phi_{8a(456\,nm)}$ = **0.209**.

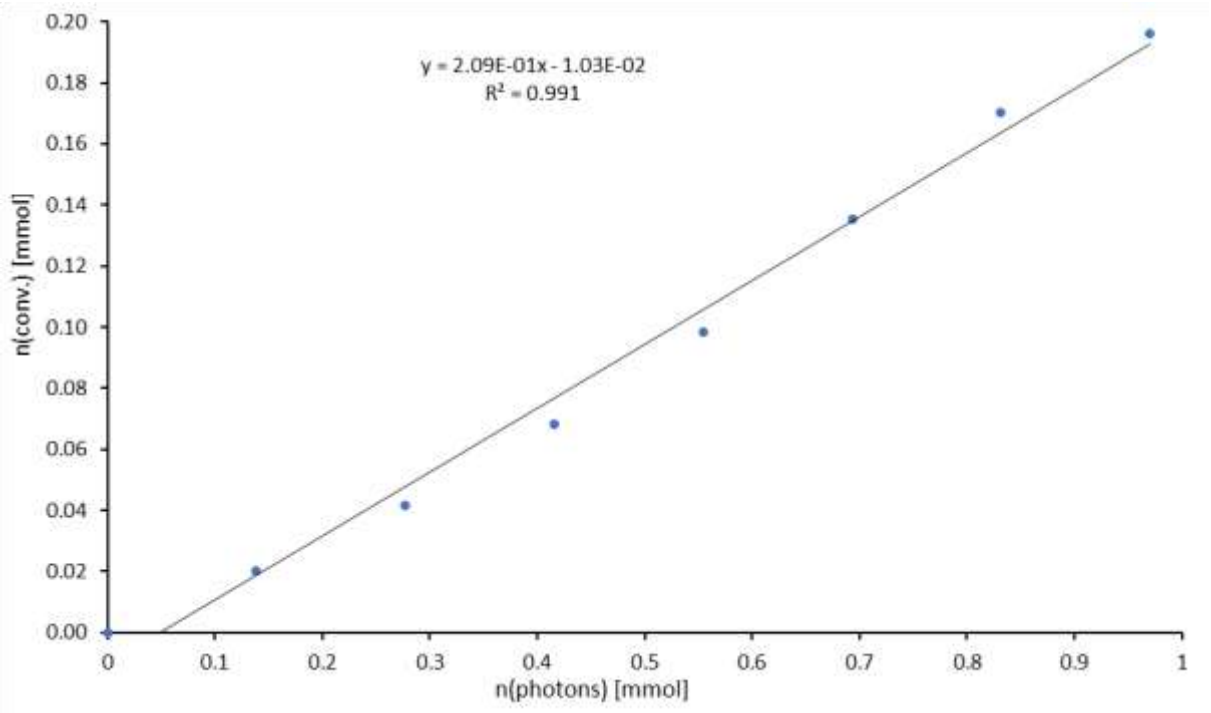


Figure S3: Amount of **8a** consumed plotted against the photon flux.

3.UV/Vis Spectra

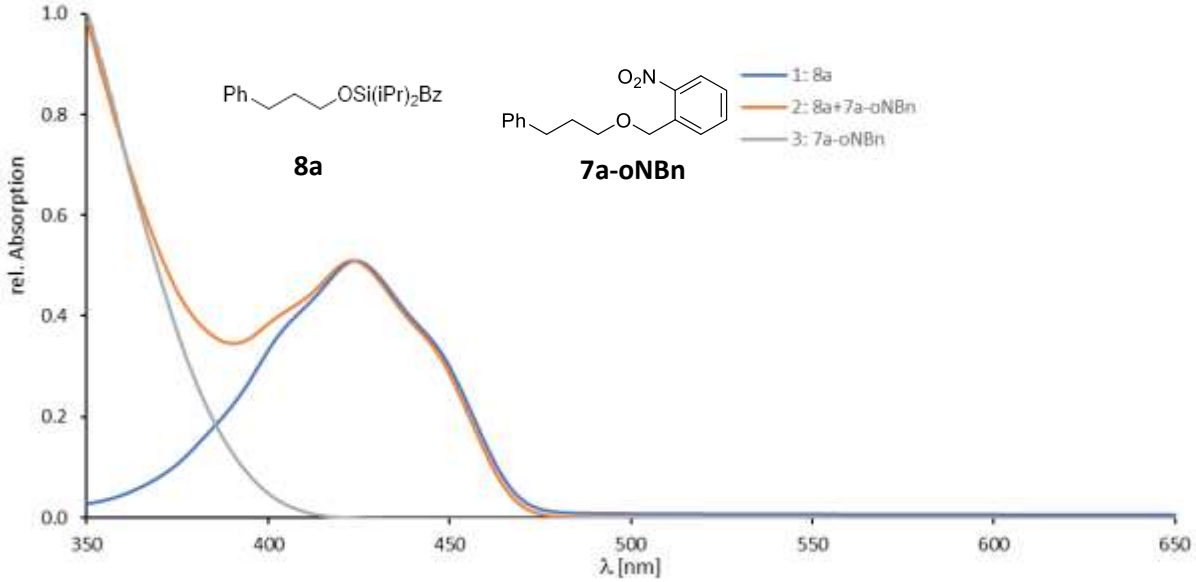
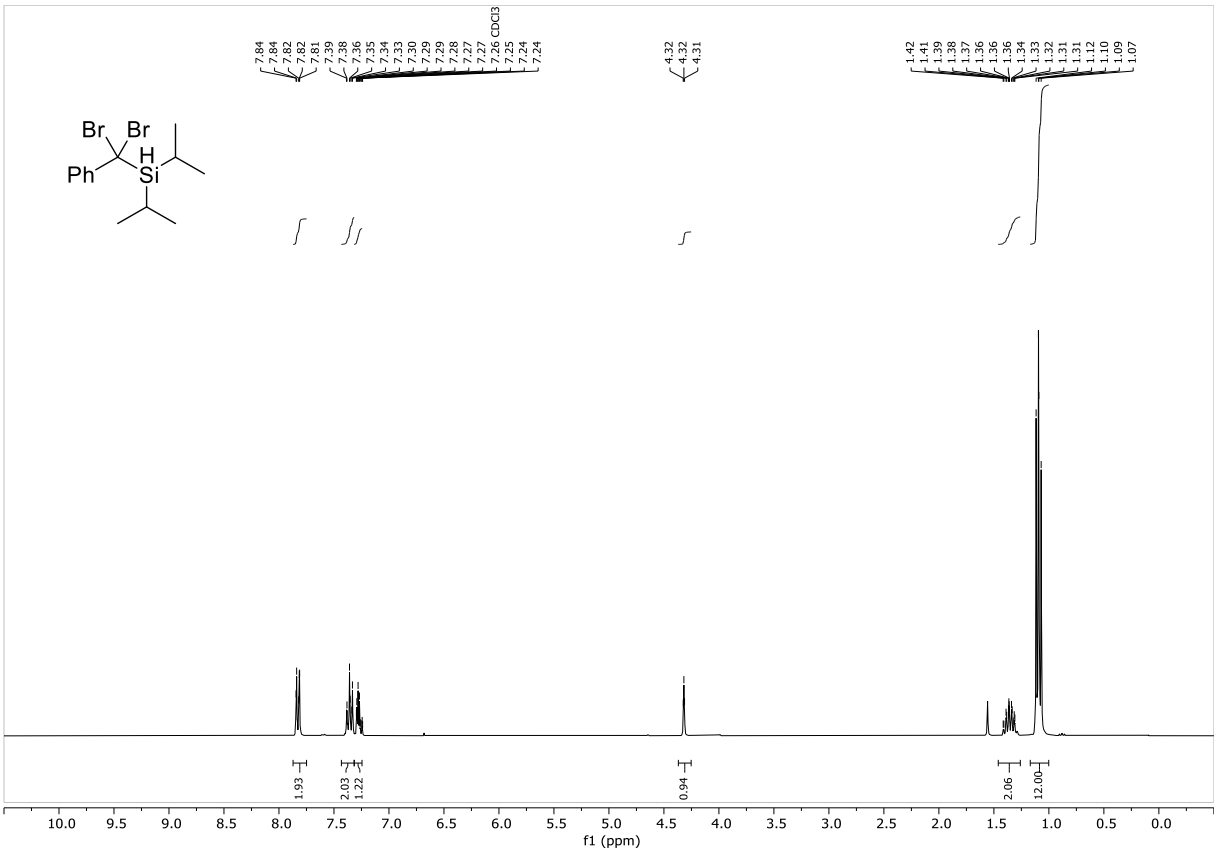
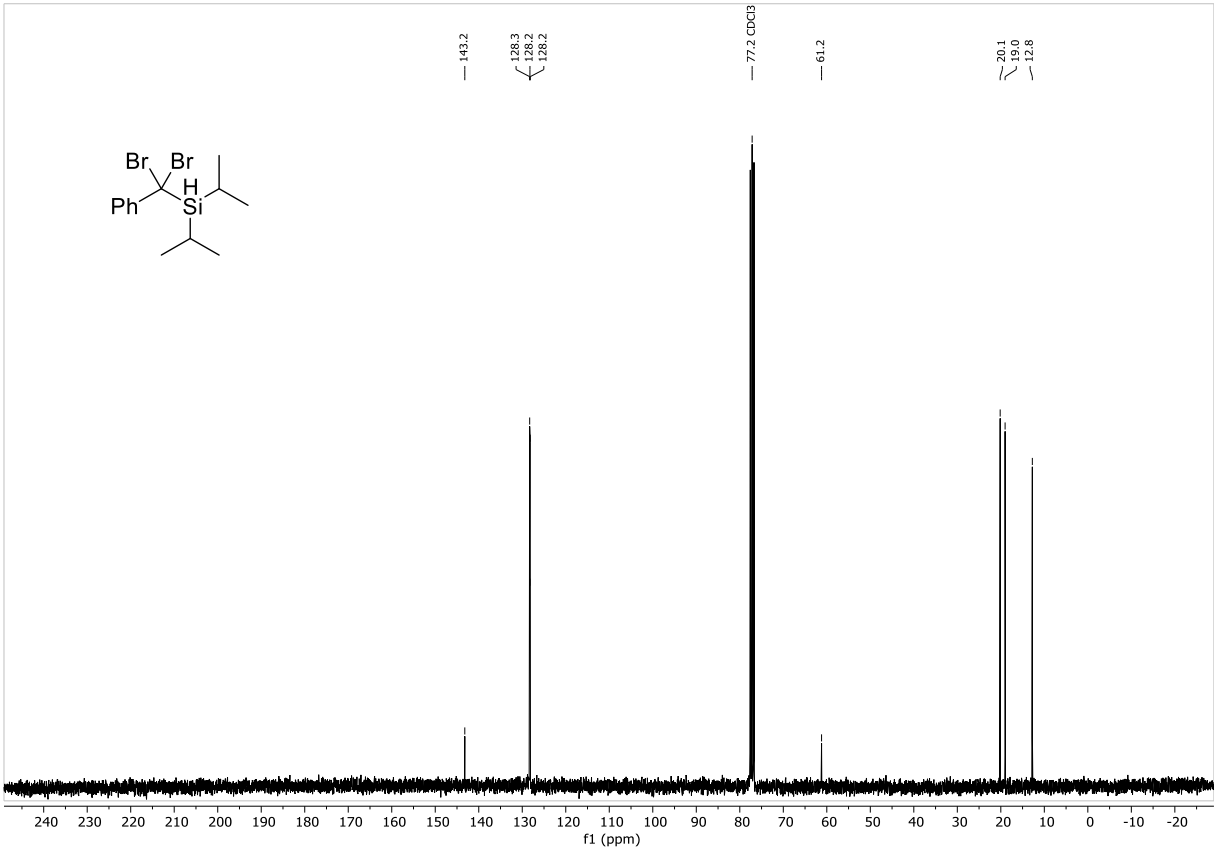


Figure S4: Spectra were recorded in Acetone. 2 and 3 were normalized to the absorption at 350 nm. 1 was normalized to the absorption of 2 at 424 nm.

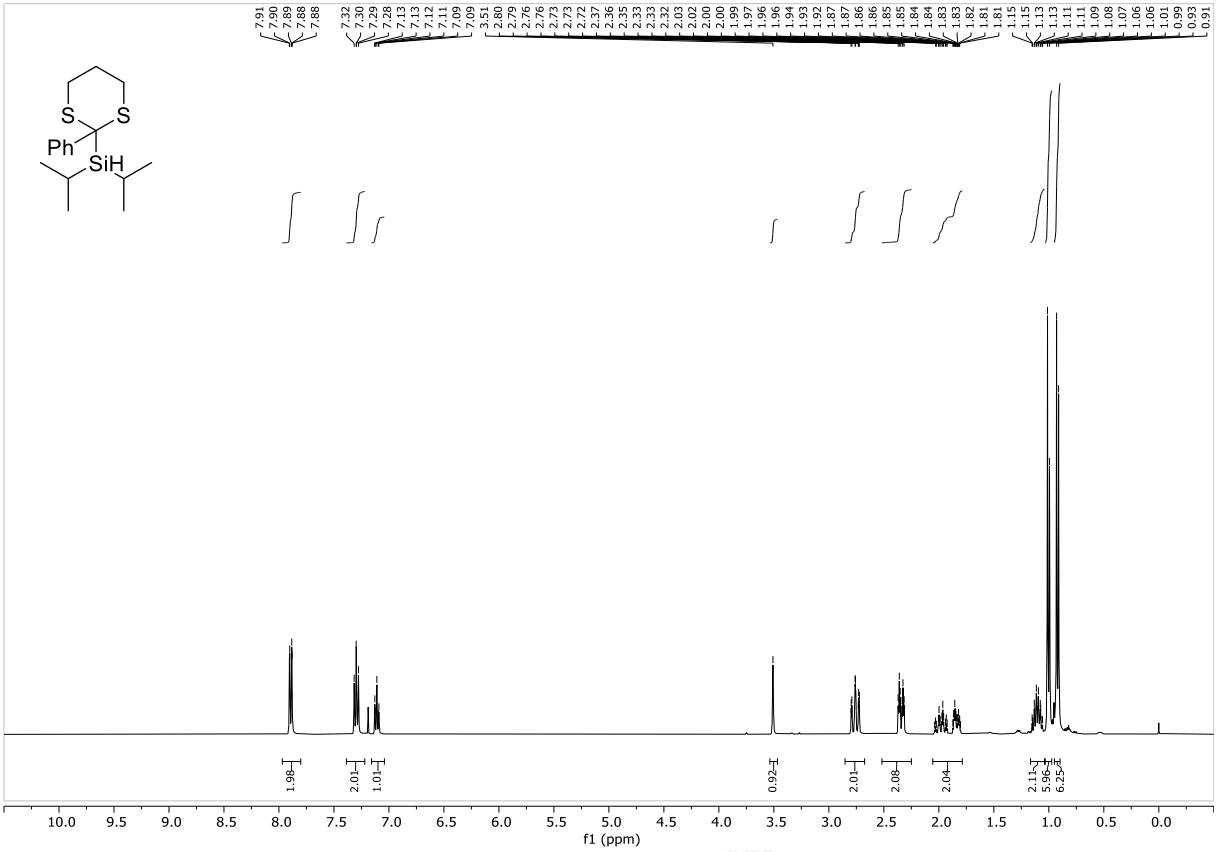
4. NMR Spectra

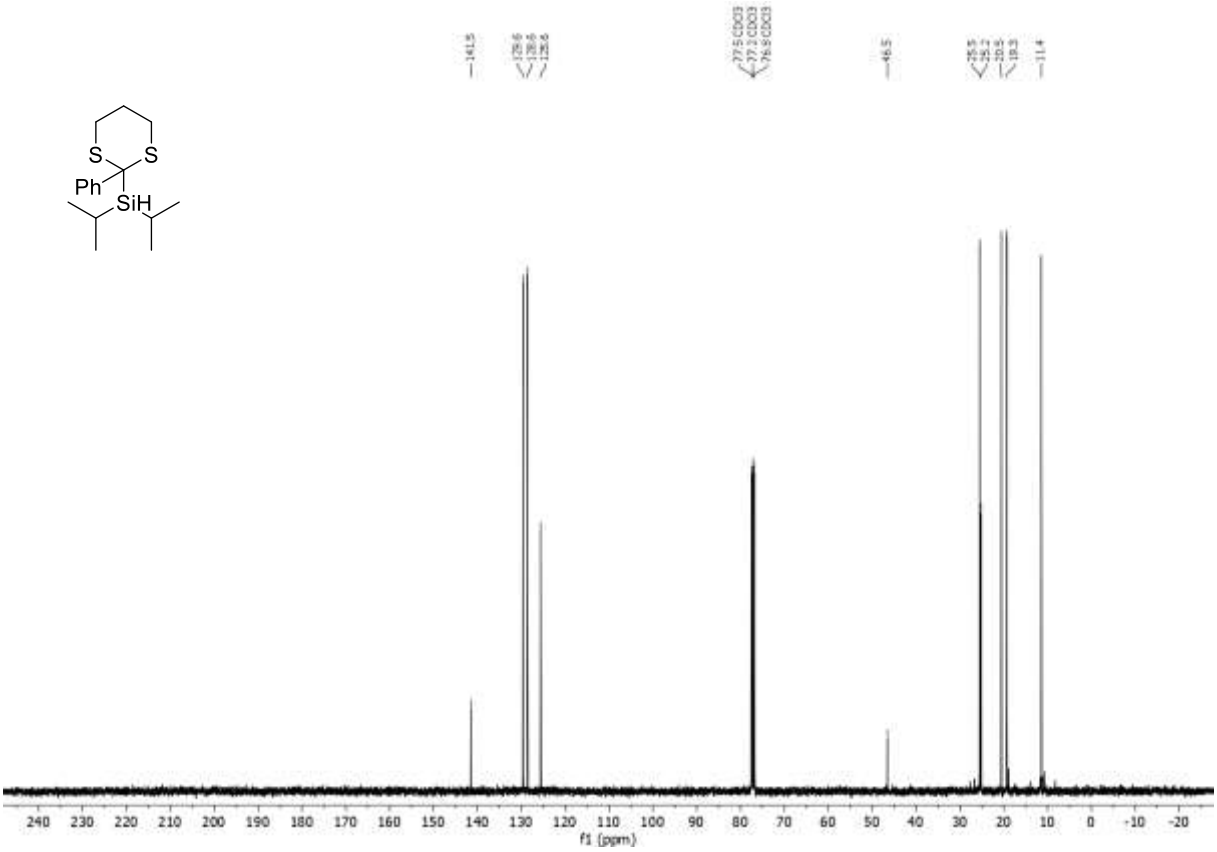
(Dibromo(phenyl)methyl)diisopropylsilane 5a



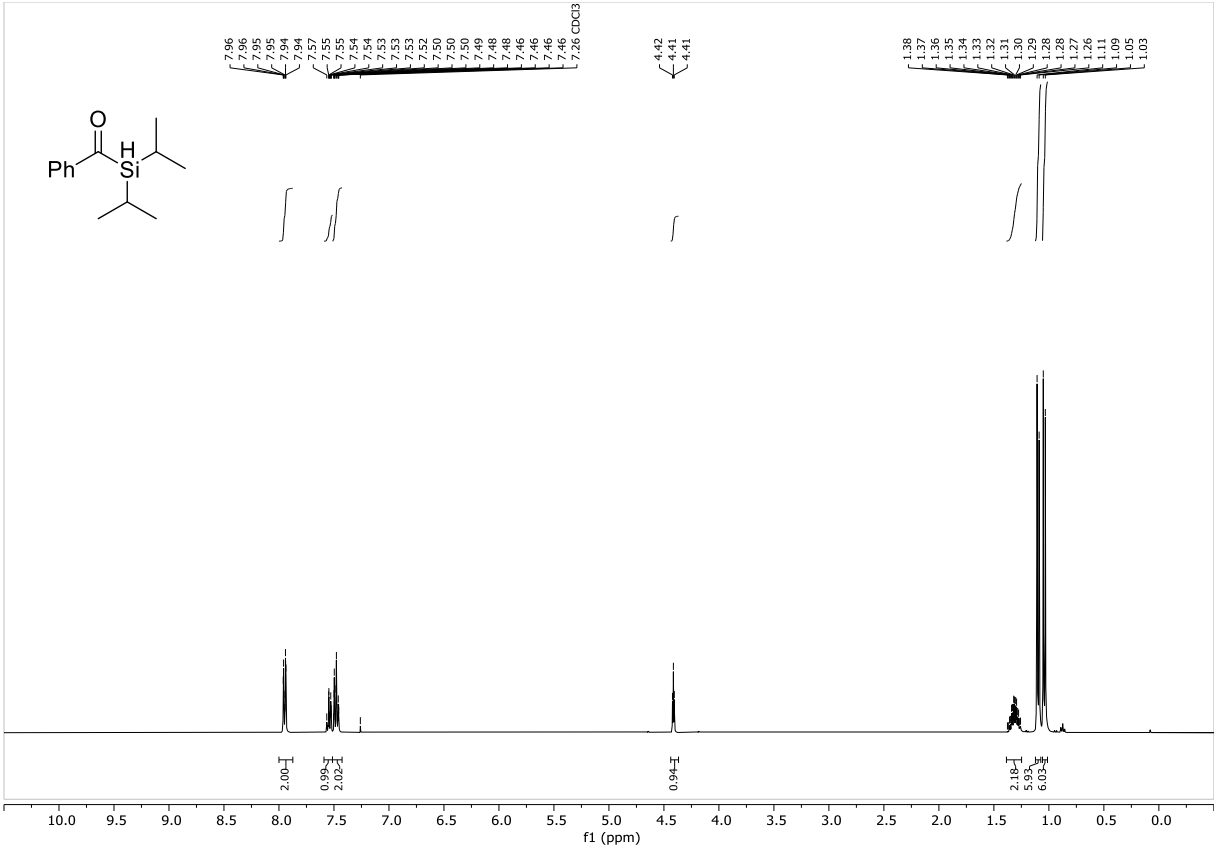


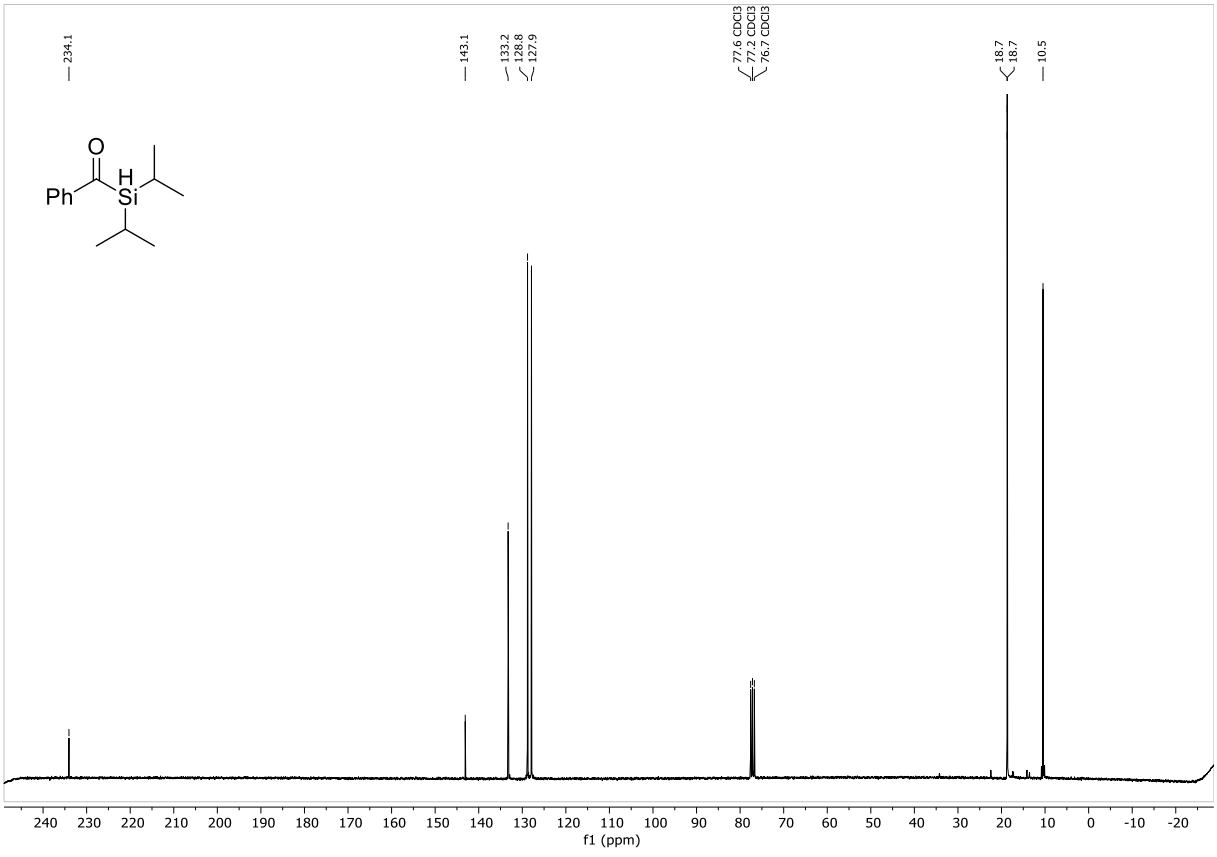
Diisopropyl(2-phenyl-1,3-dithian-2-yl)silane



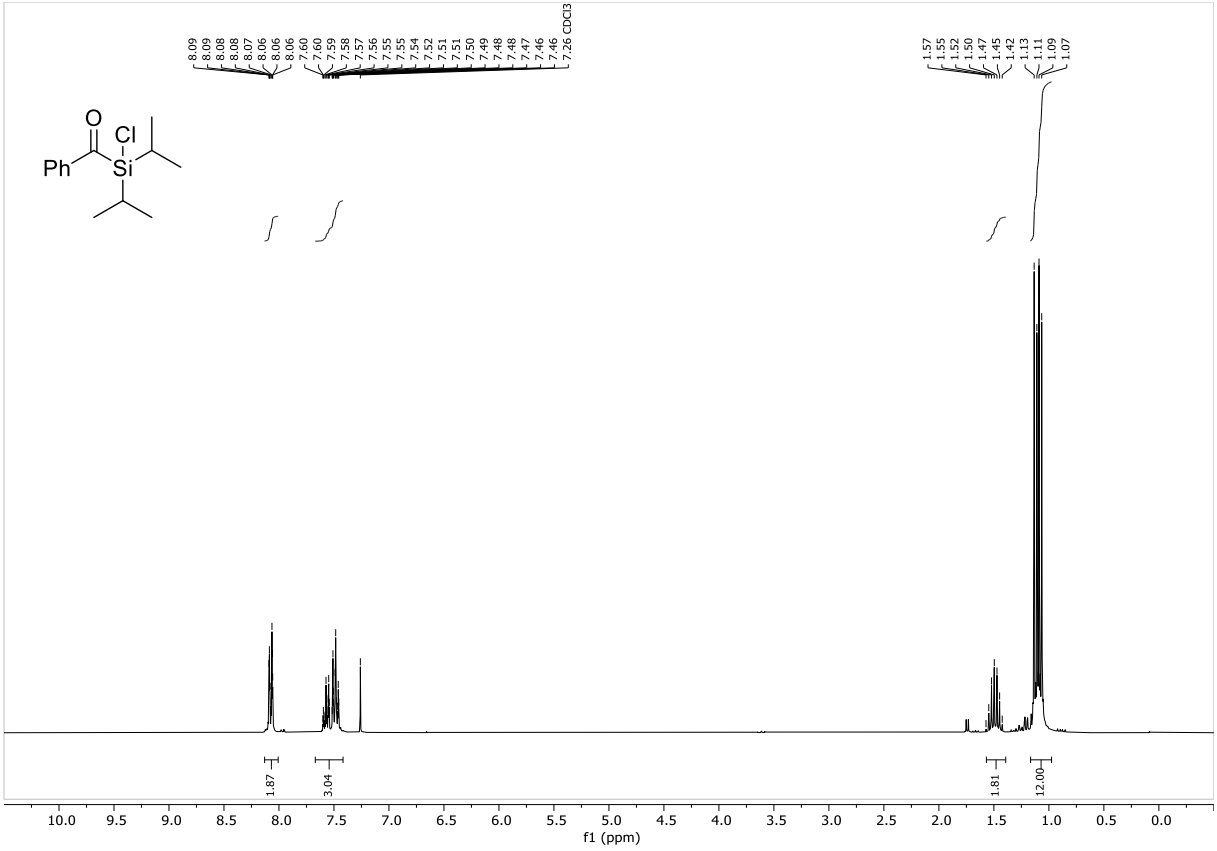


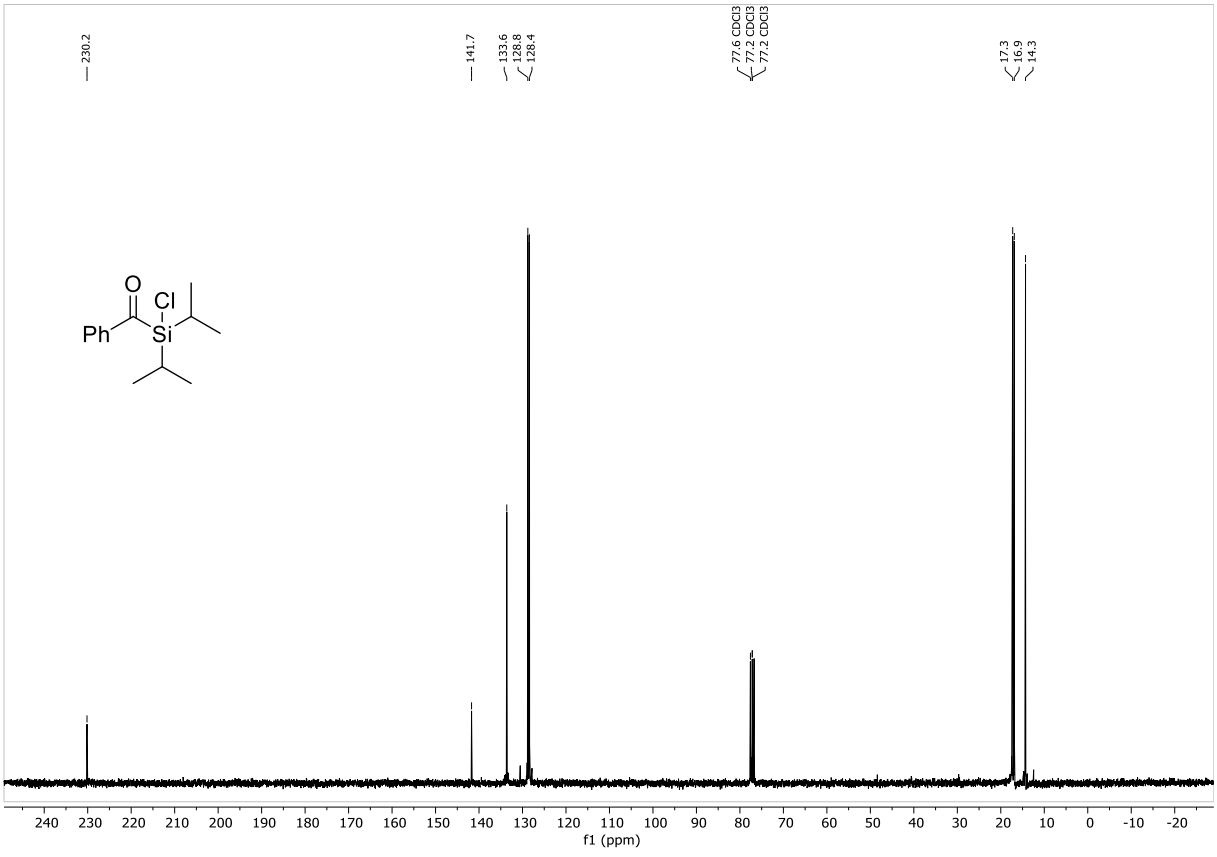
Diisopropyl benzoyl silane 6a



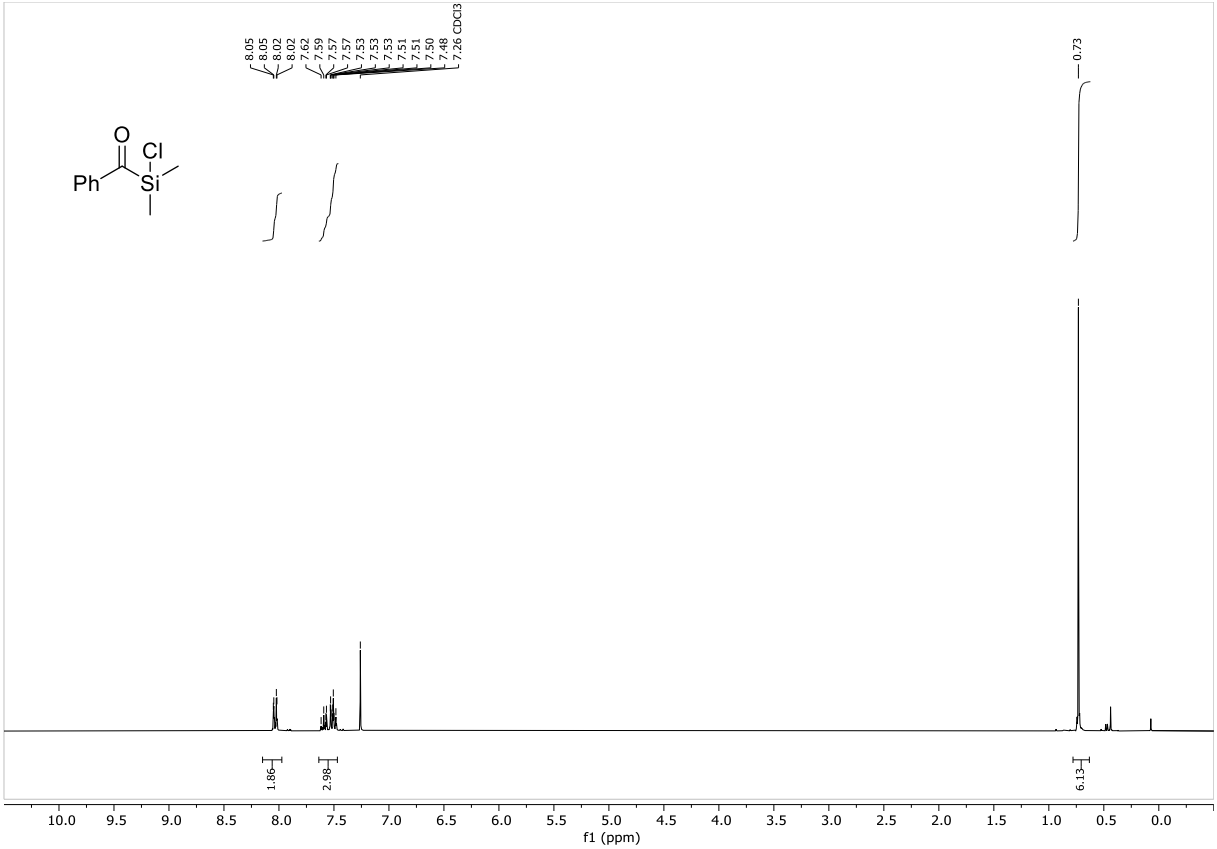


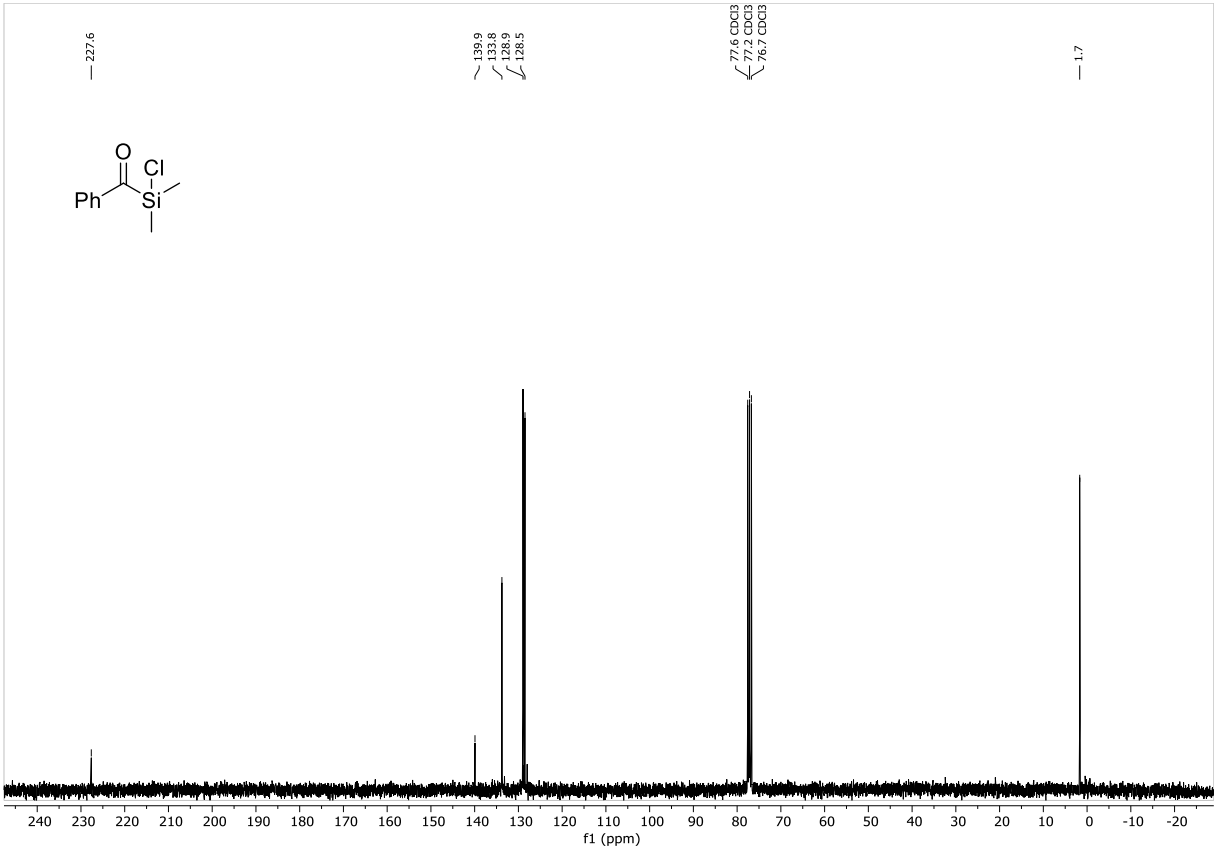
(Chlorodiisopropylsilyl)(phenyl)methanone 1a



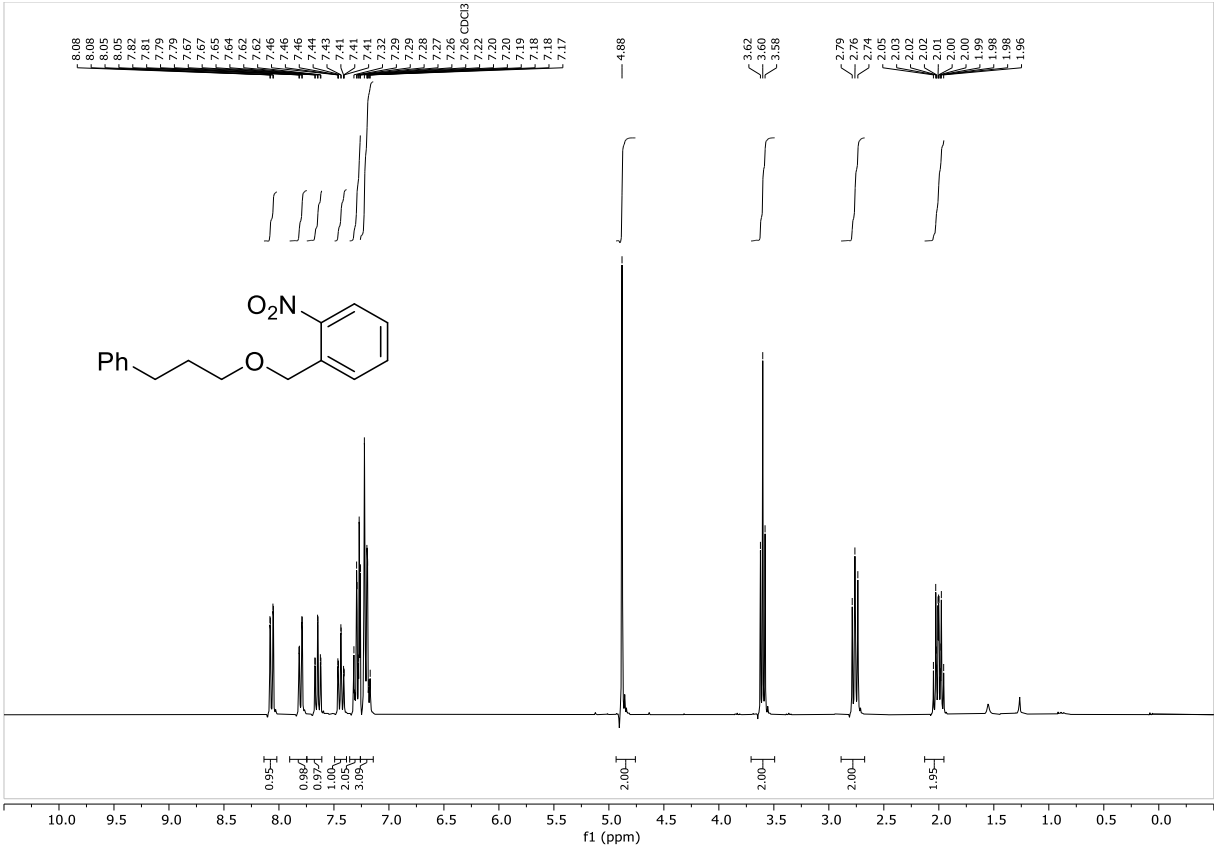


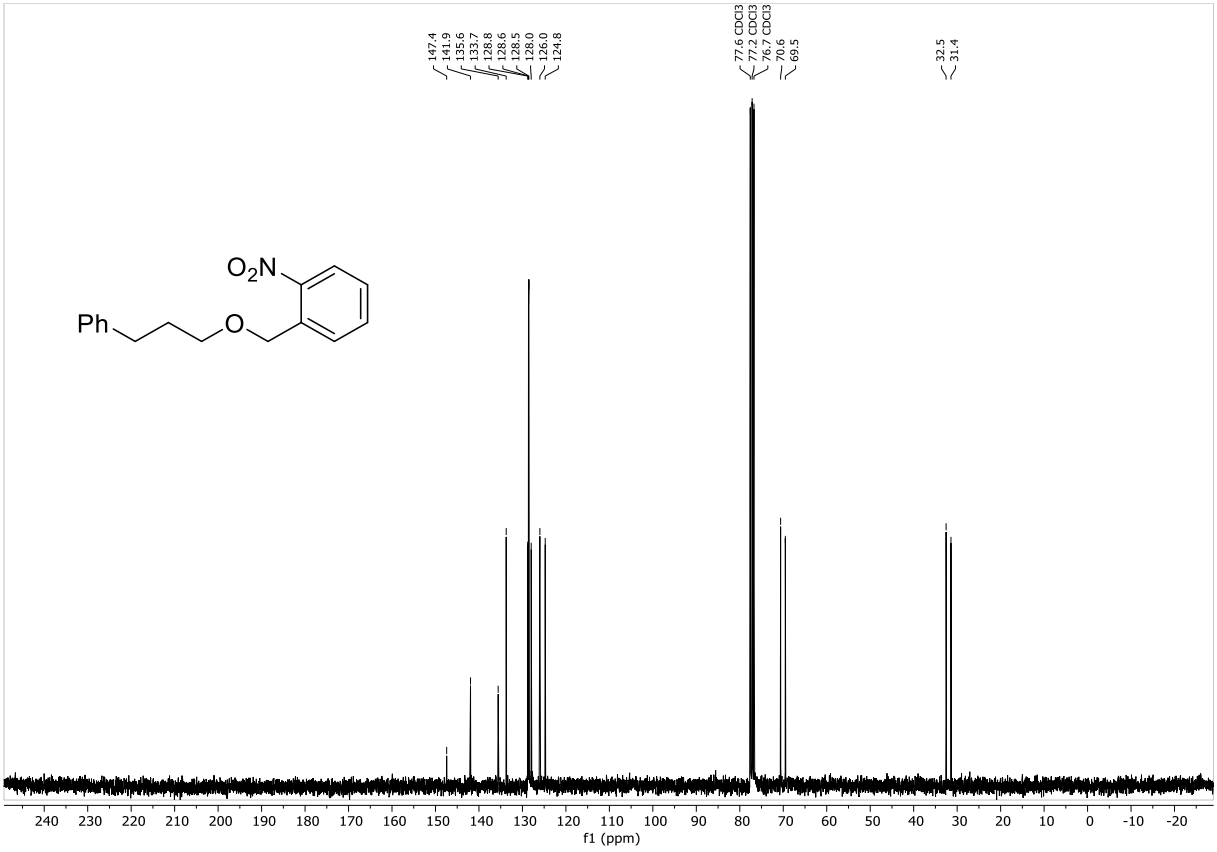
(Chlorodimethylsilyl)(phenyl)methanone 1b



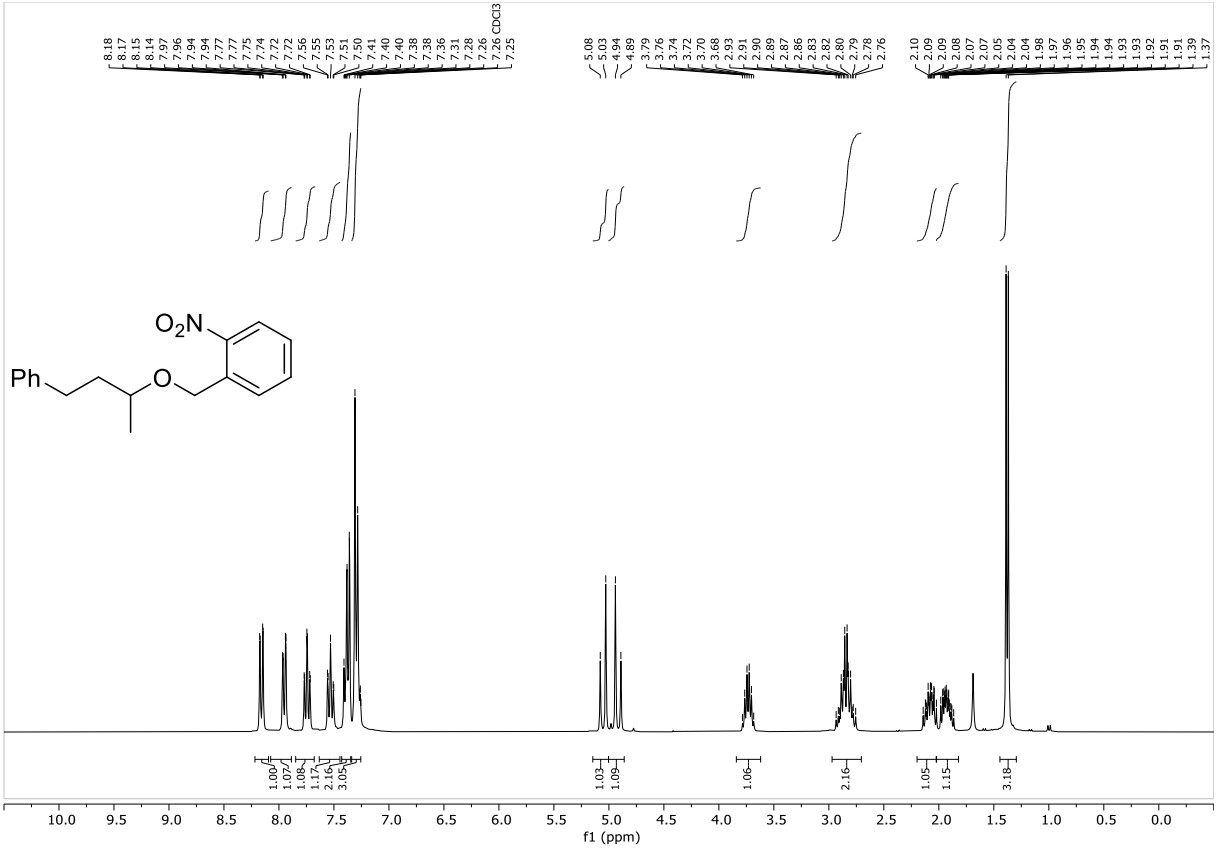


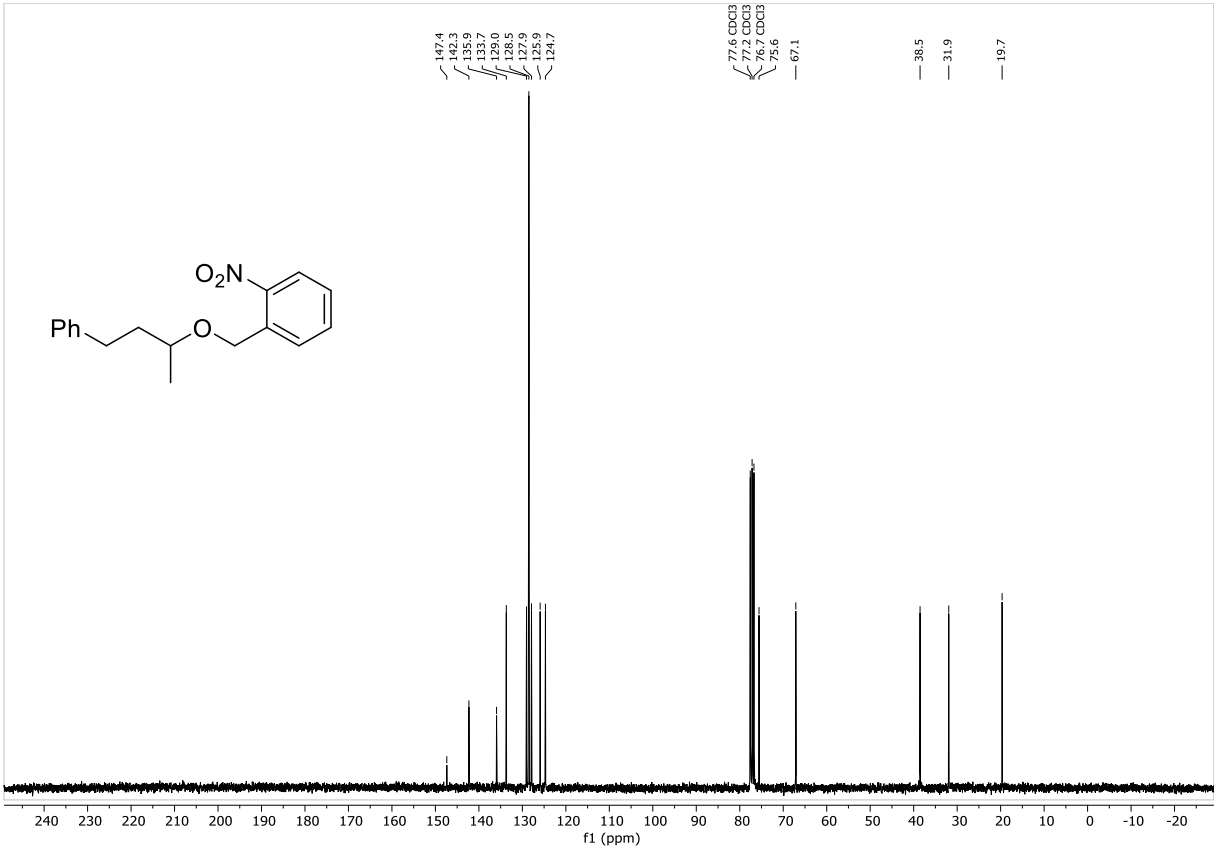
1-Nitro-2-((3-phenylpropoxy)methyl)benzene 7a-oNBn



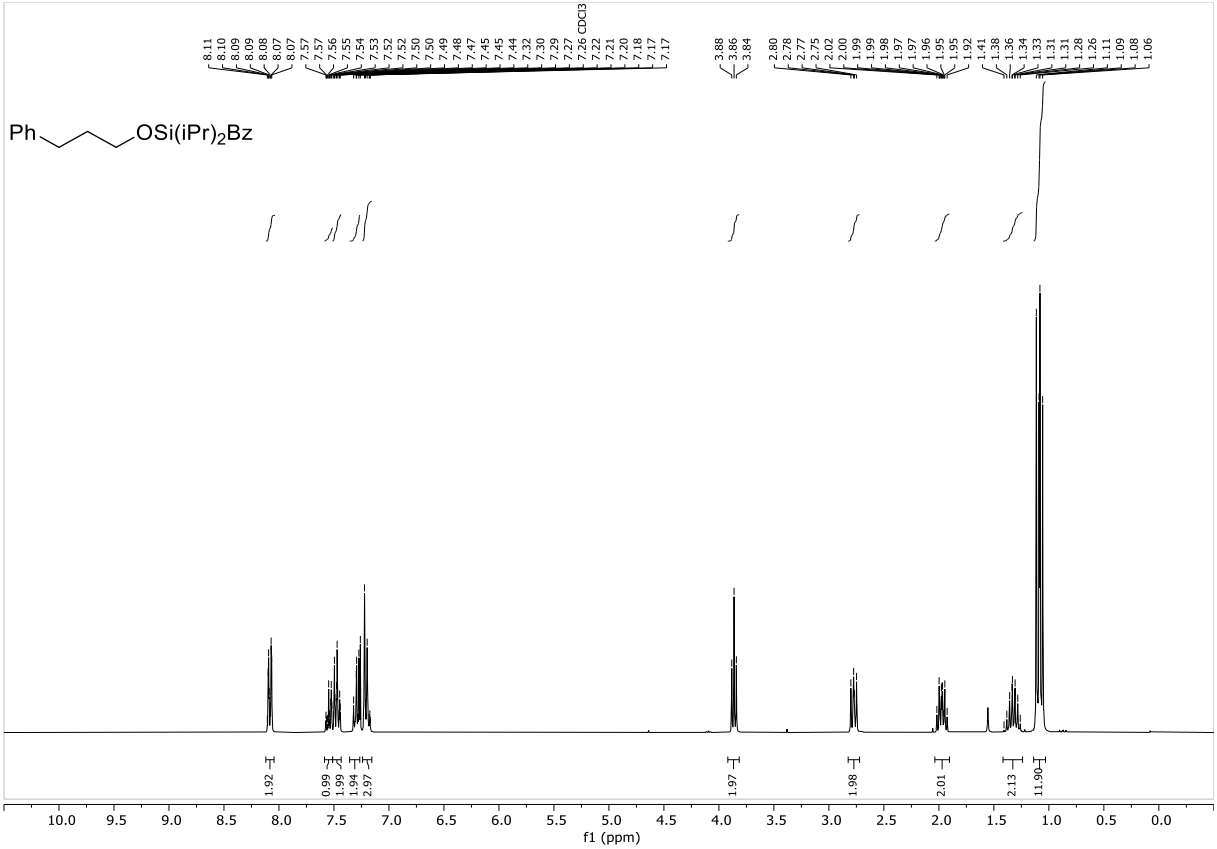


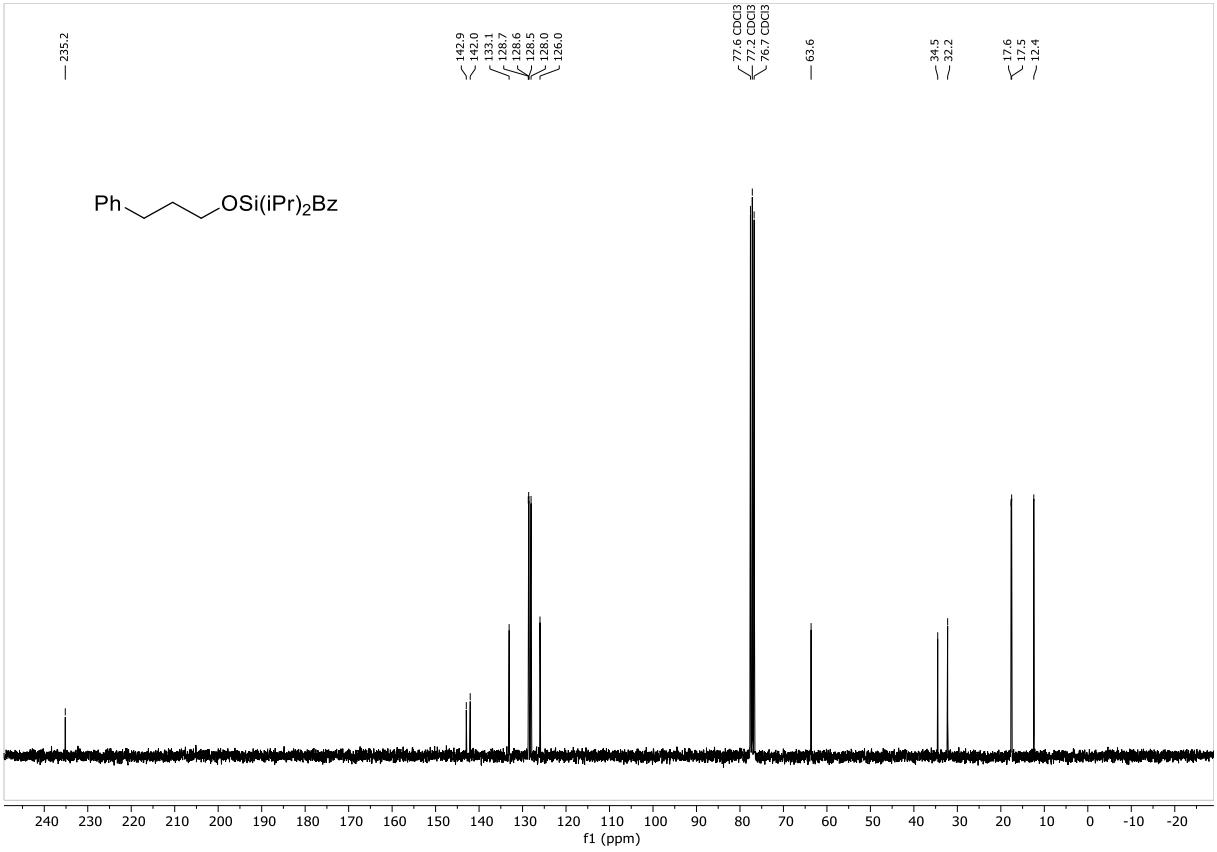
1-Nitro-2-(((4-phenylbutan-2-yl)oxy)methyl)benzene 7b-oNBn



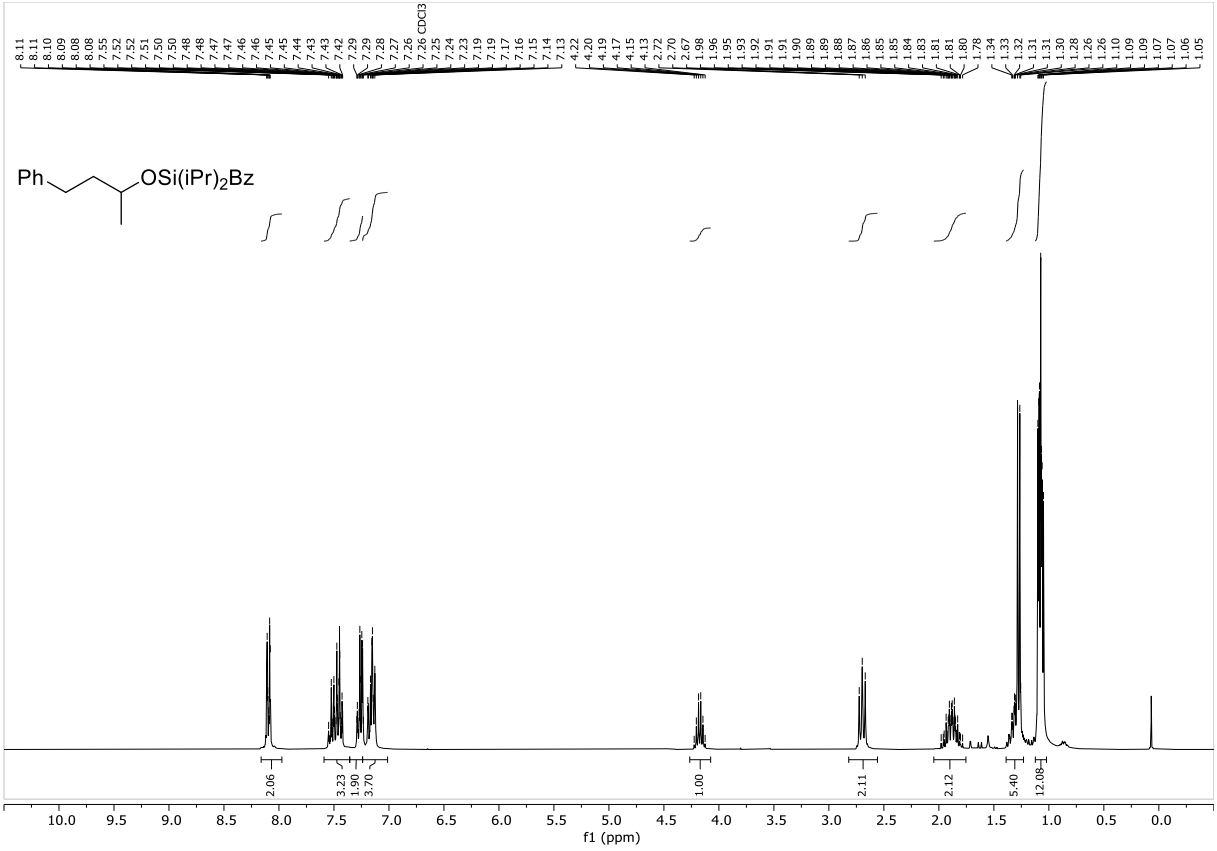


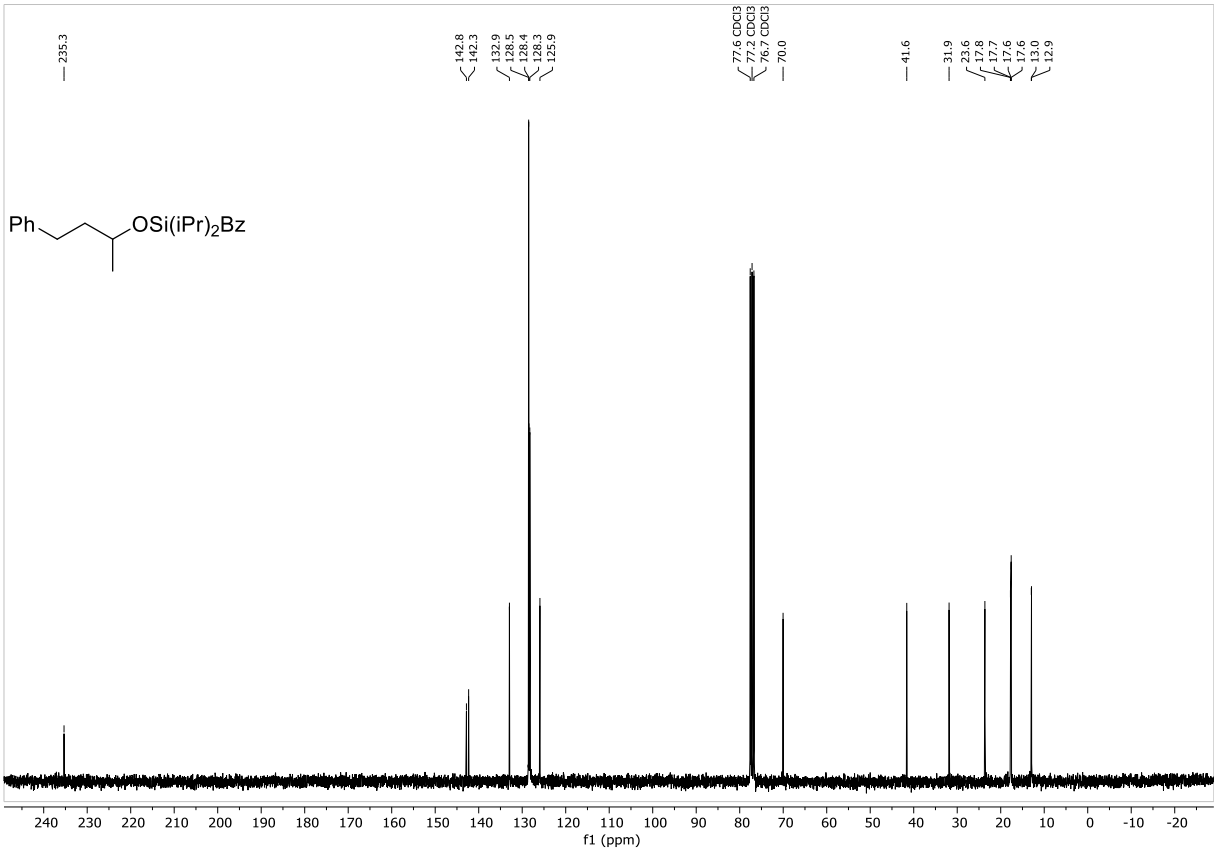
(Diisopropyl(3-phenylpropoxy)silyl)(phenyl)methanone 8a



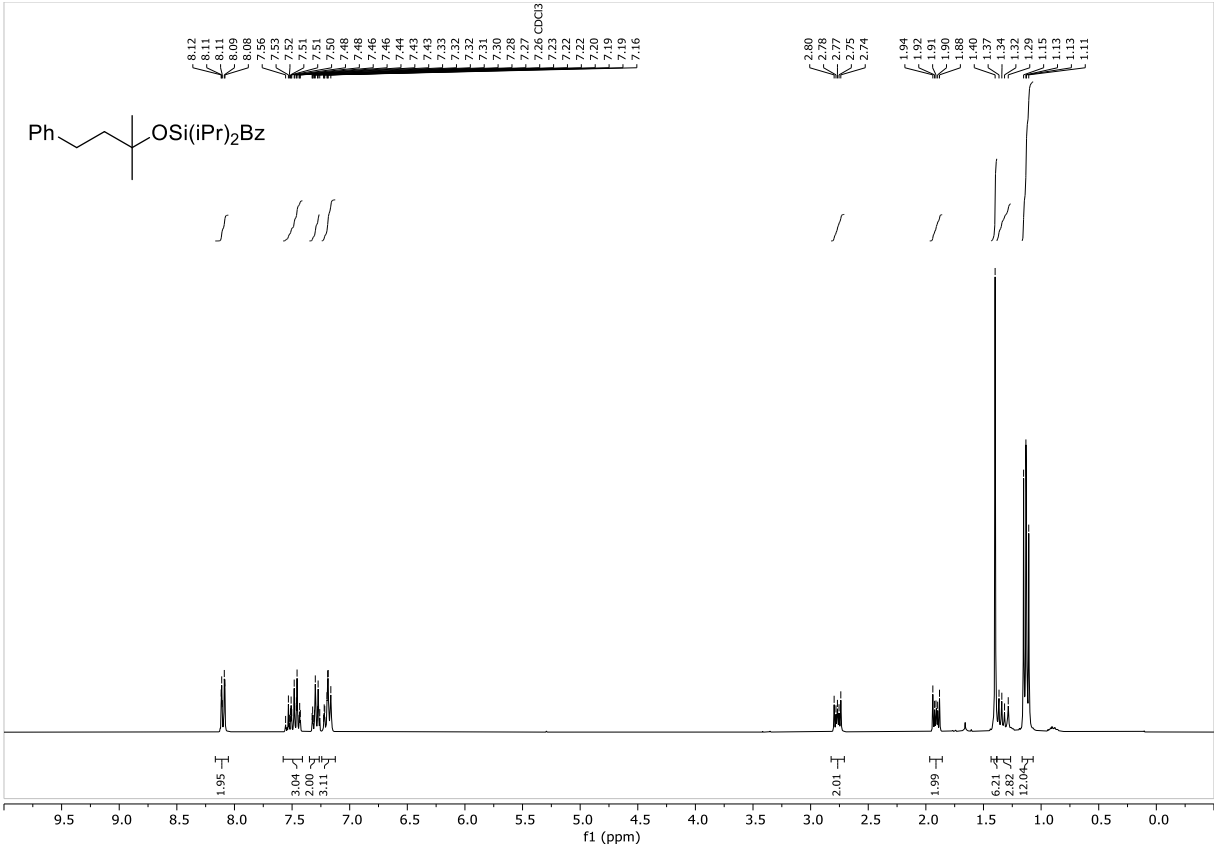


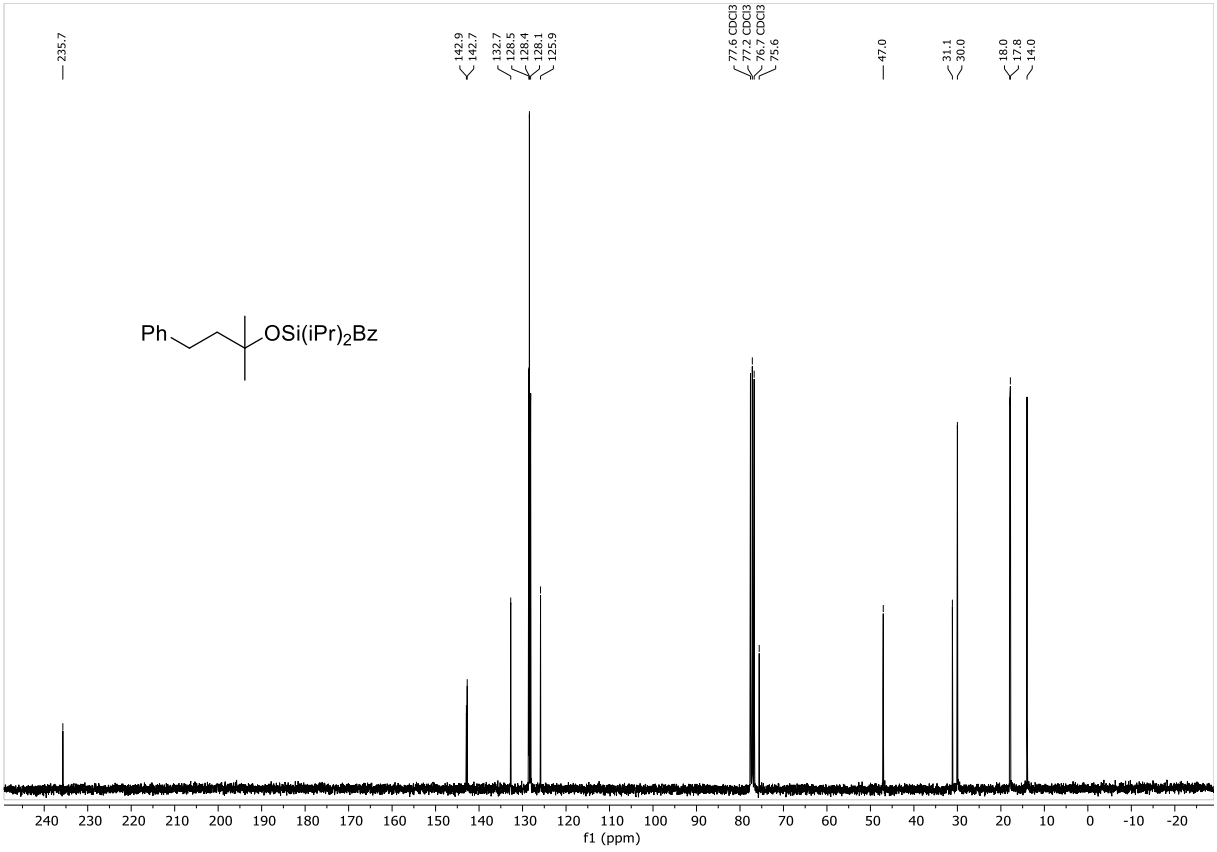
(Diisopropyl((4-phenylbutan-2-yl)oxy)silyl)(phenyl)methanone 8b



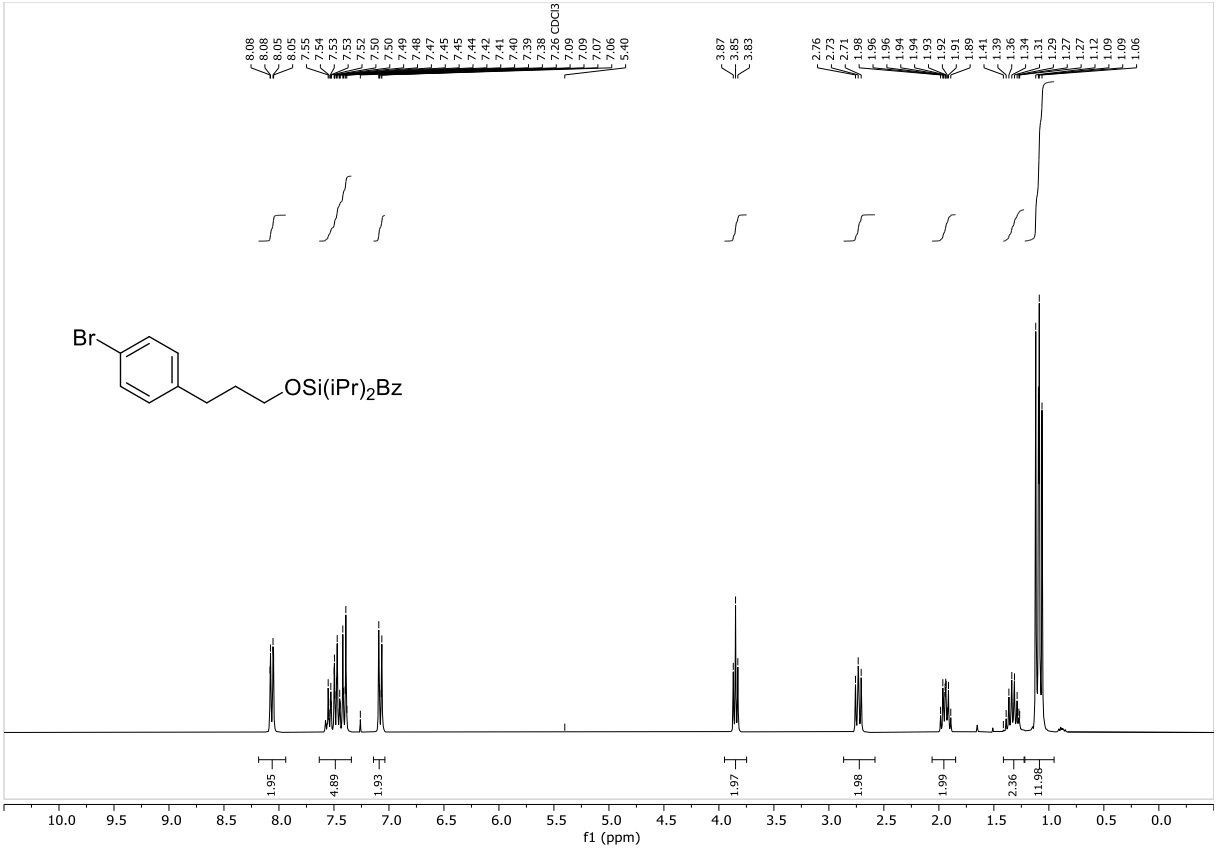


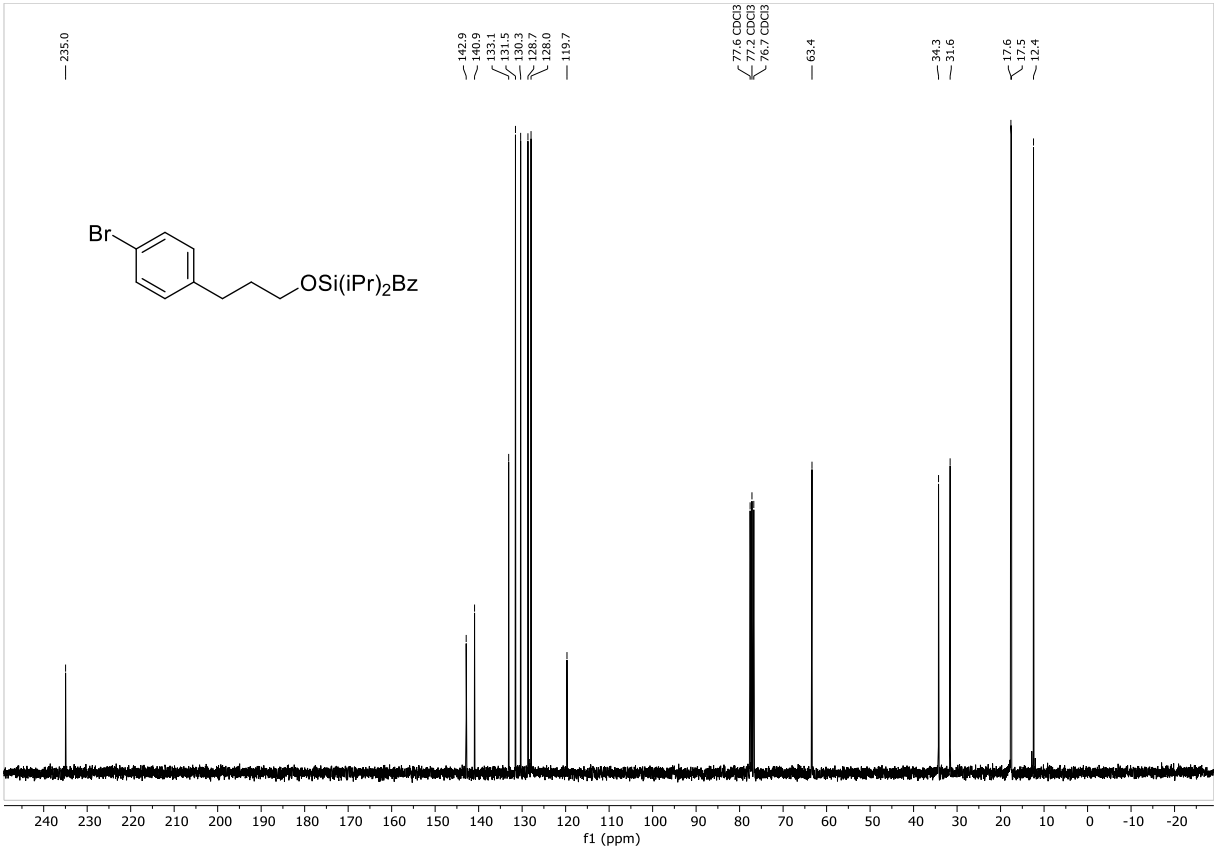
(Diisopropyl((2-methyl-4-phenylbutan-2-yl)oxy)silyl)(phenyl)methanone 8c



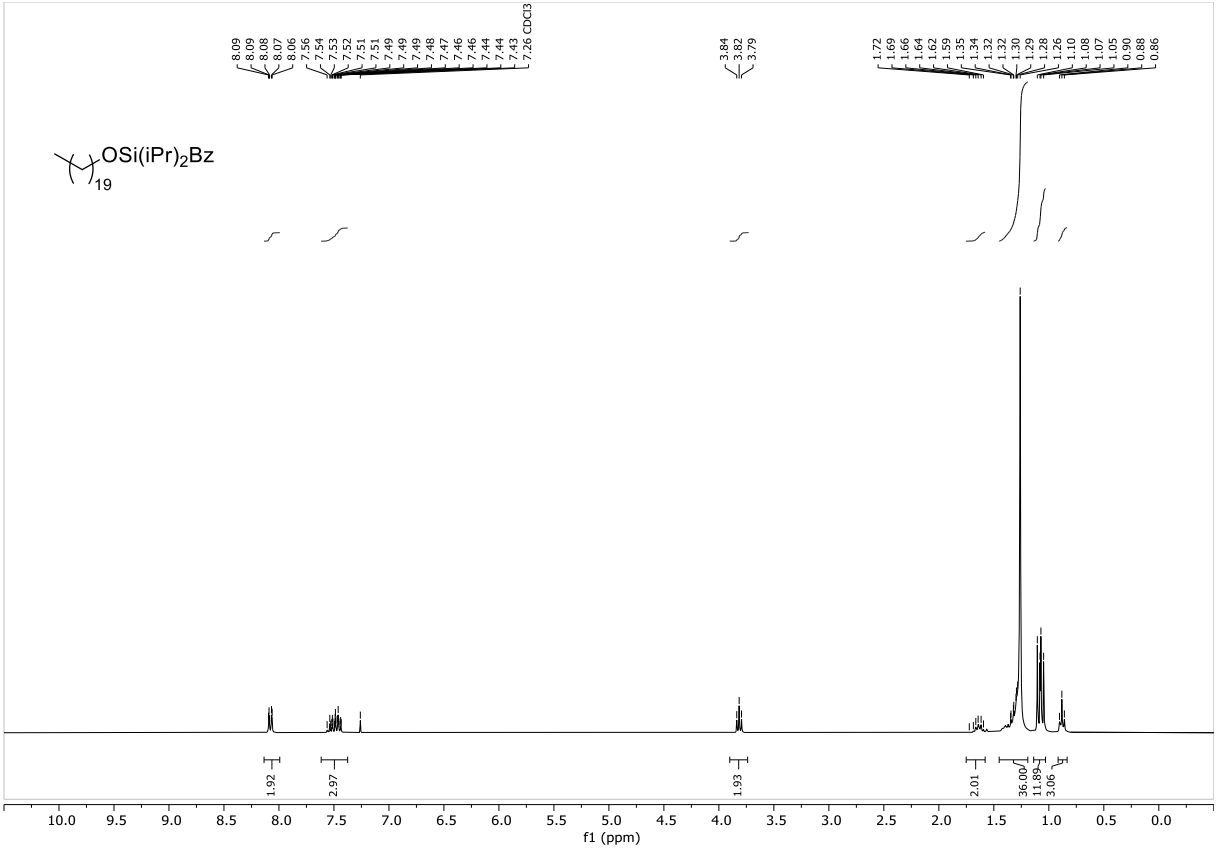


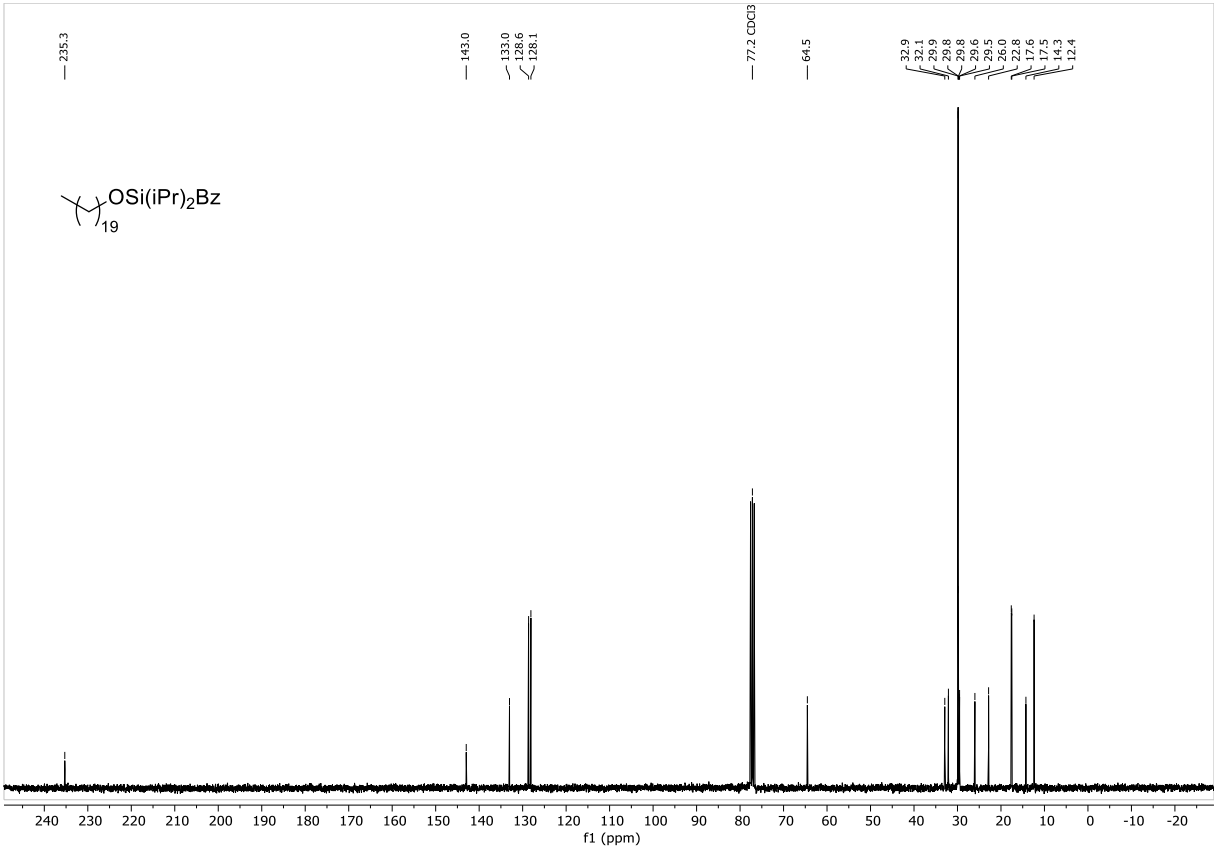
((3-(4-Bromophenyl)propoxy)diisopropylsilyl)(phenyl)methanone 8d



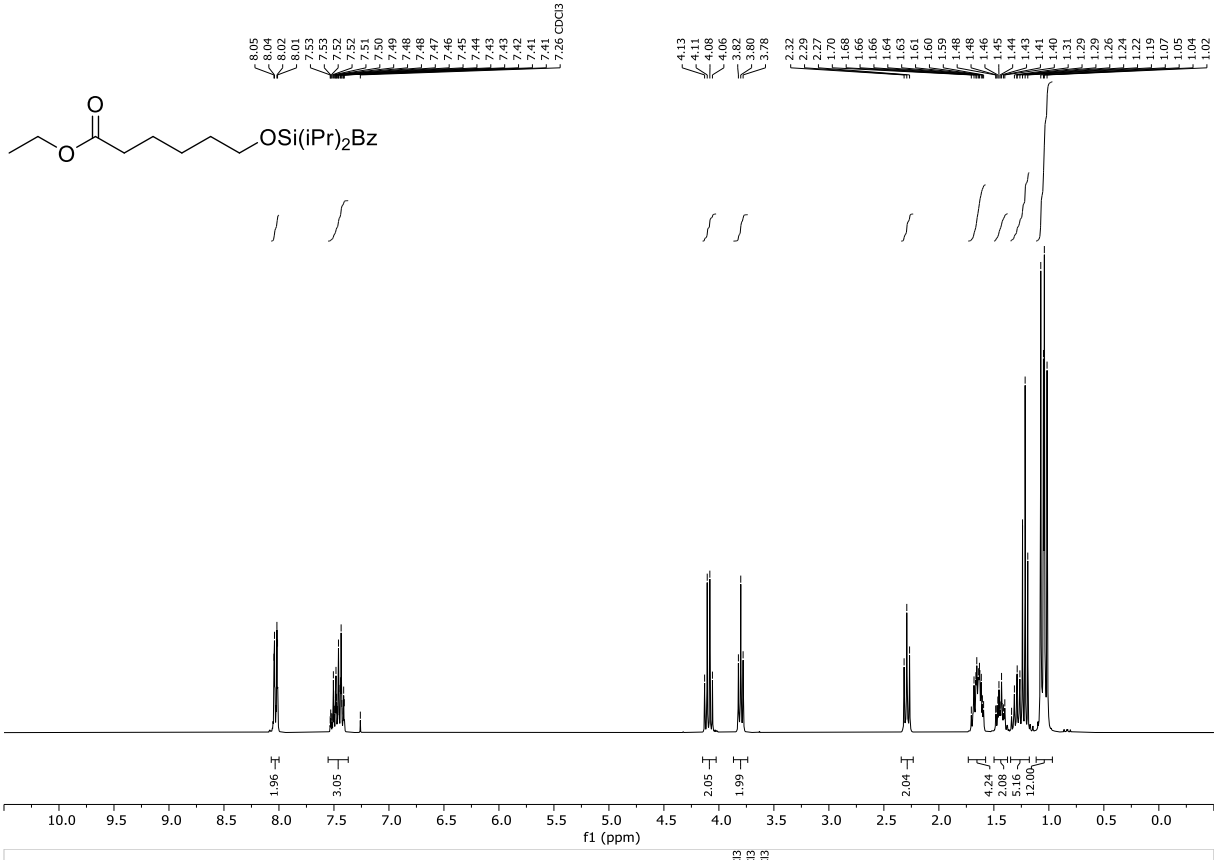


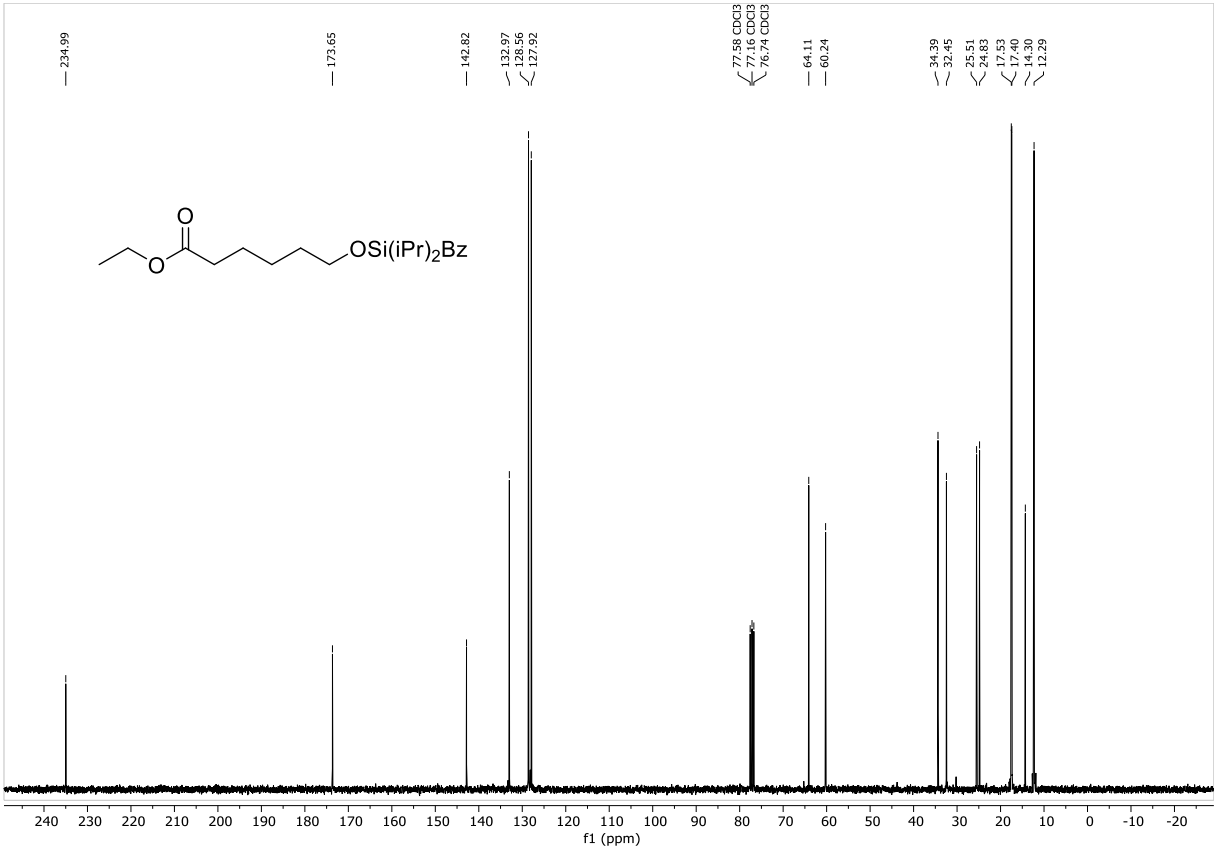
((Icosyloxy)diisopropylsilyl)(phenyl)methanone 8e



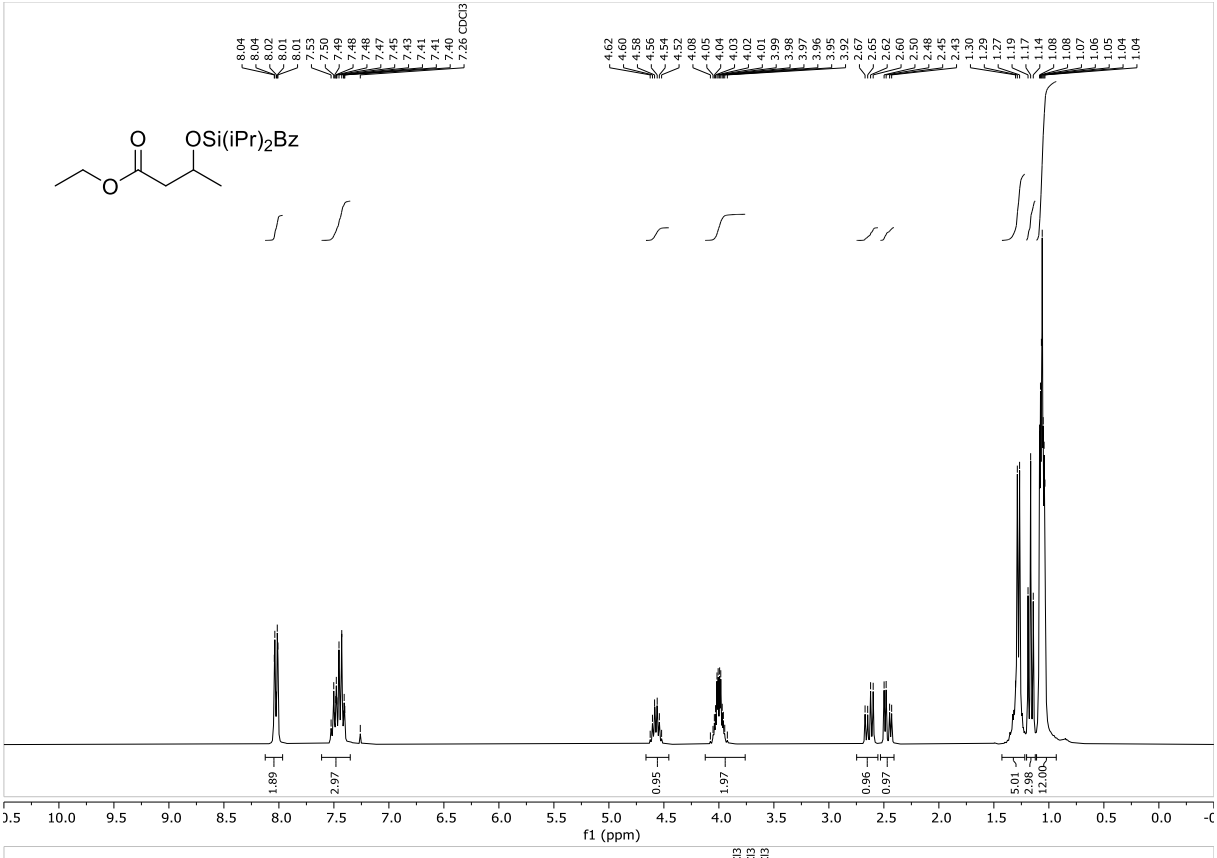


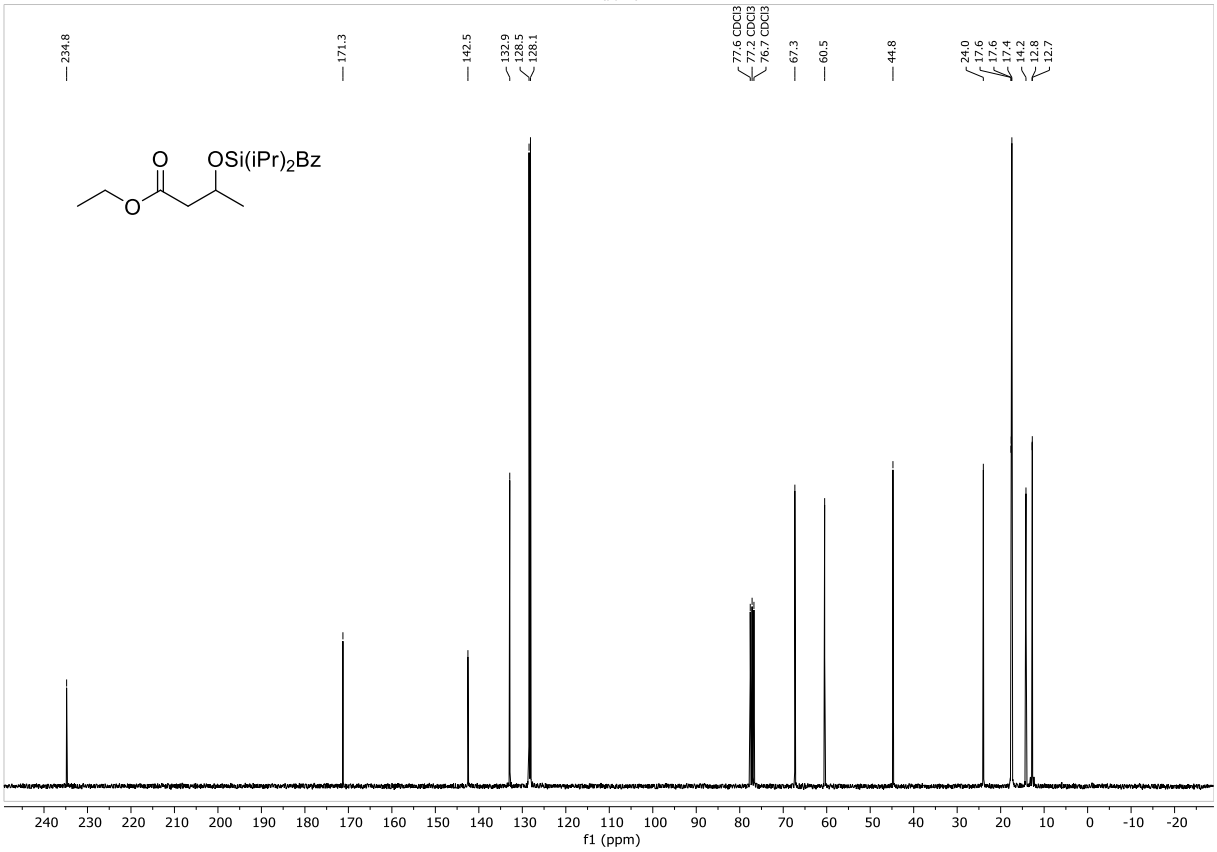
Ethyl 6-((benzoyldiisopropylsilyl)oxy)hexanoate 8f



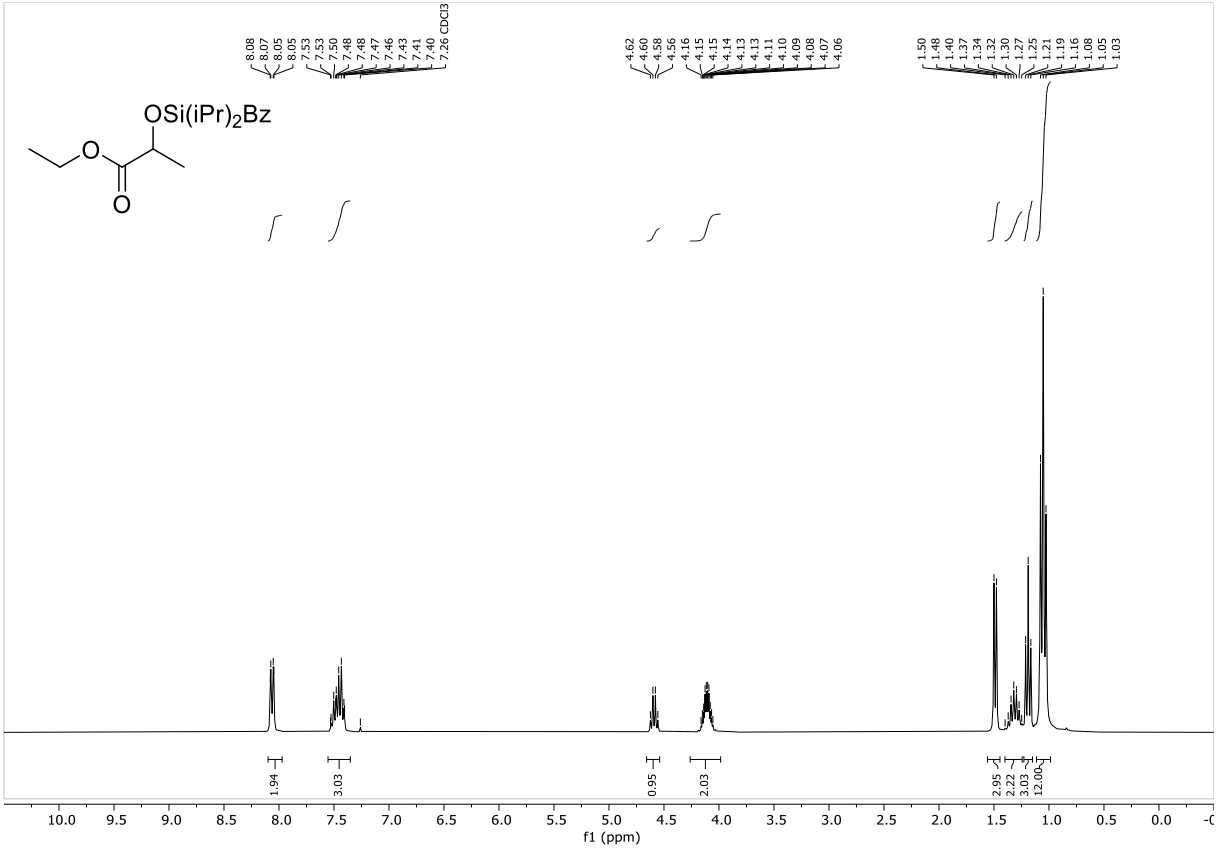


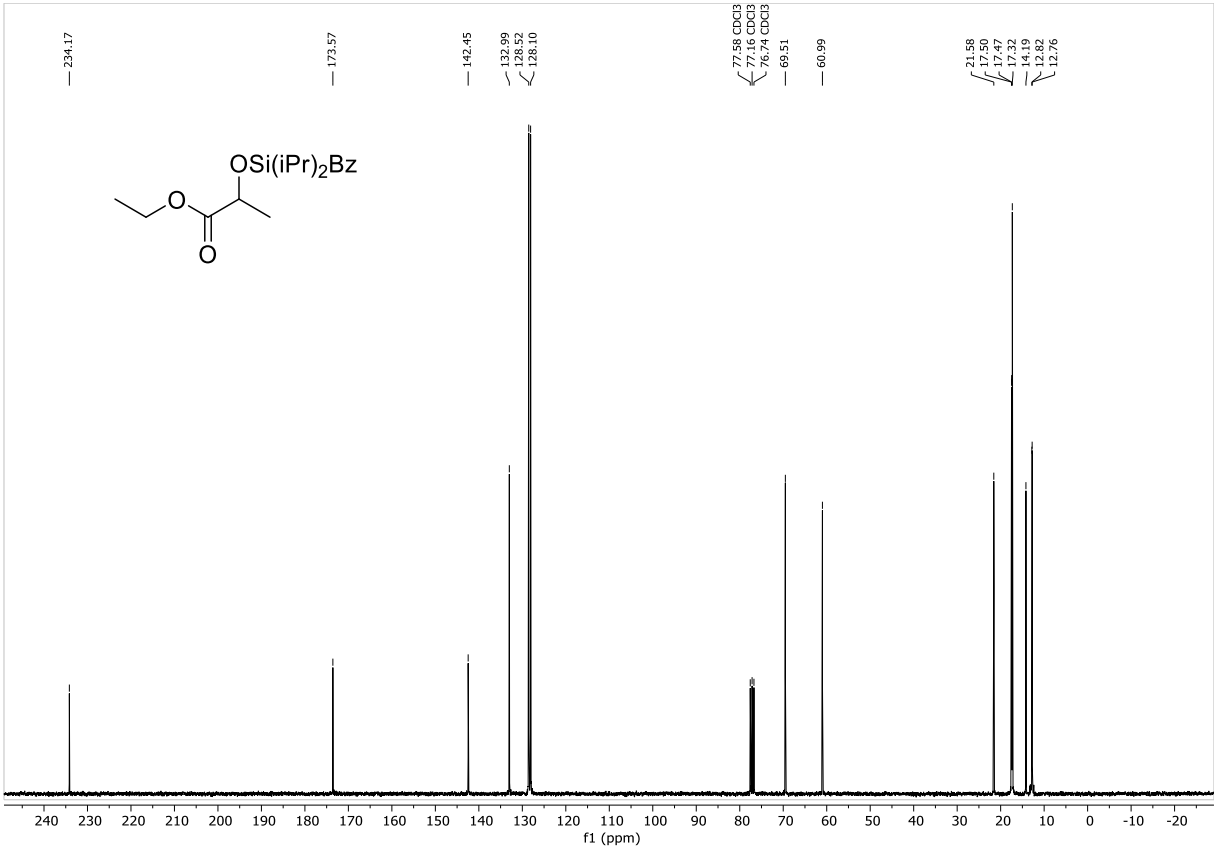
Ethyl 3-((benzoyldiisopropylsilyl)oxy)butanoate 8g



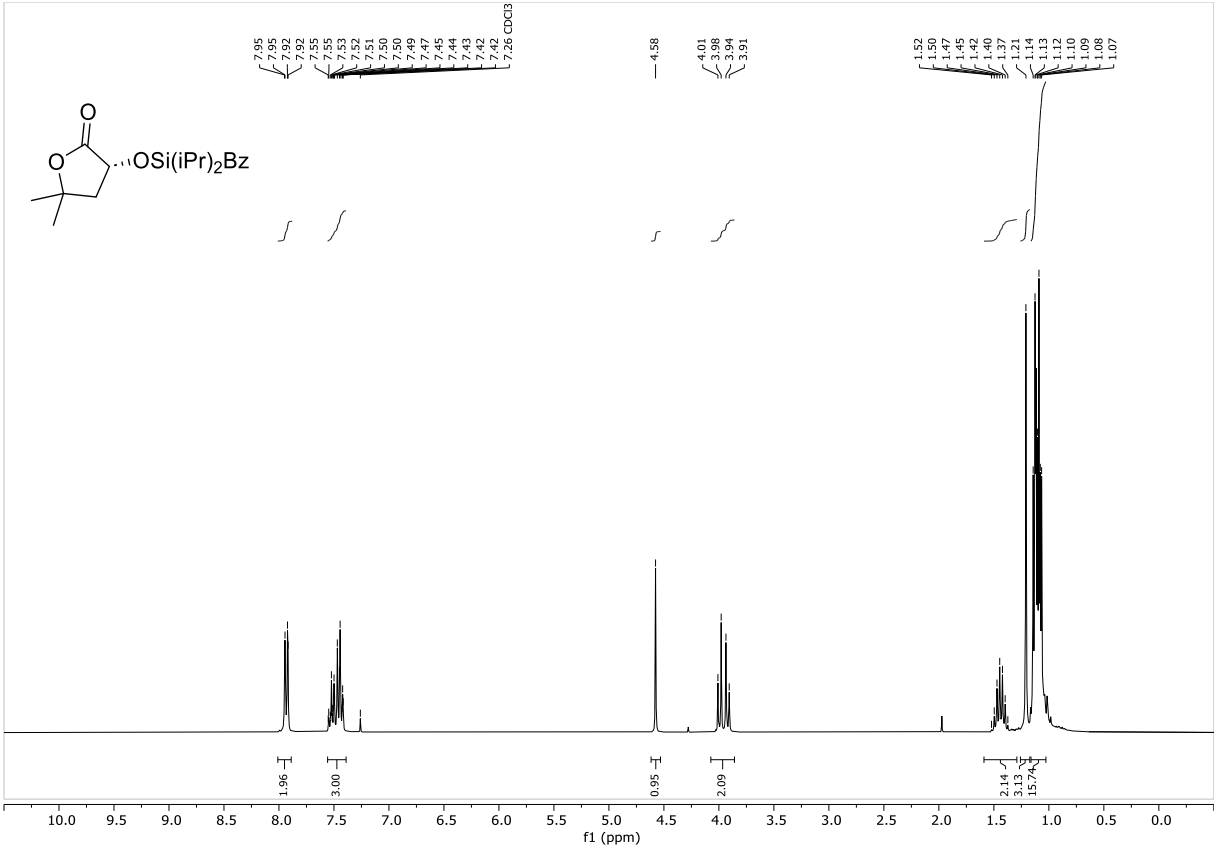


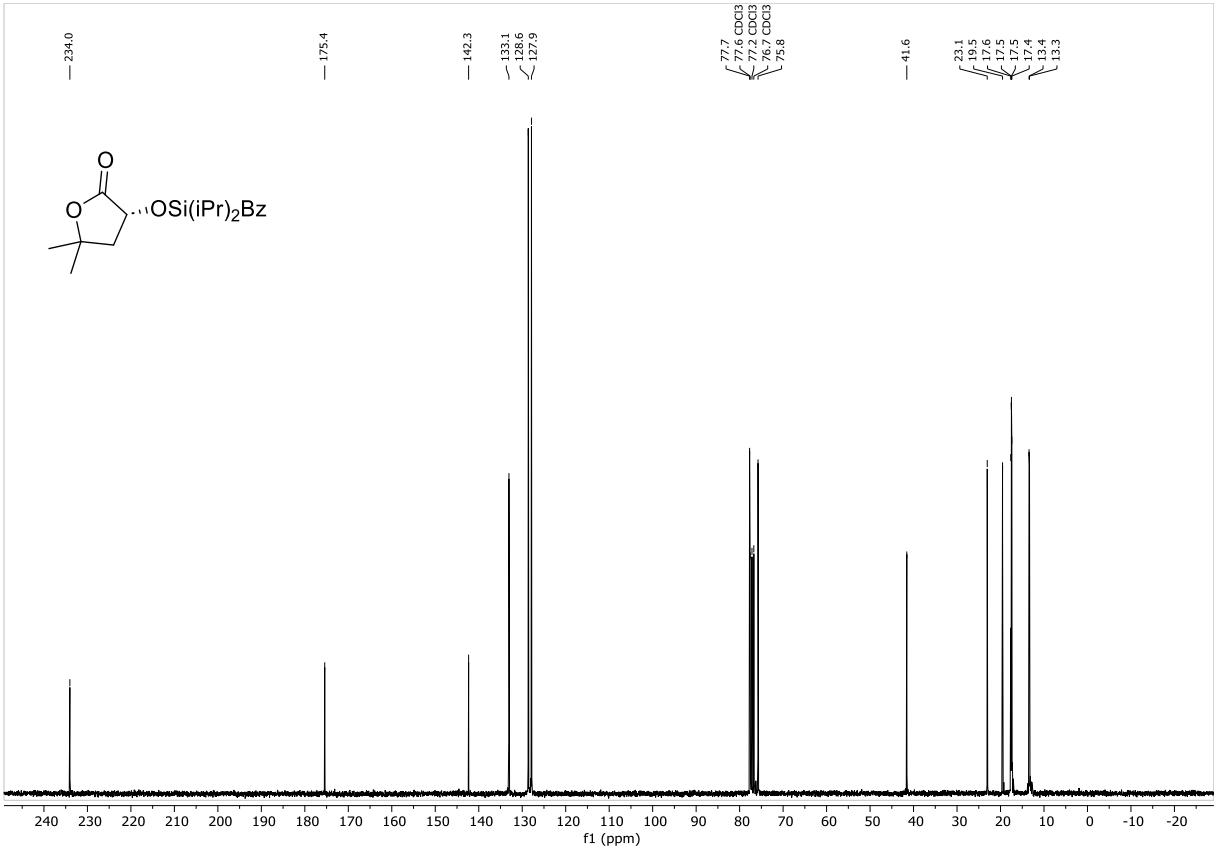
Ethyl 2-((benzoyldiisopropylsilyl)oxy)propanoate 8h



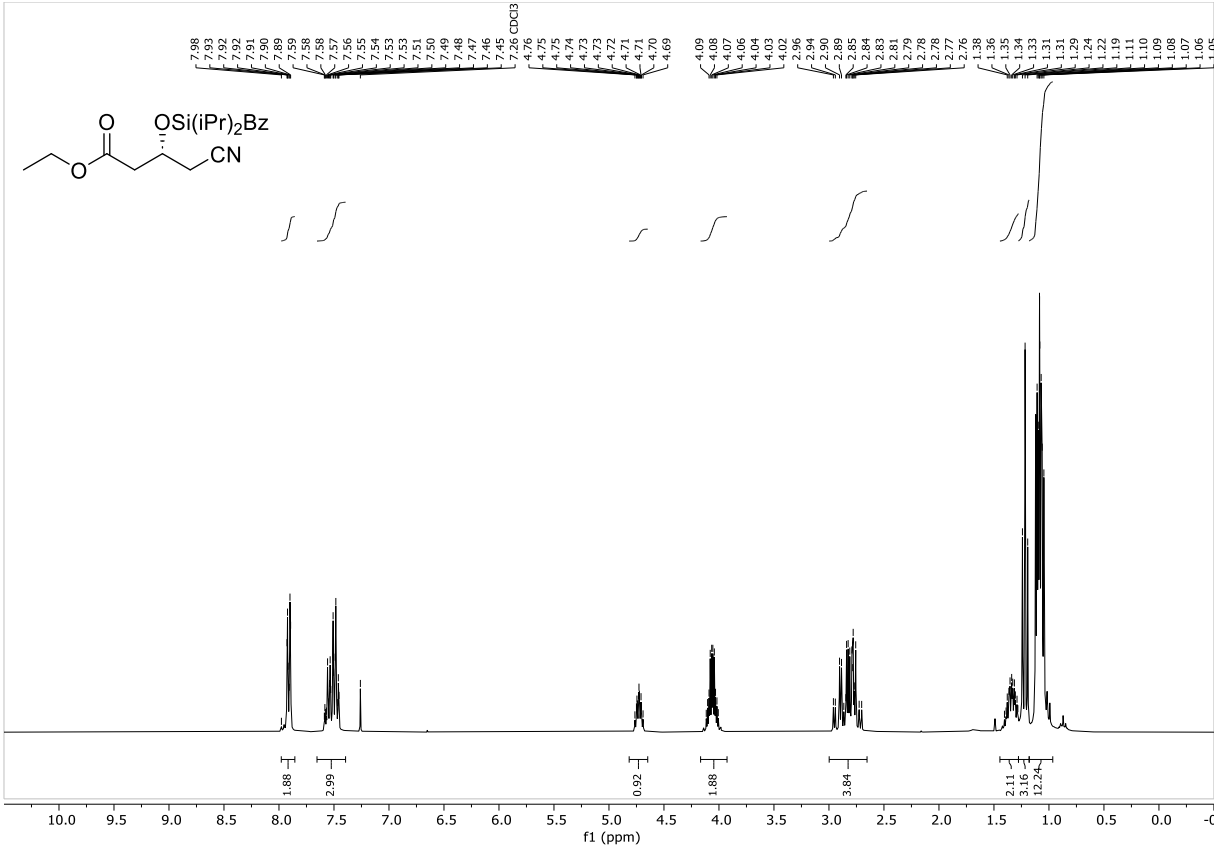


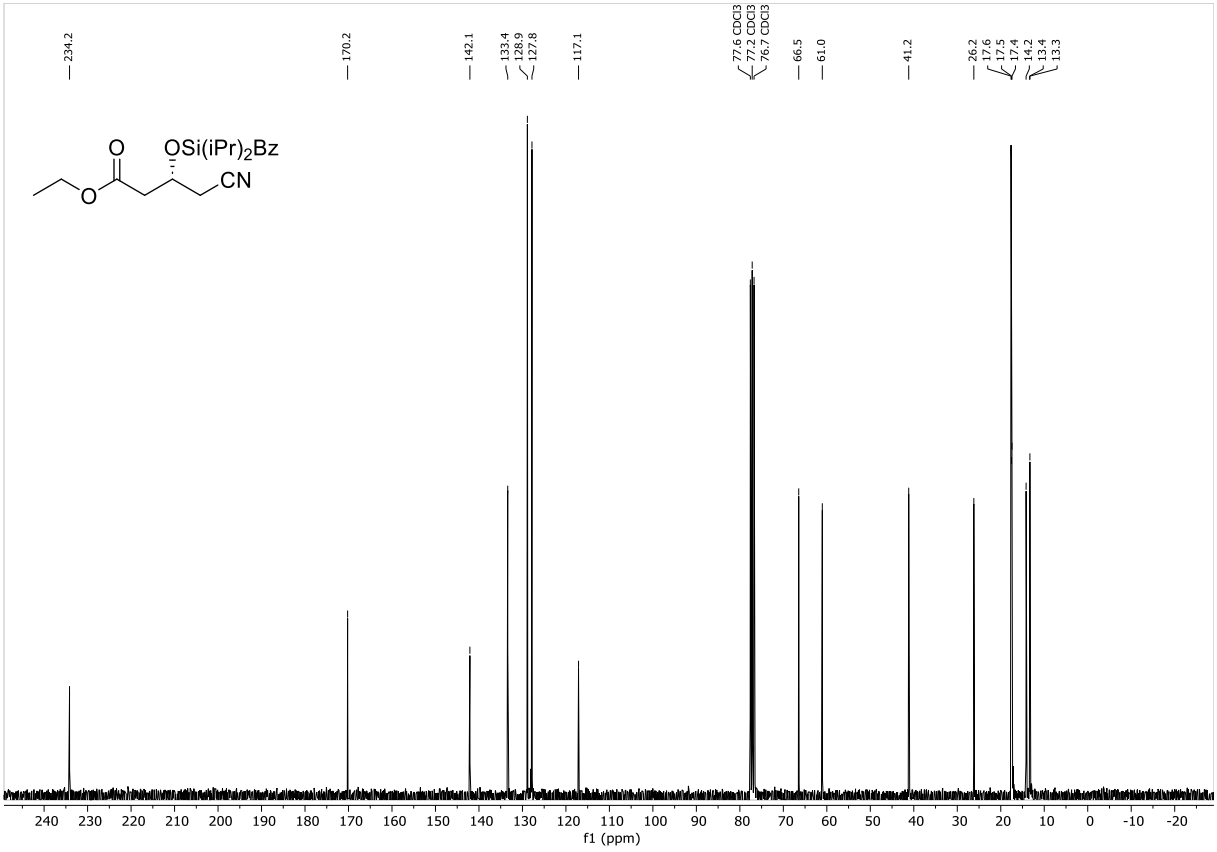
(R)-3-((Benzoyldiisopropylsilyl)oxy)-5,5-dimethyldihydrofuran-2(3H)-one 8i



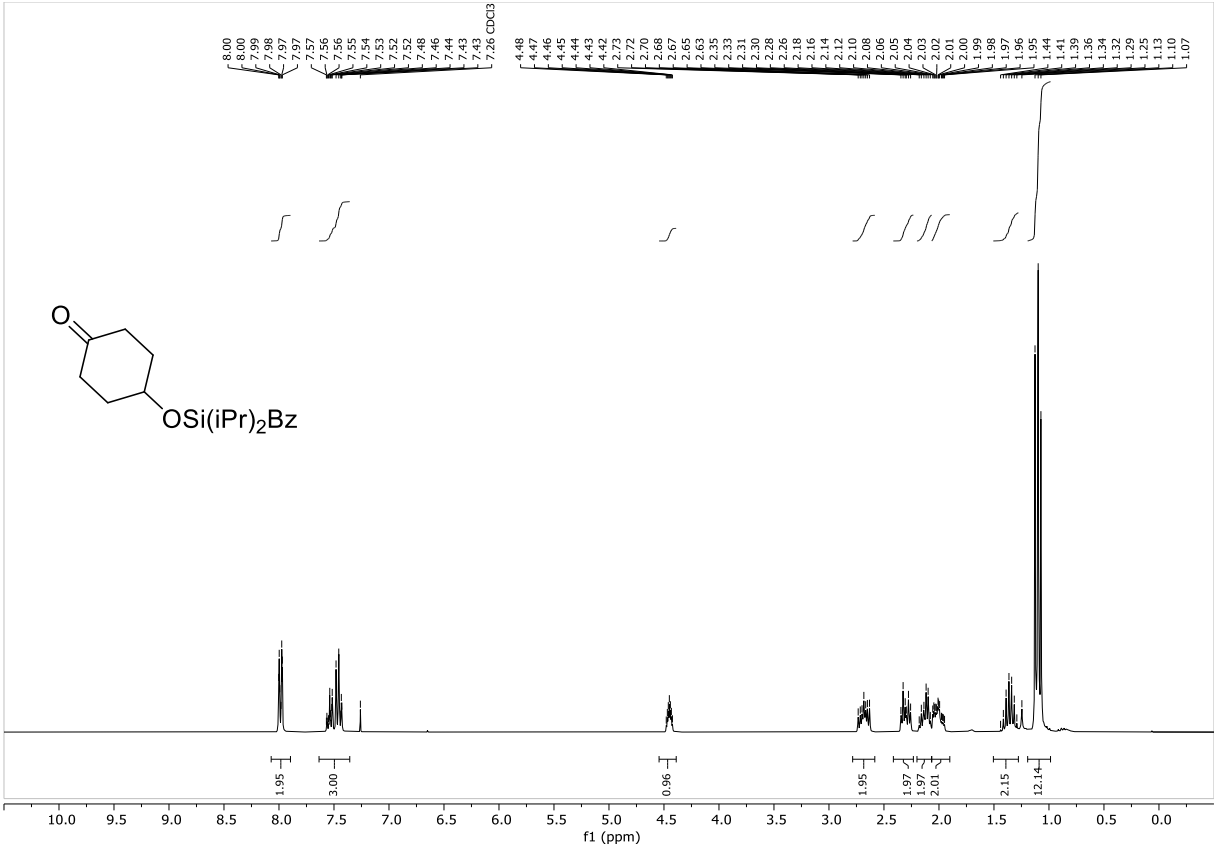


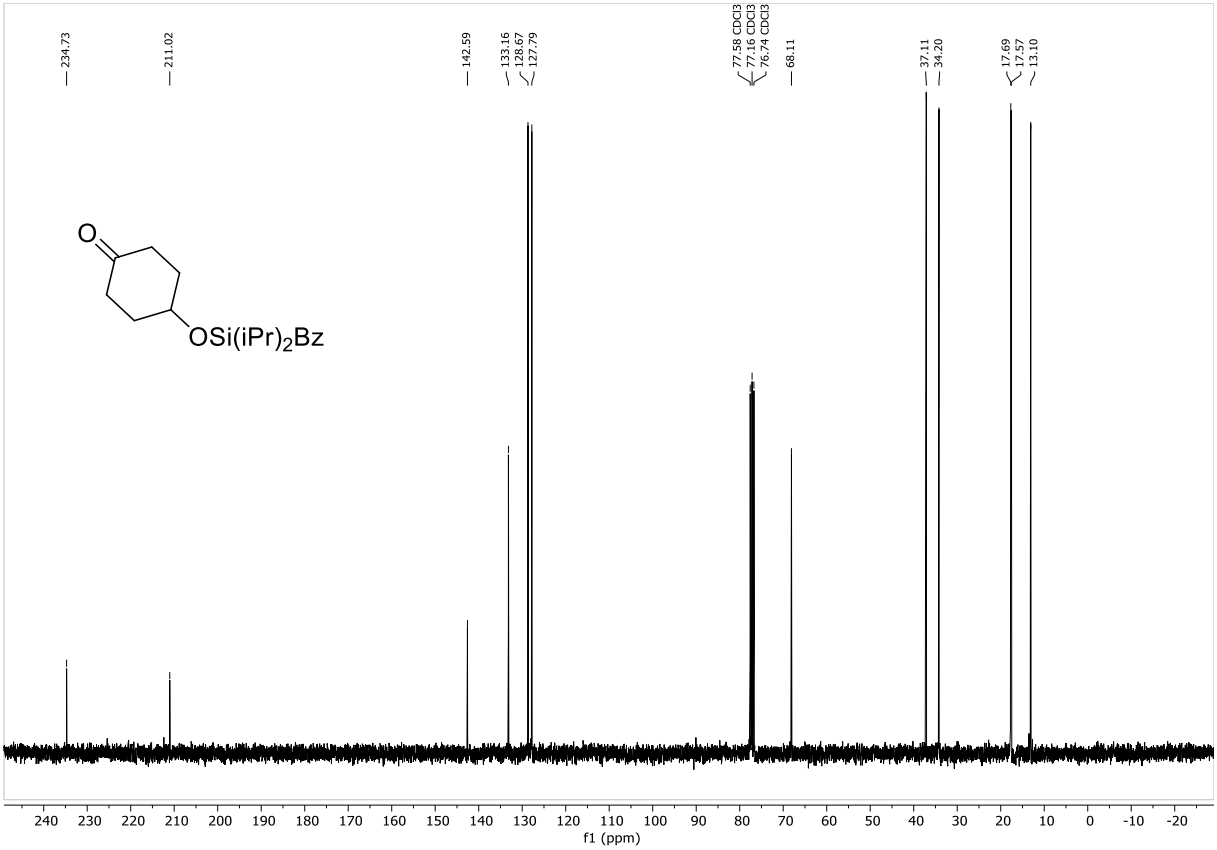
Ethyl (R)-3-((benzoyldiisopropylsilyl)oxy)-4-cyanobutanoate 8j



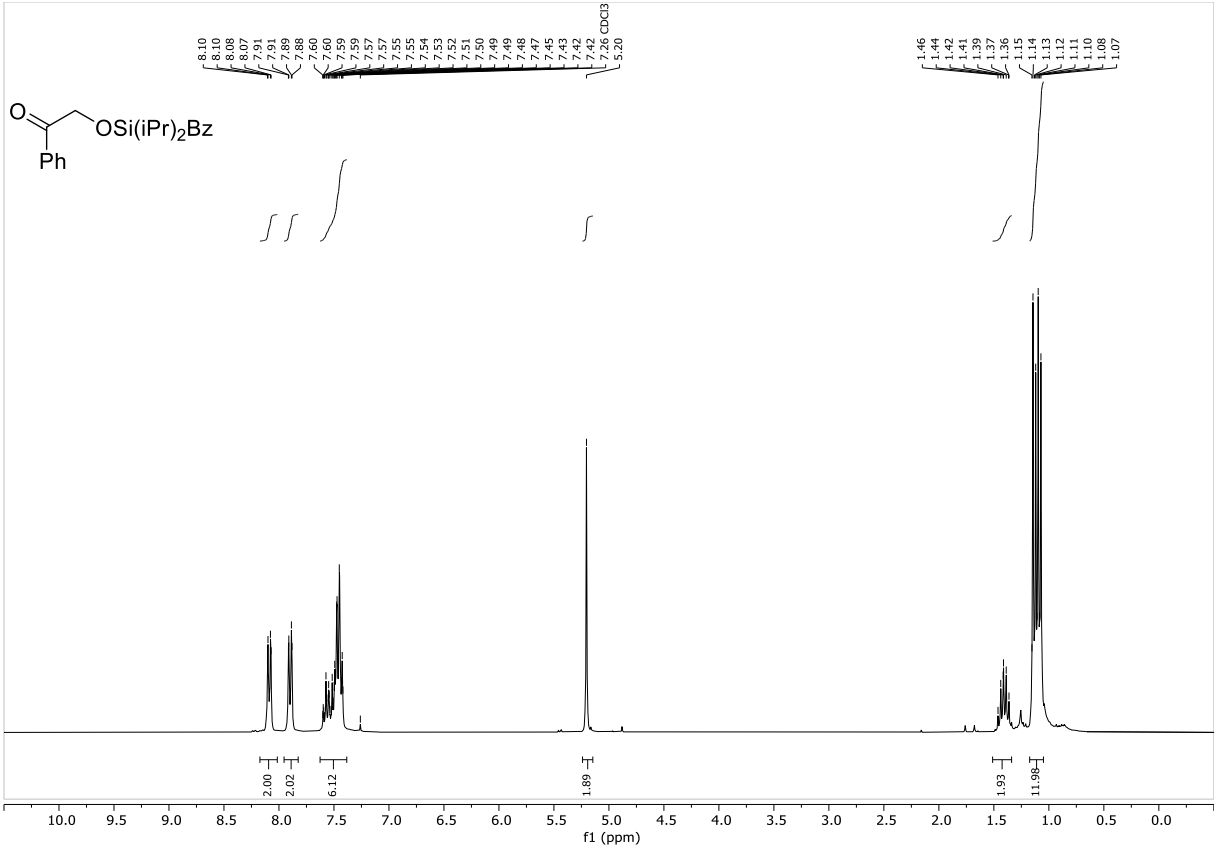


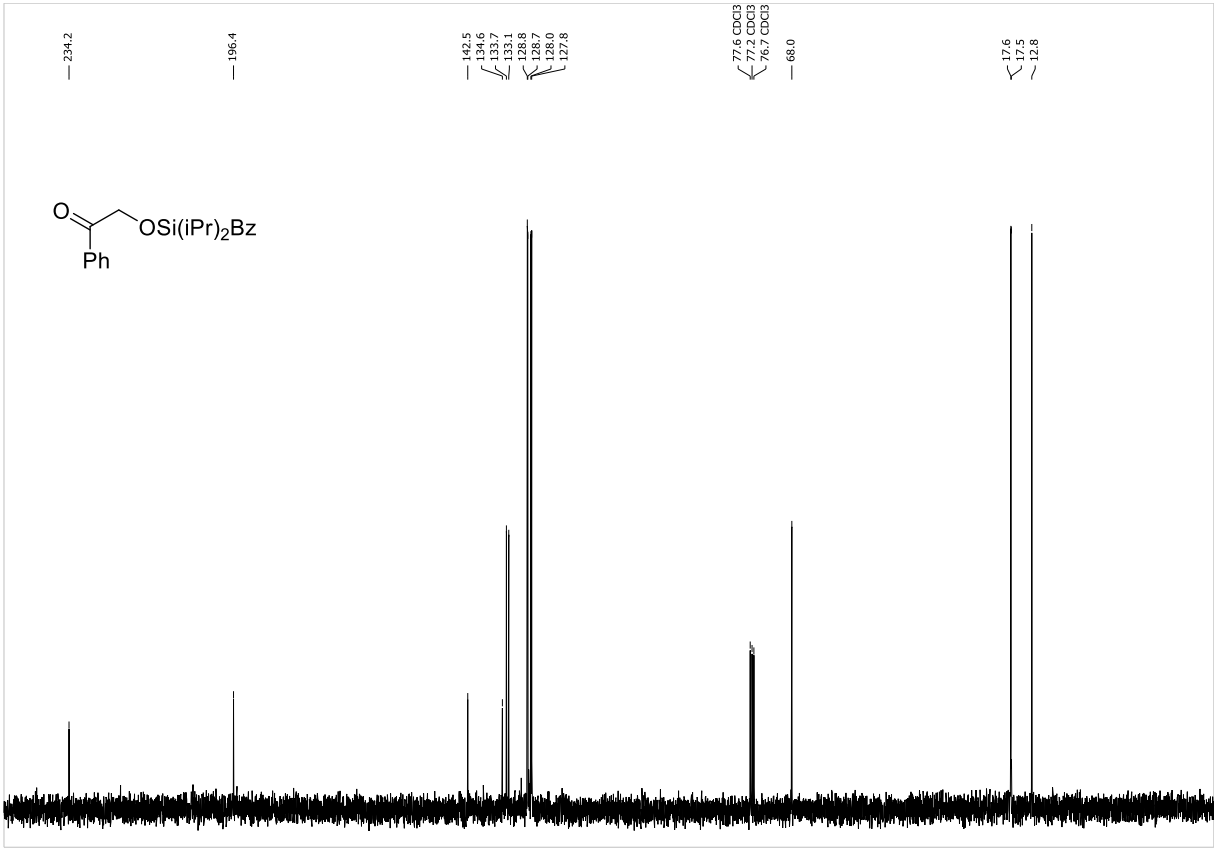
4-((Benzoyldiisopropylsilyl)oxy)cyclohexan-1-one 8k



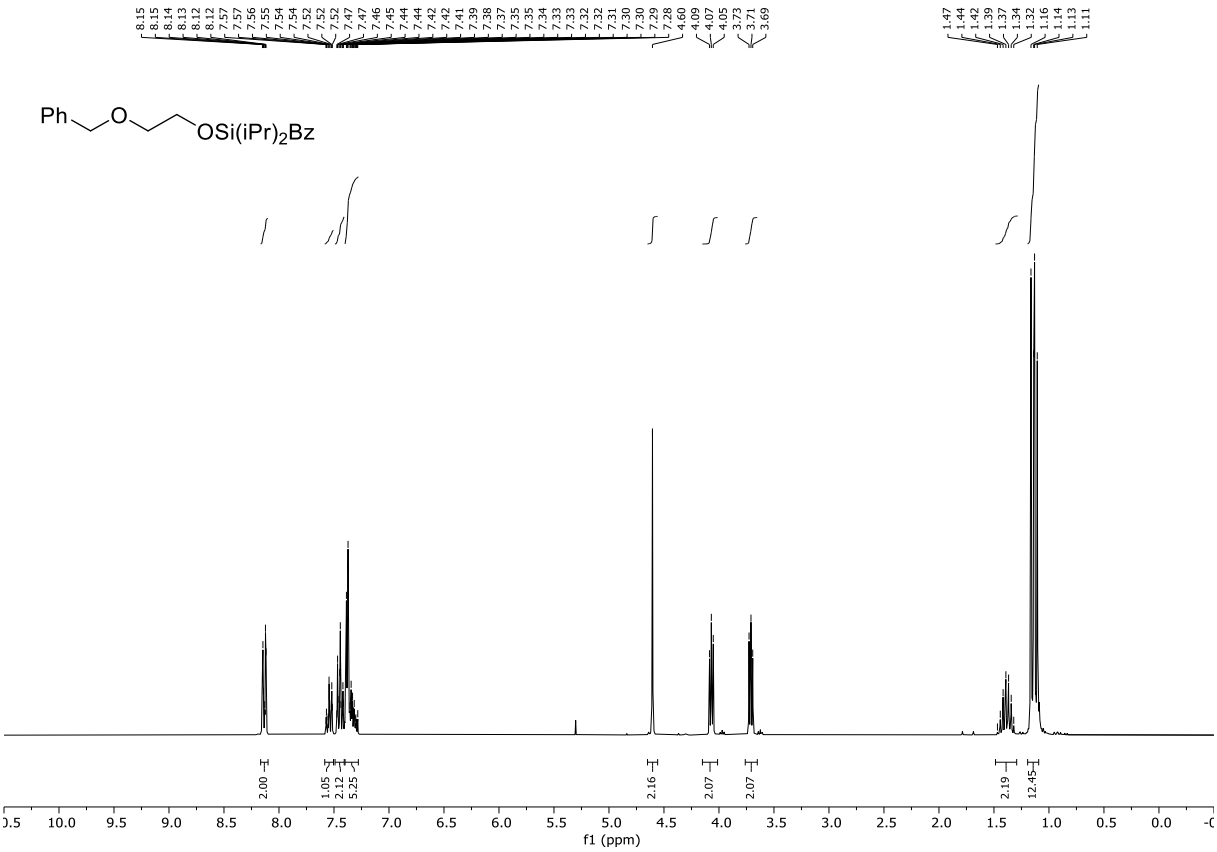


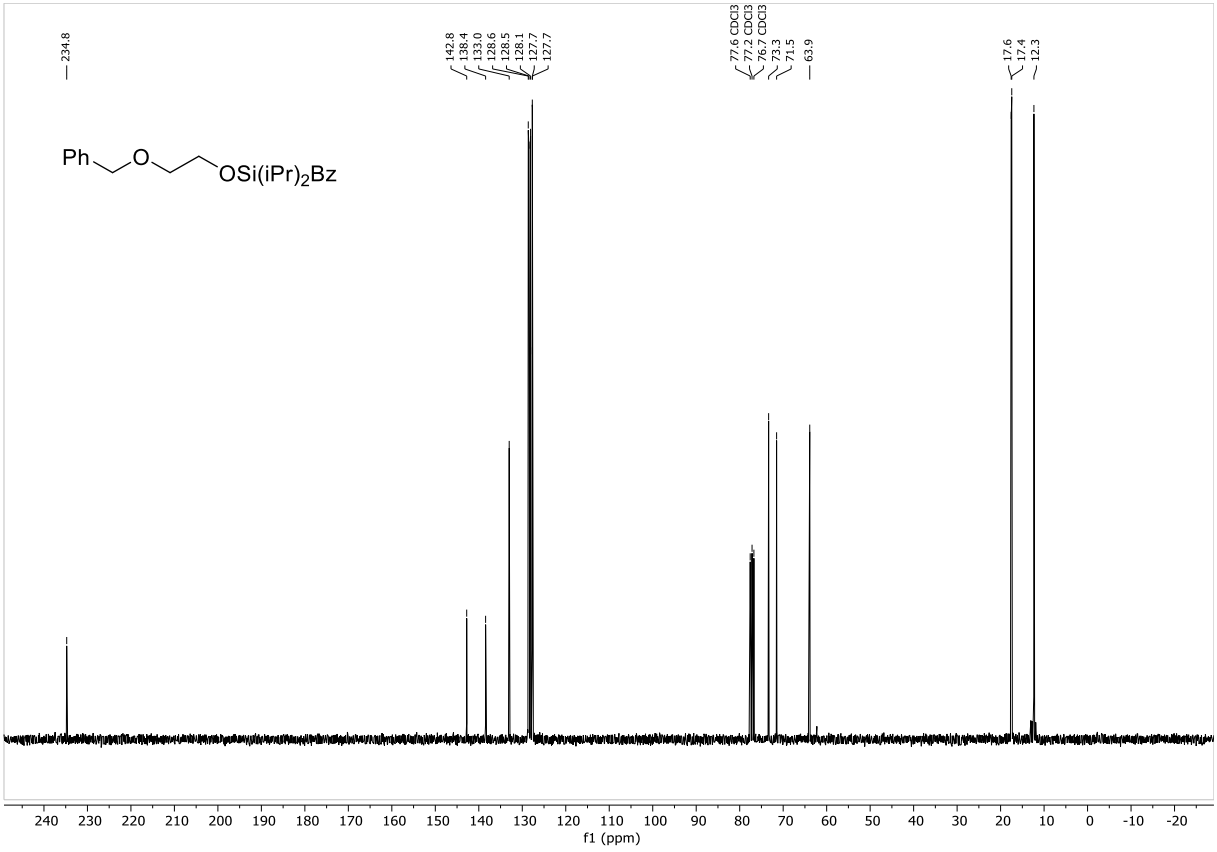
2-((Benzoyldiisopropylsilyl)oxy)-1-phenylethan-1-one 8l



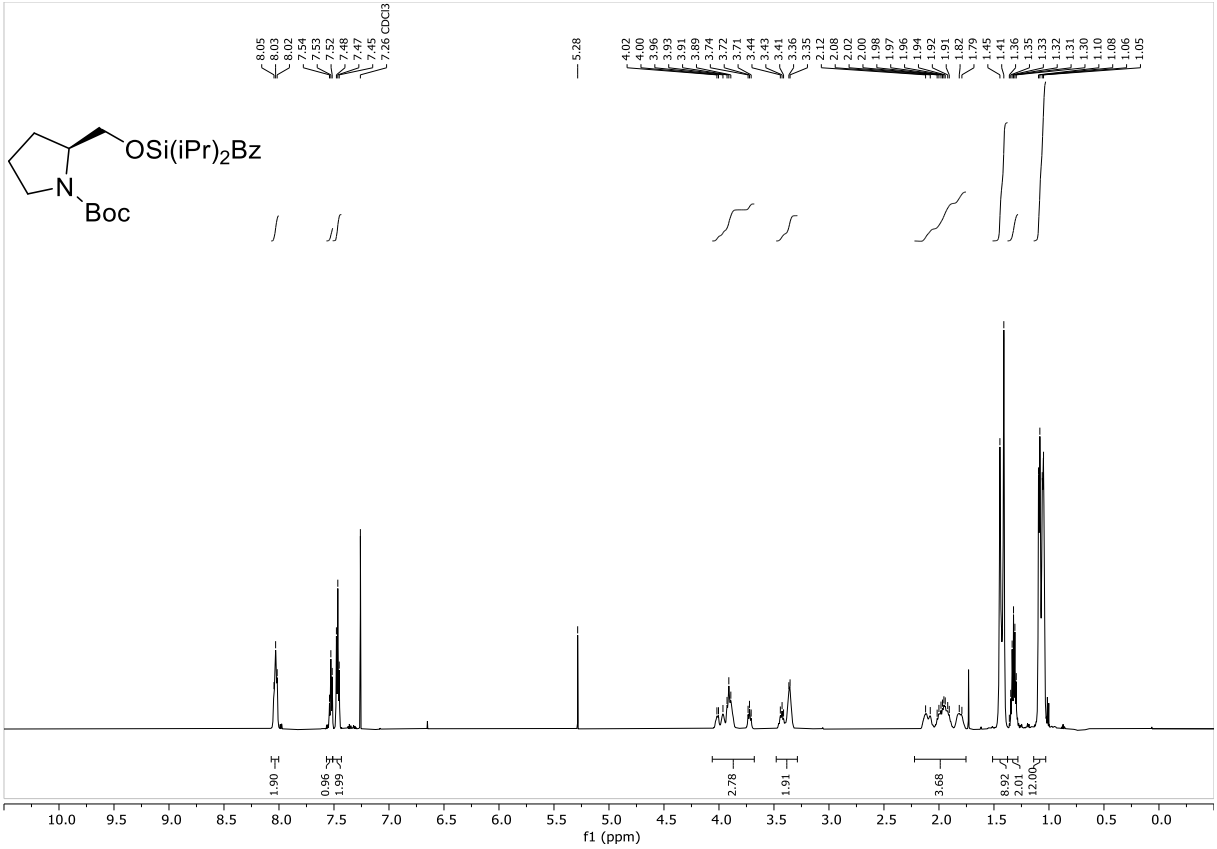


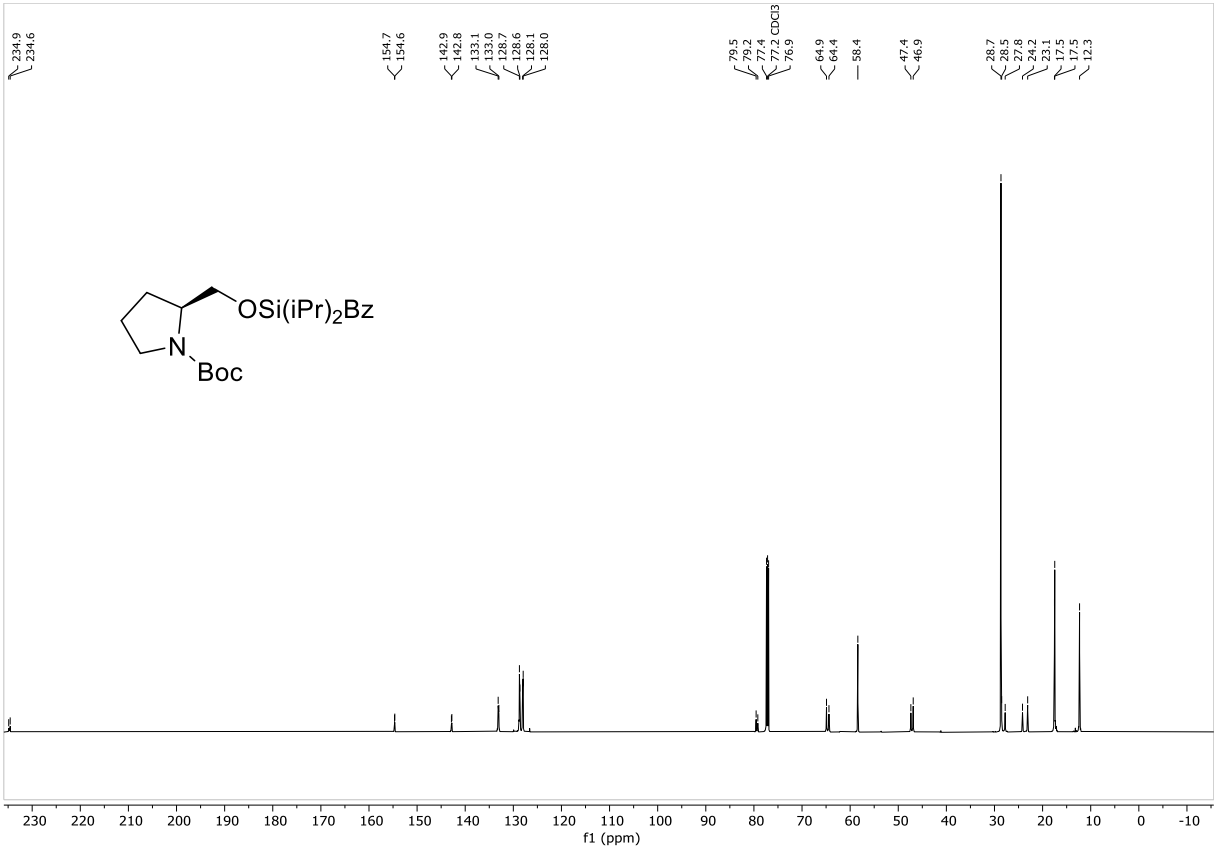
((2-(Benzyloxy)ethoxy)diisopropylsilyl)(phenyl)methanone 8m



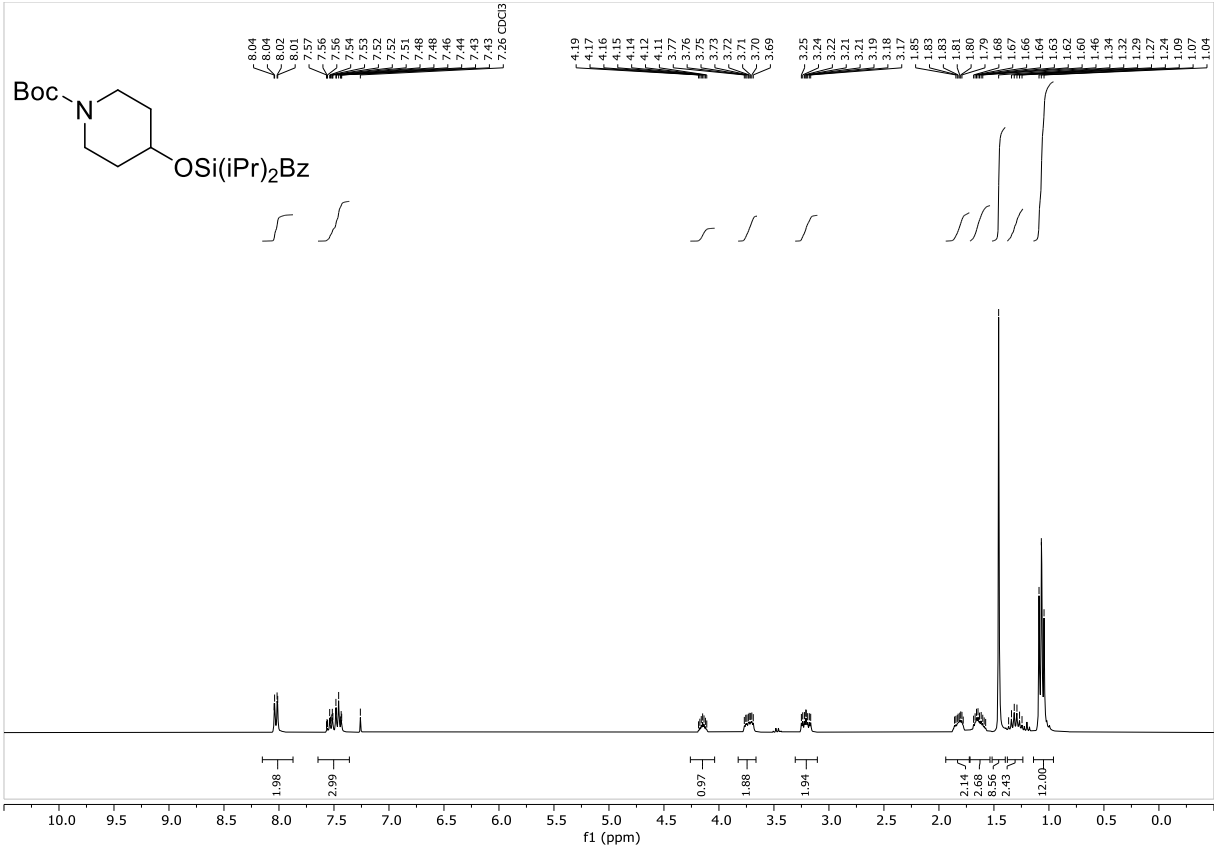


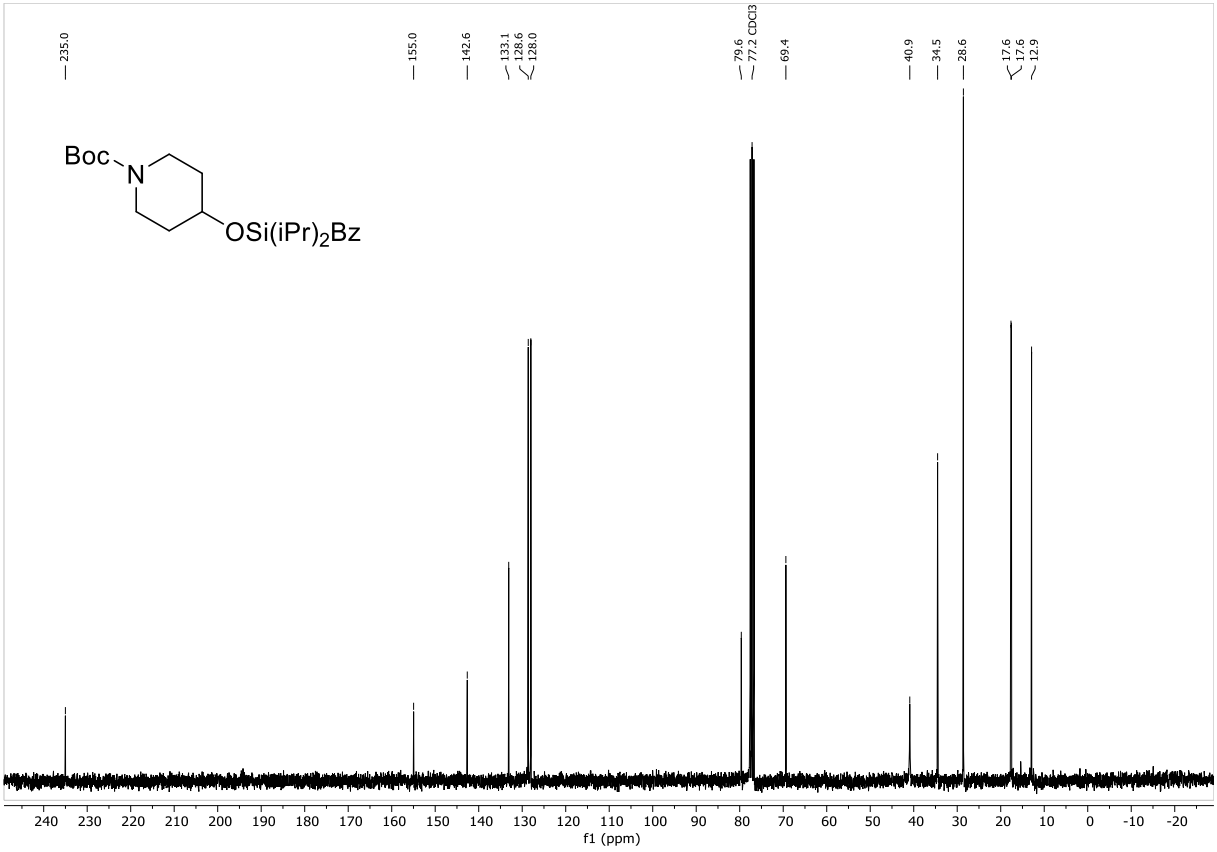
***tert*-Butyl 2-(((benzoyldiisopropylsilyl)oxy)methyl)pyrrolidine-1-carboxylate 8n**



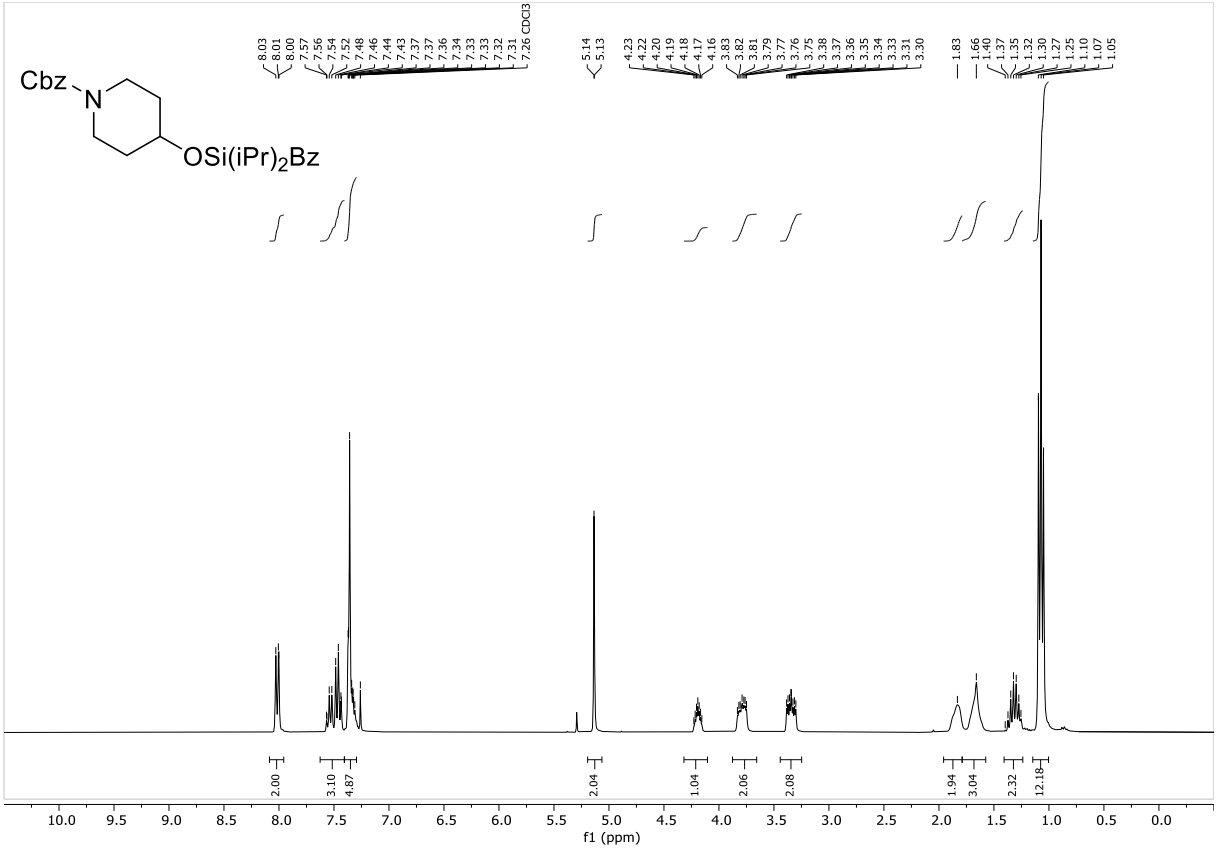


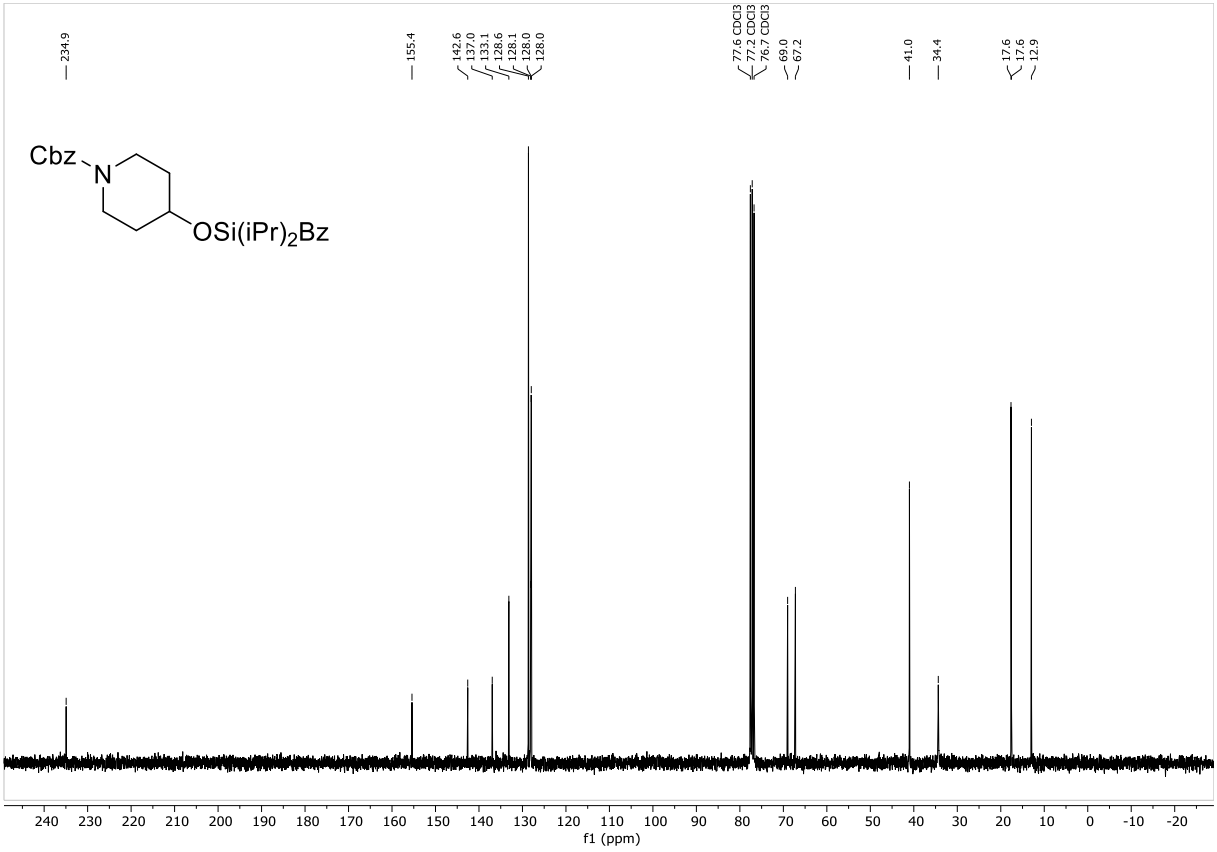
tert-Butyl 4-((benzoyldiisopropylsilyl)oxy)piperidine-1-carboxylate 8o



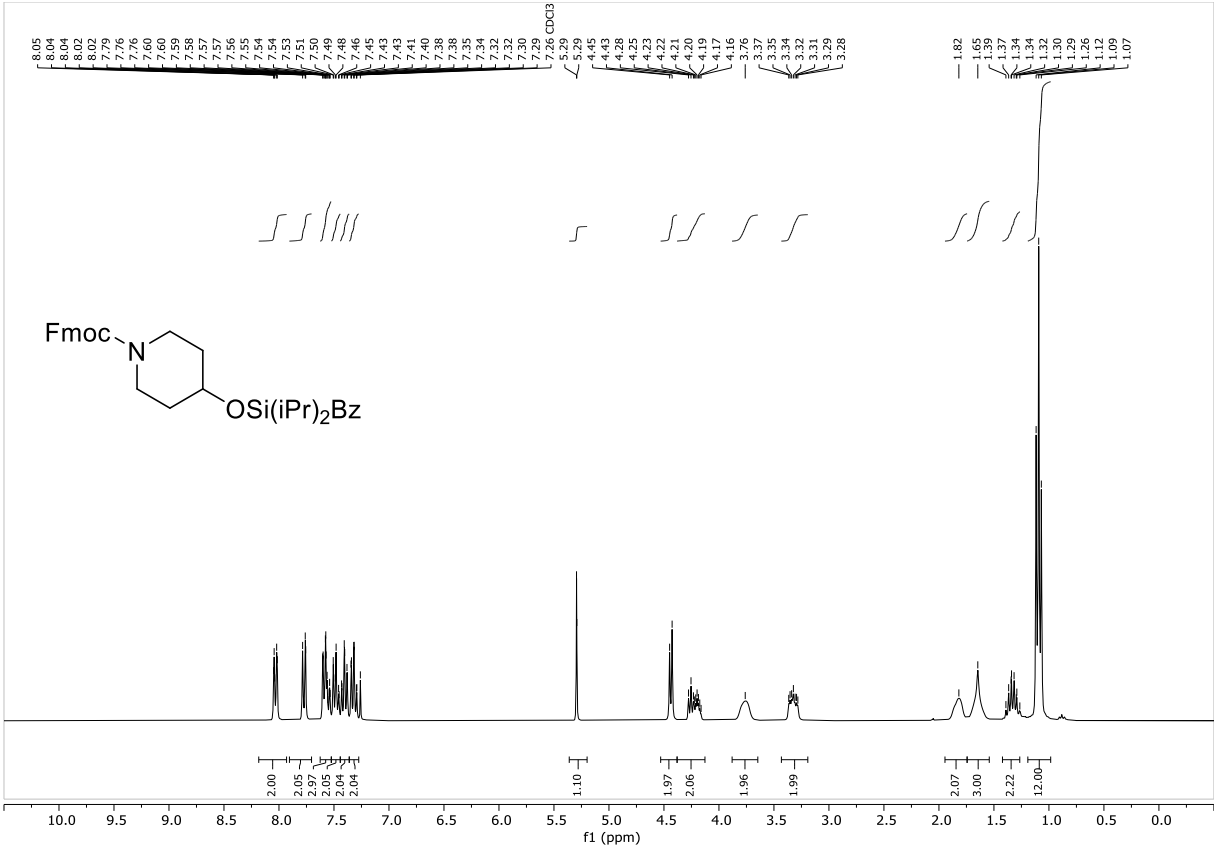


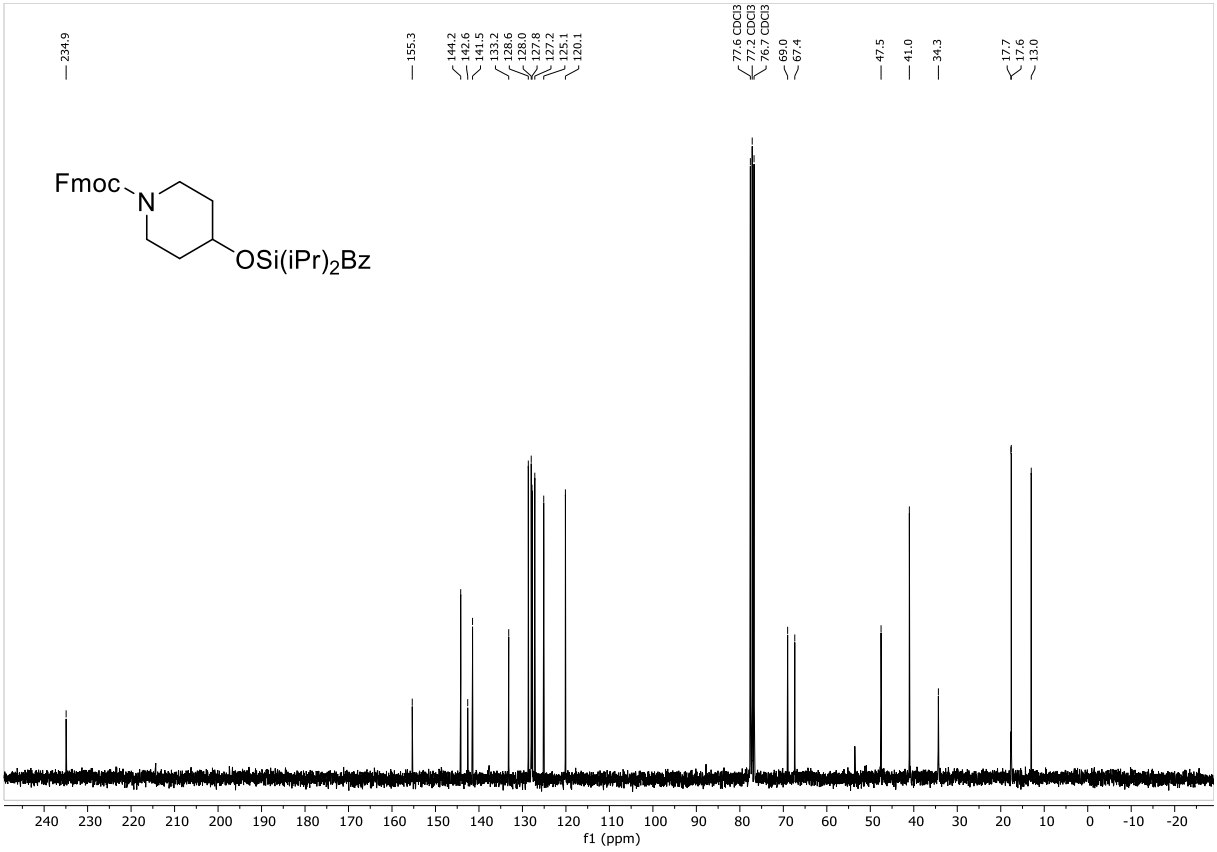
Benzyl 4-((benzoyldiisopropylsilyl)oxy)piperidine-1-carboxylate 8p



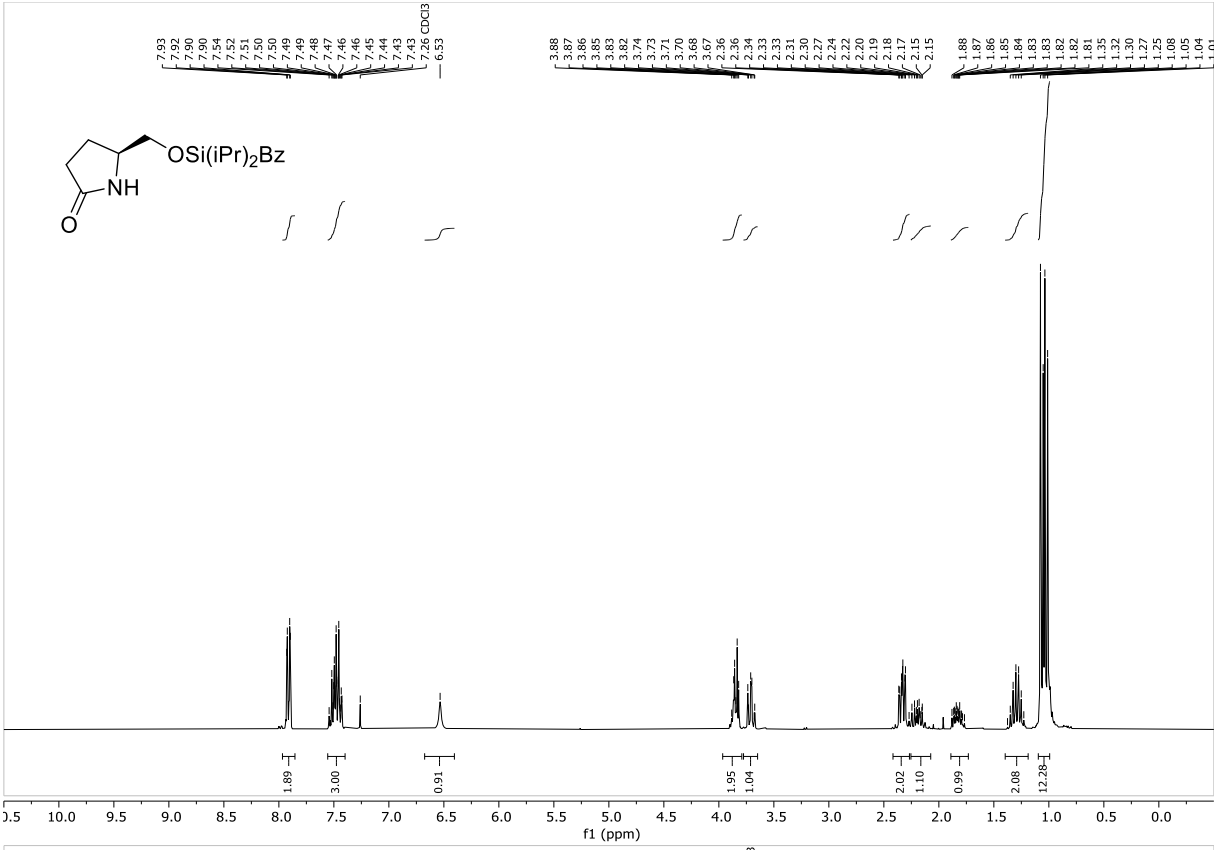


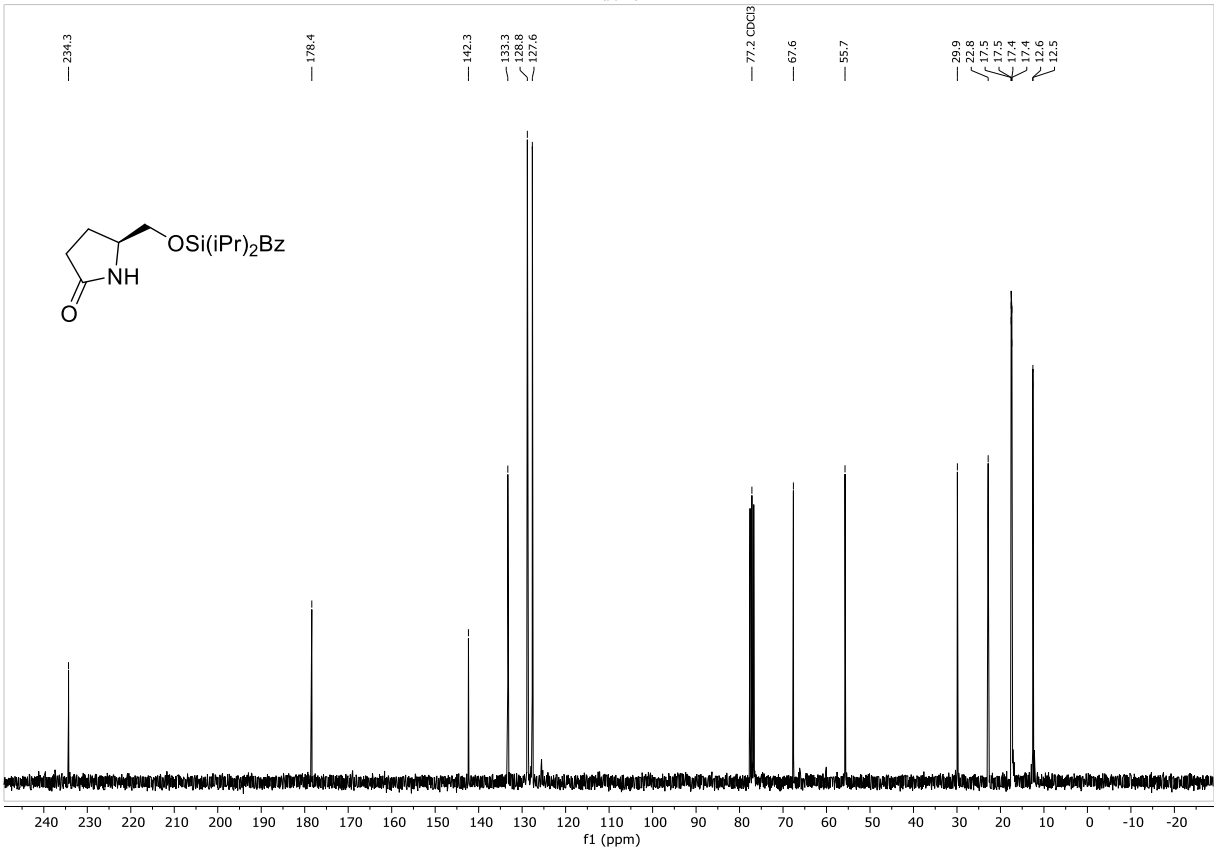
(9H-Fluoren-9-yl)methyl 4-((benzoyldiisopropylsilyl)oxy)piperidine-1-carboxylate 8q



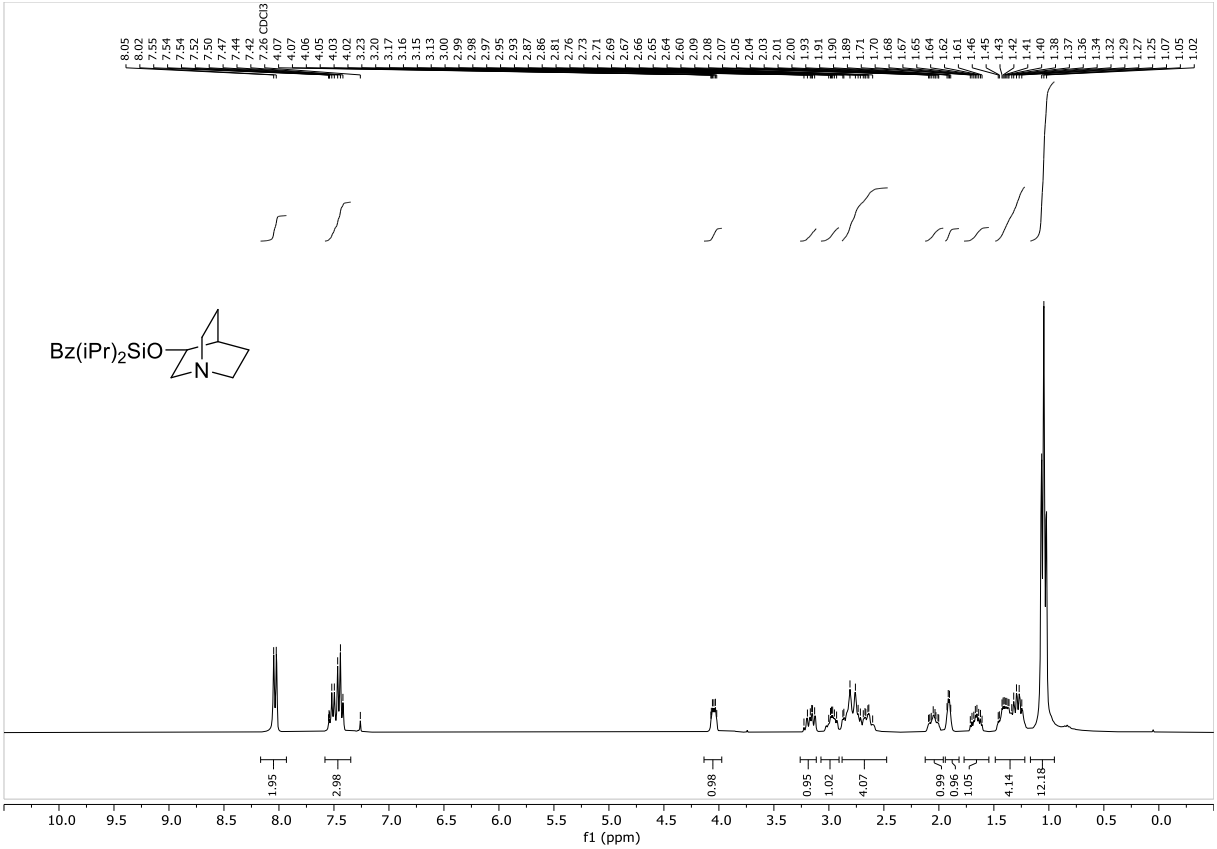


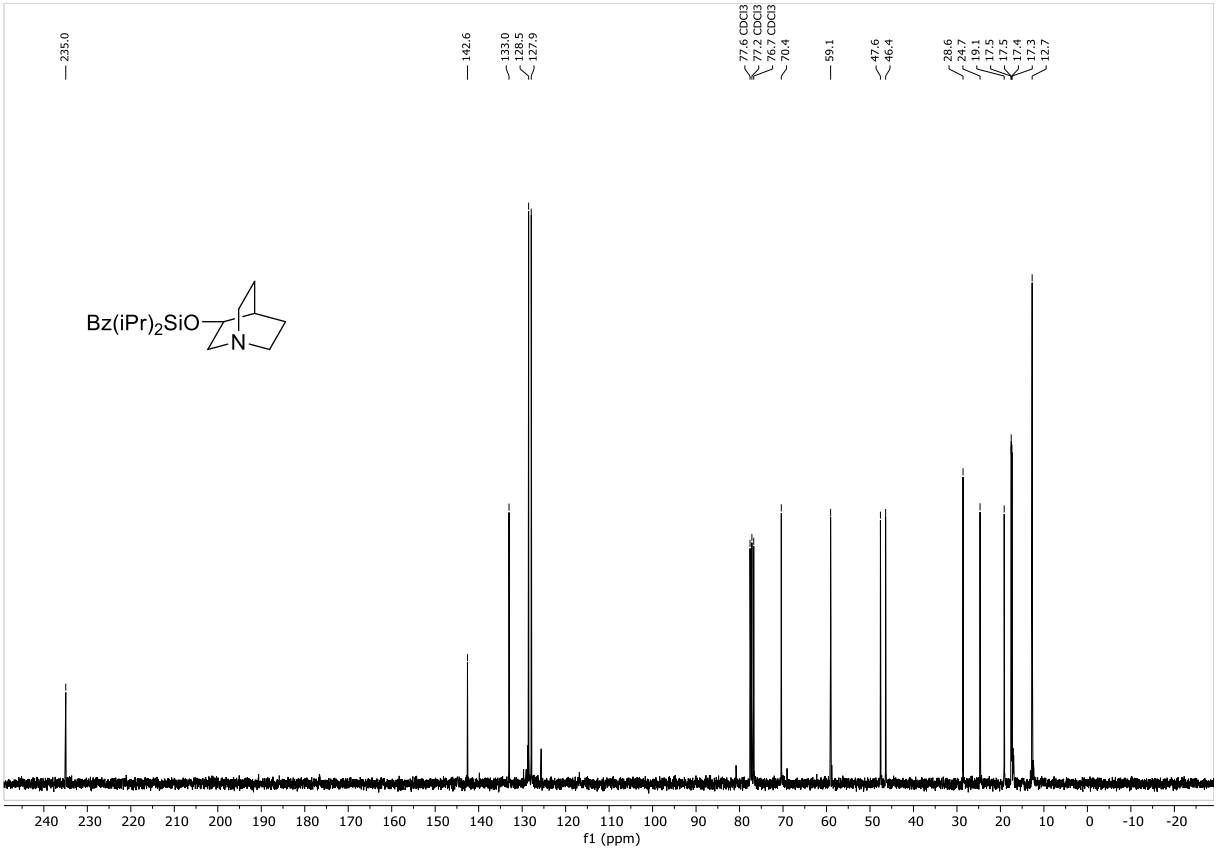
(S)-5-(((Benzoyldiisopropylsilyl)oxy)methyl)pyrrolidin-2-one 8r



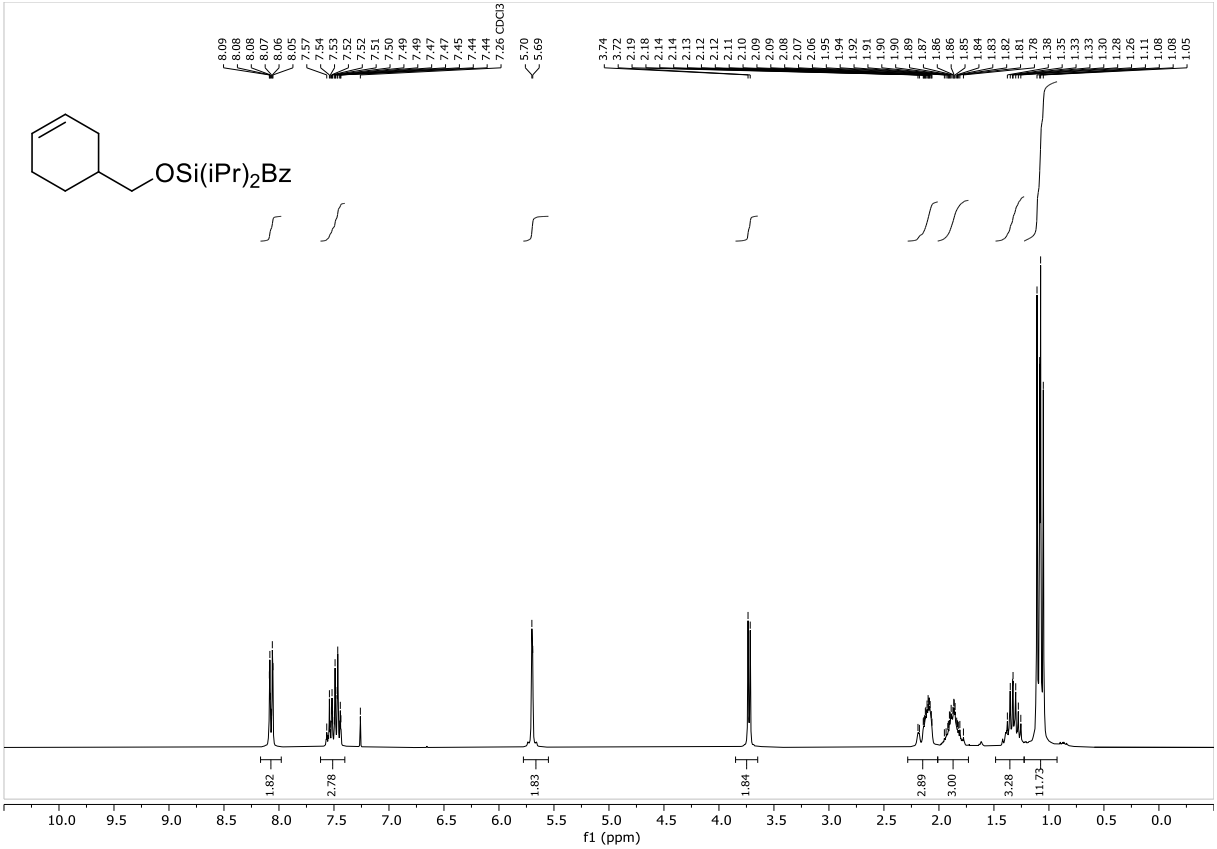


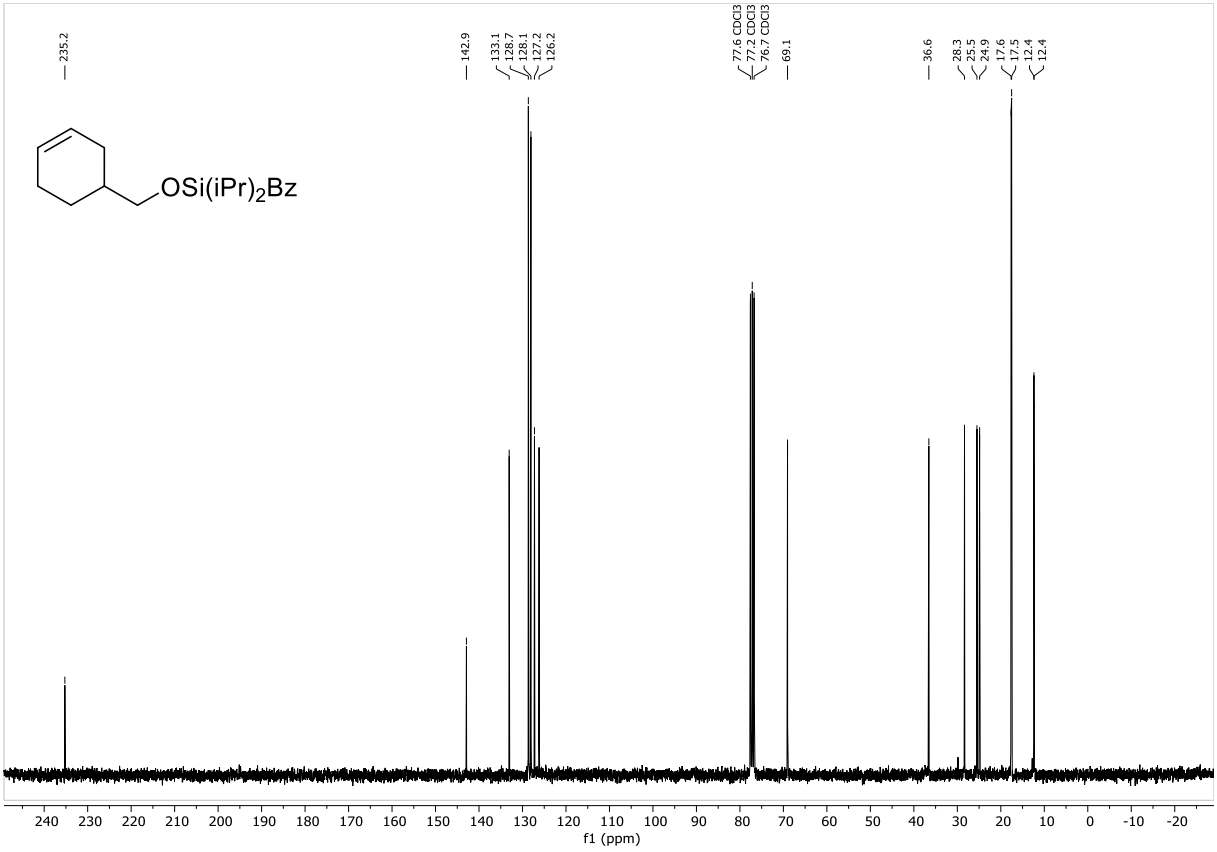
(Diisopropyl(((1R,3S,4R)-quinuclidin-3-yl)oxy)silyl)(phenyl)methanone 8s



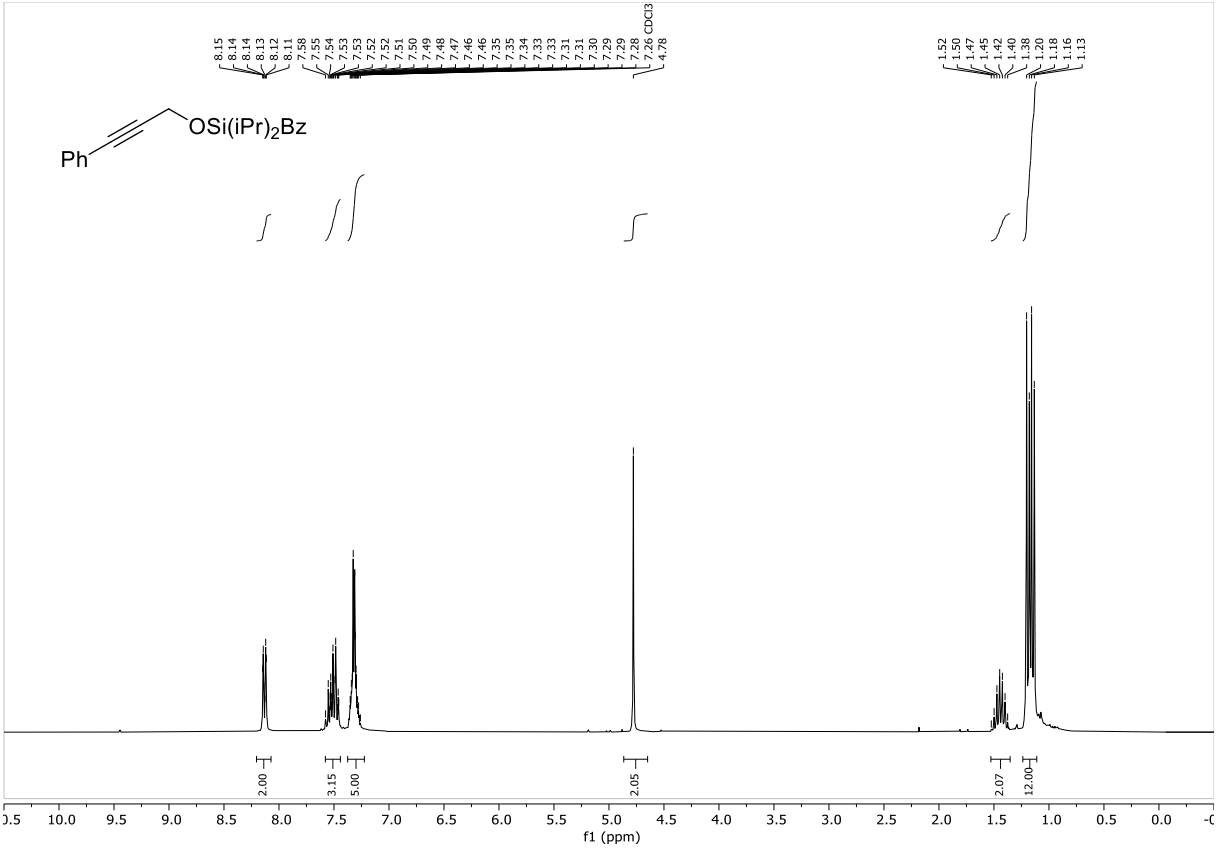


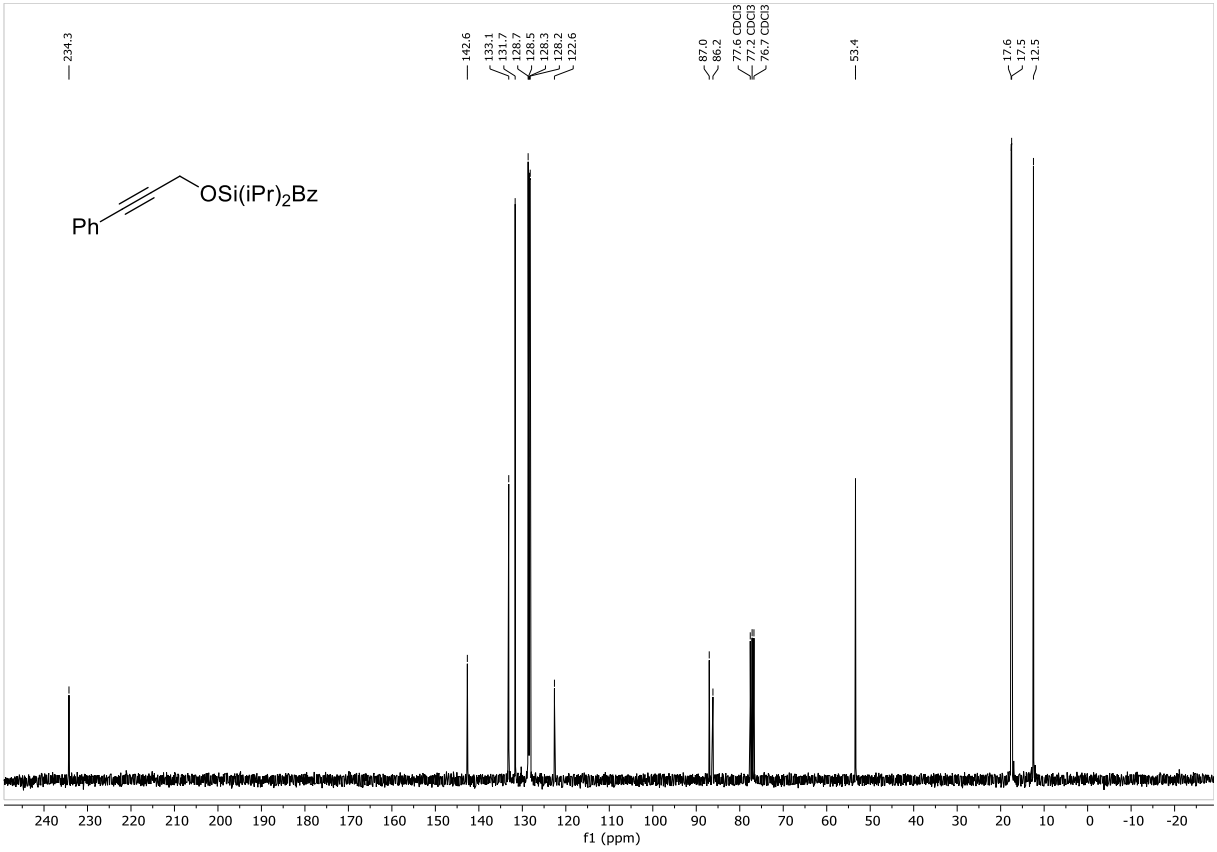
((Cyclohex-3-en-1-ylmethoxy)diisopropylsilyl)(phenyl)methanone 8t



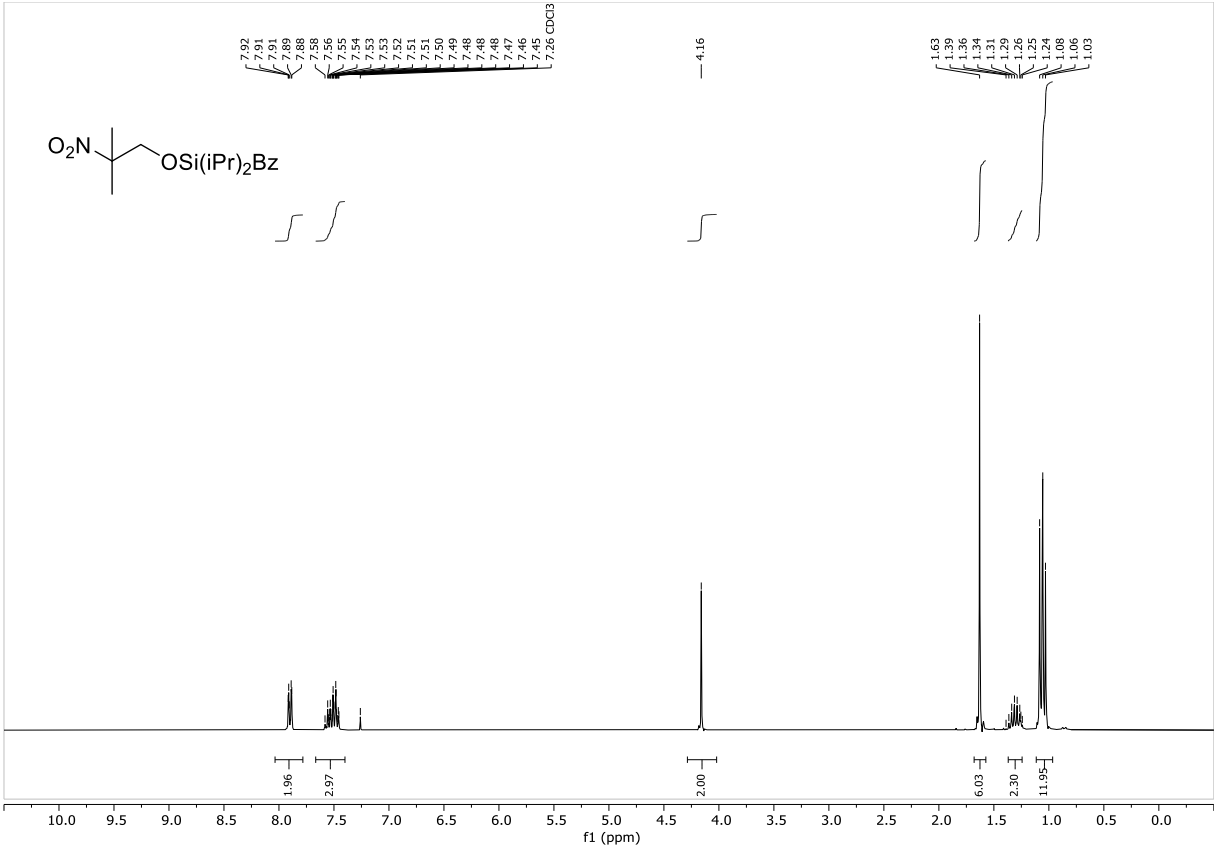


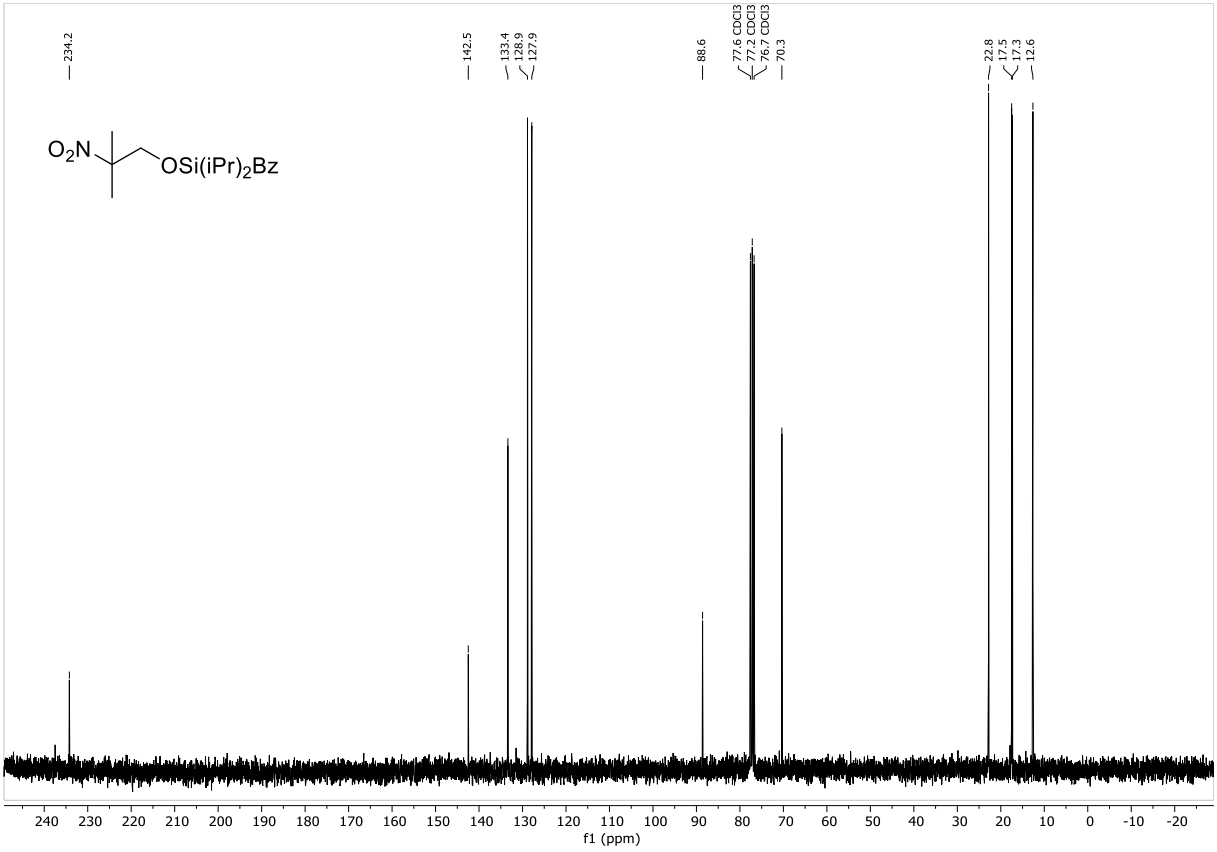
(Diisopropyl((3-phenylprop-2-yn-1-yl)oxy)silyl)(phenyl)methanone 8u



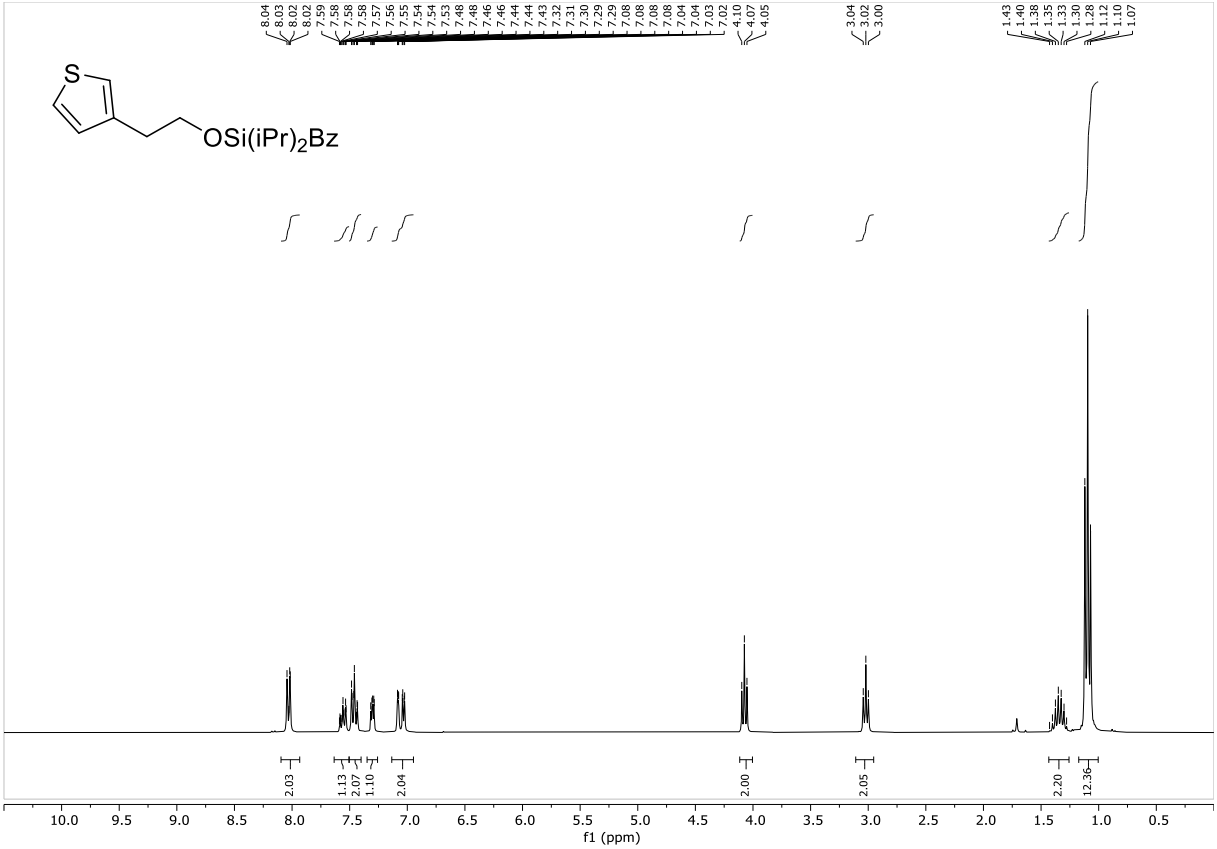


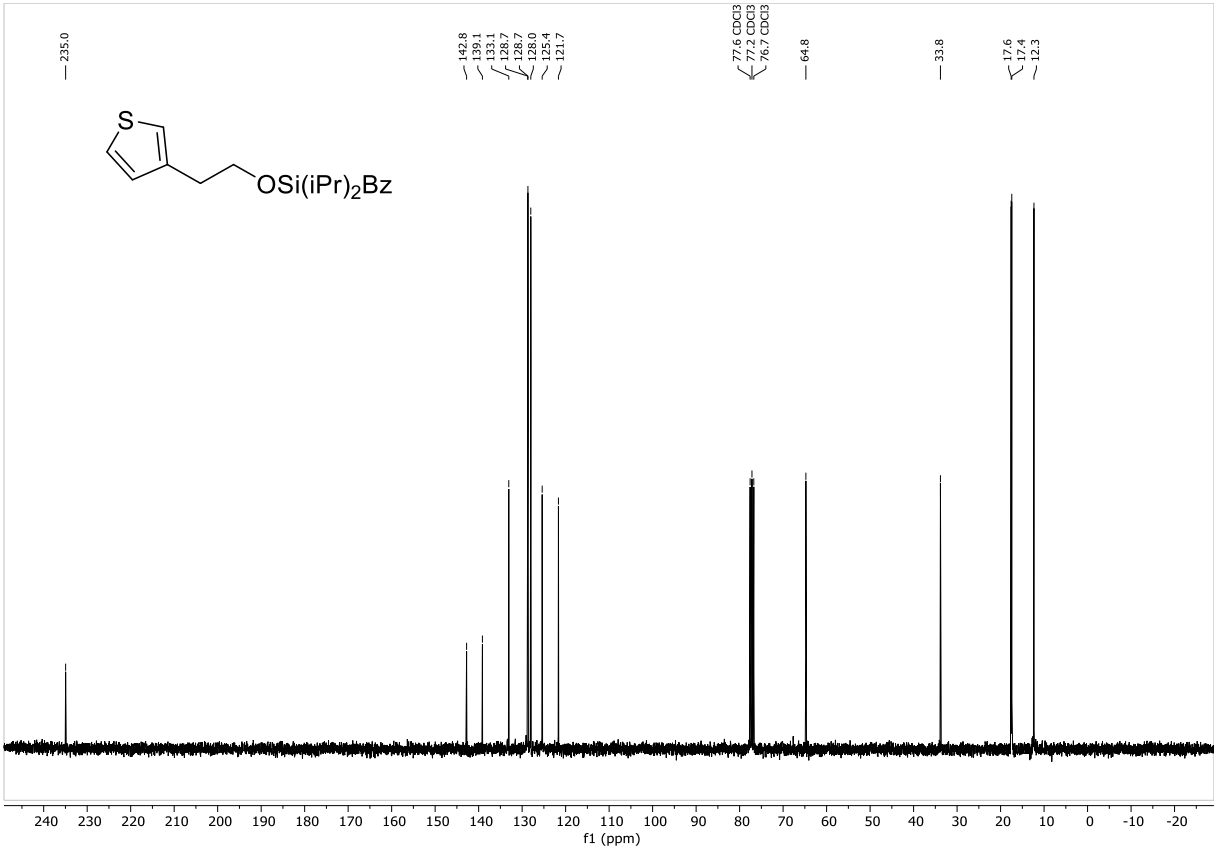
(Diisopropyl(2-methyl-2-nitropropoxy)silyl)(phenyl)methanone 8v



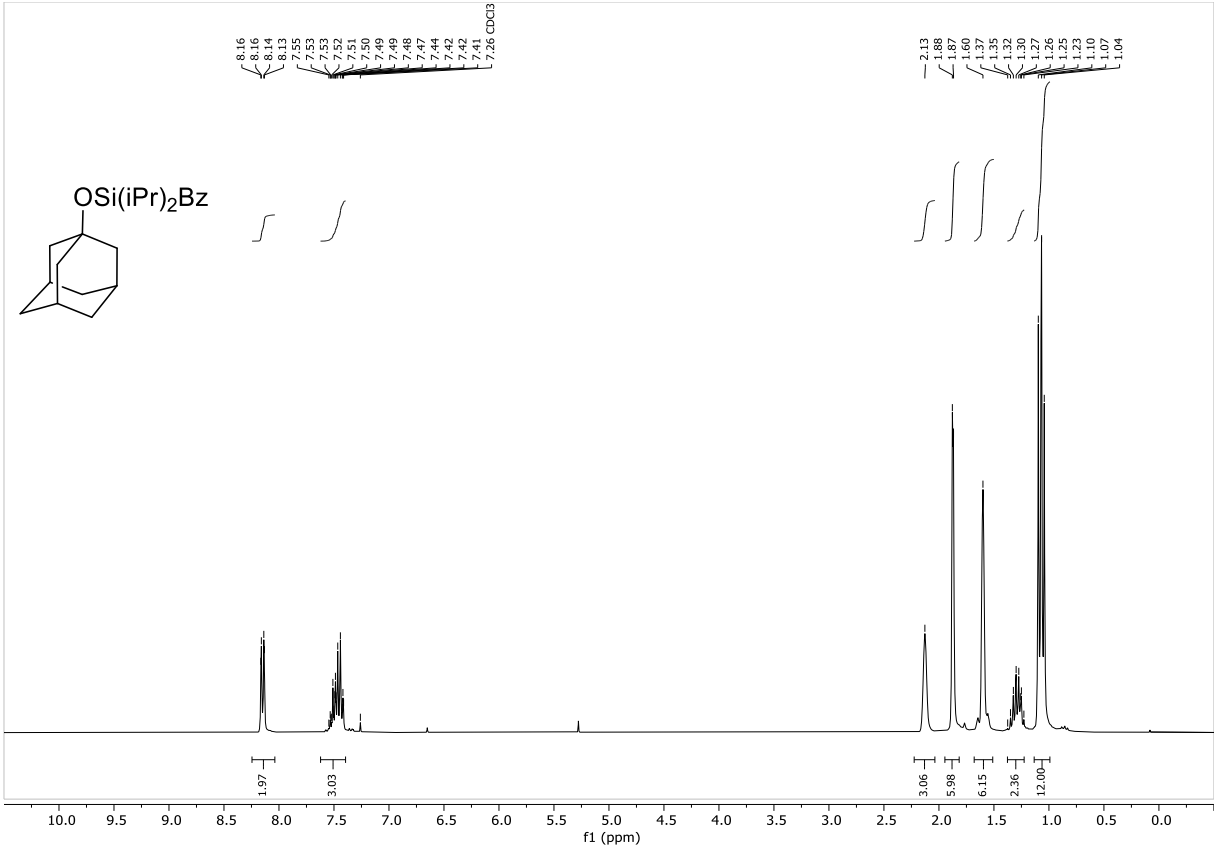


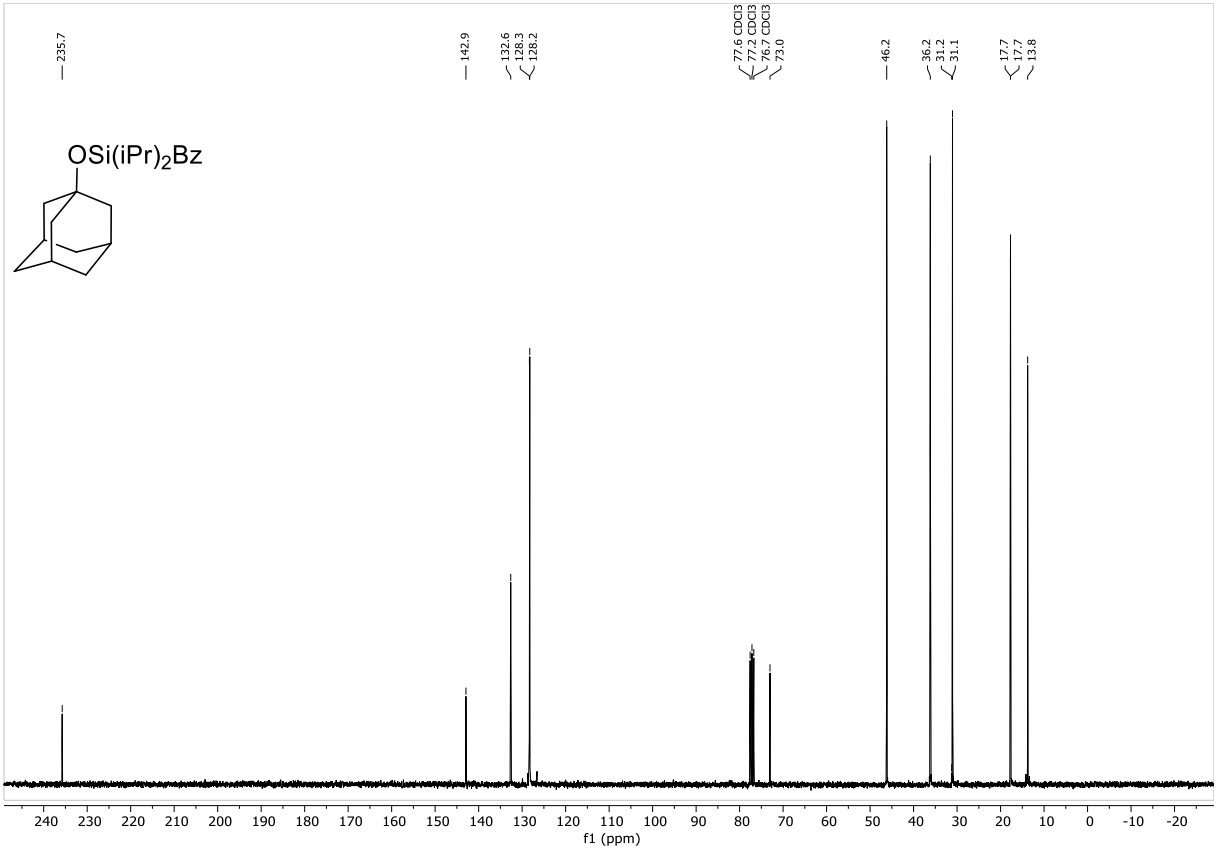
(Diisopropyl(2-(thiophen-2-yl)ethoxy)silyl)(phenyl)methanone 5w



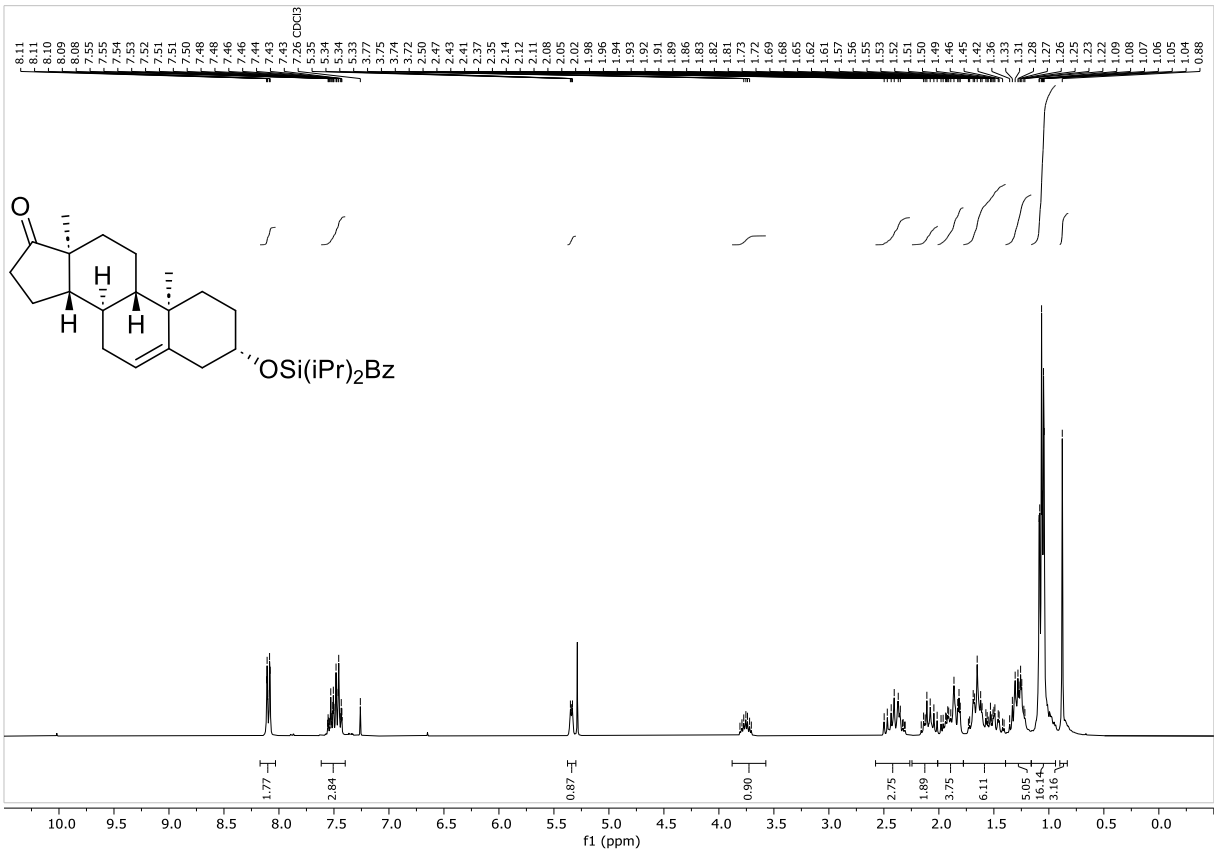


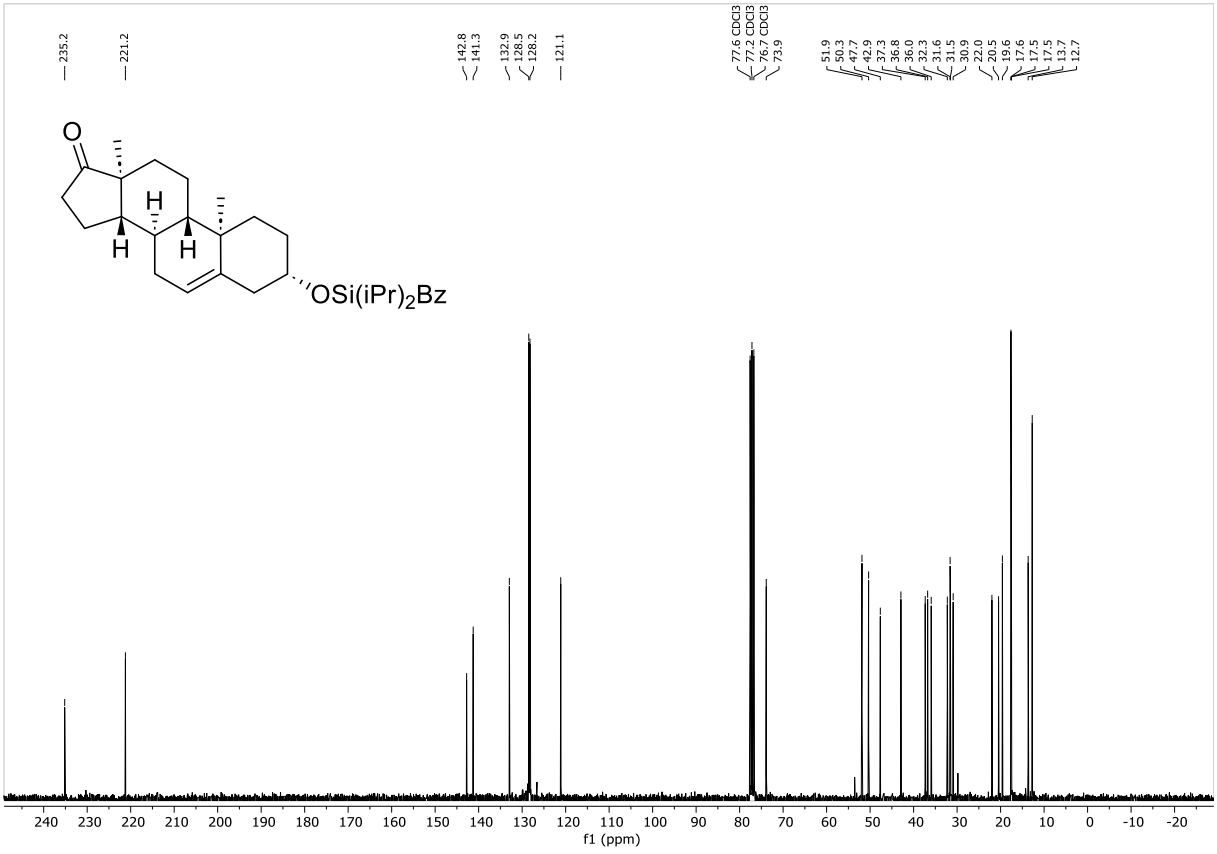
((((3s,5s,7s)-Adamantan-1-yl)oxy)diisopropylsilyl)(phenyl)methanone 8x



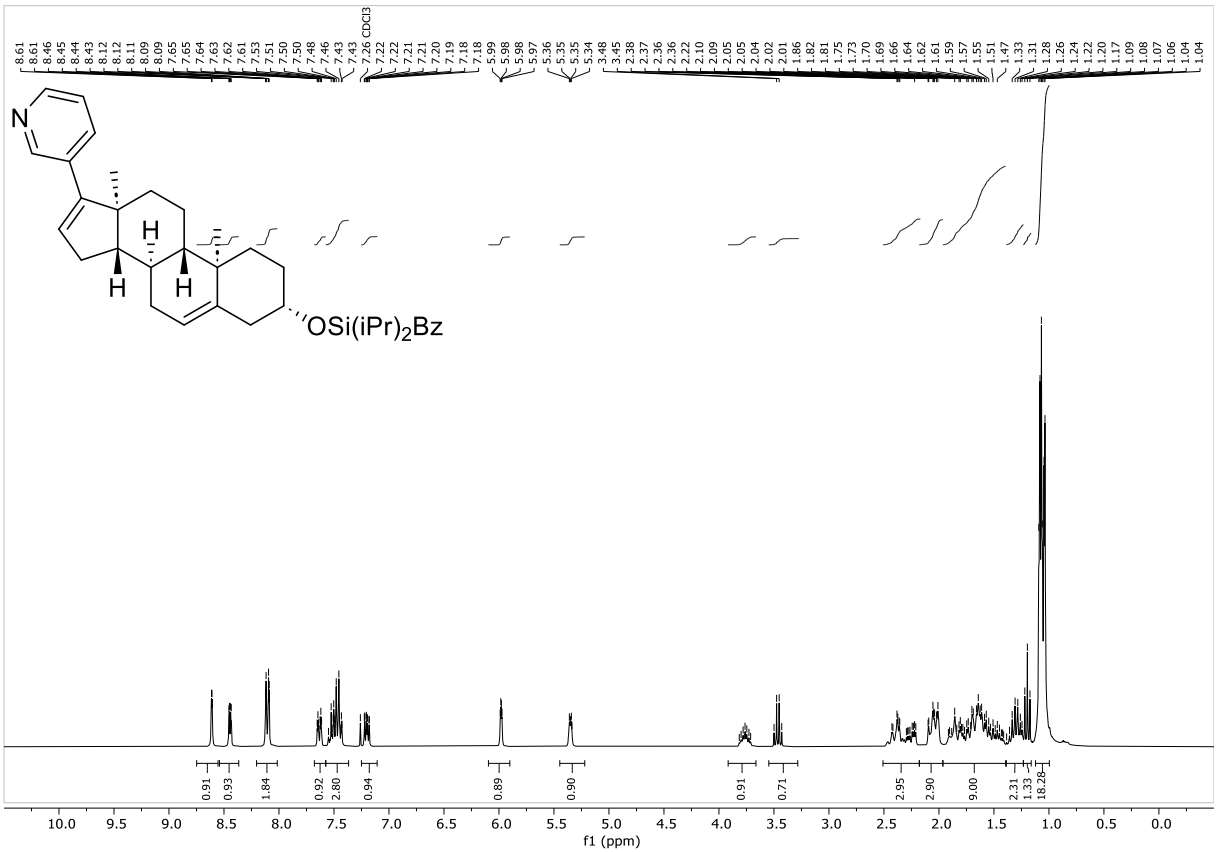


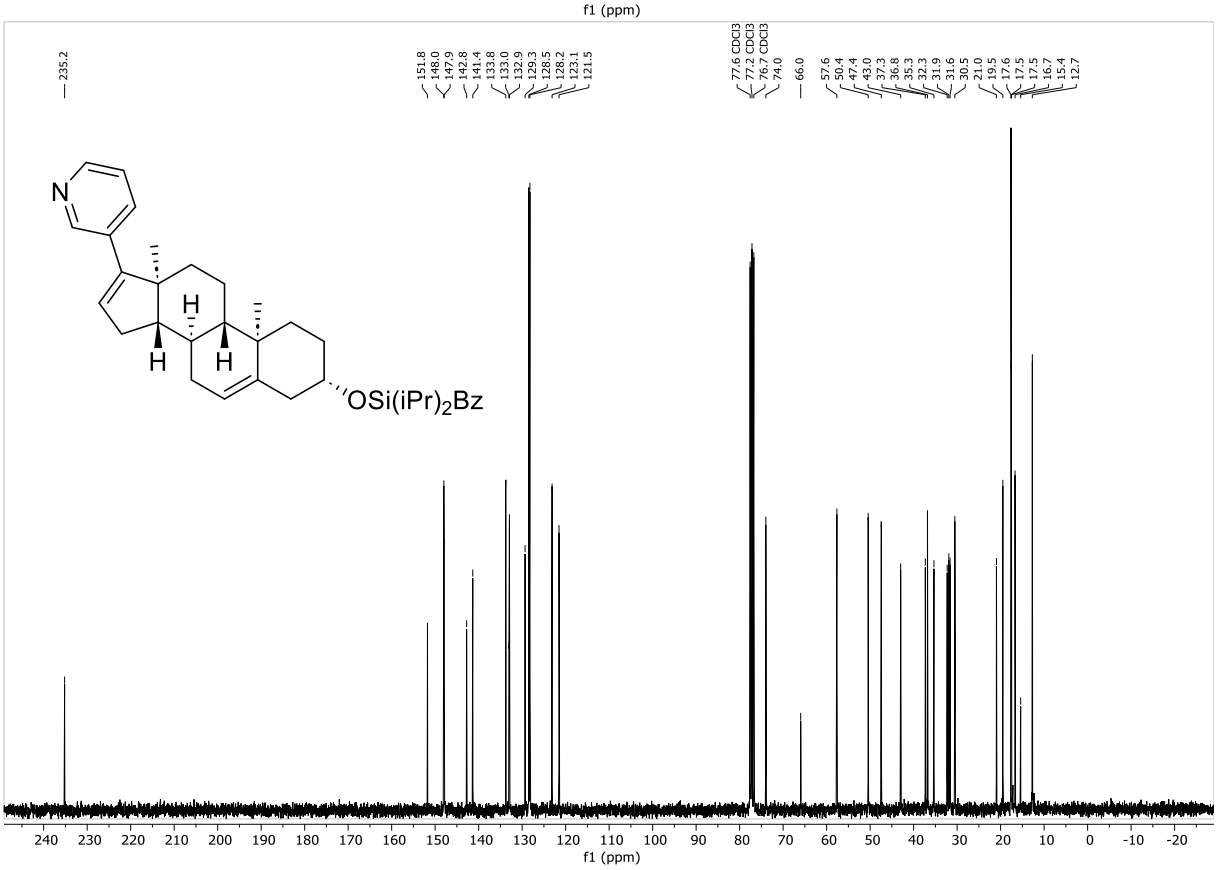
(3S,8R,9S,10R,13S,14S)-3-((Benzoyldiisopropylsilyl)oxy)-10,13-dimethyl-1,2,3,4,7,8,9,10,11,12,13,14,15,16-tetradecahydro-17H-cyclopenta[a]phenanthren-17-one 8y



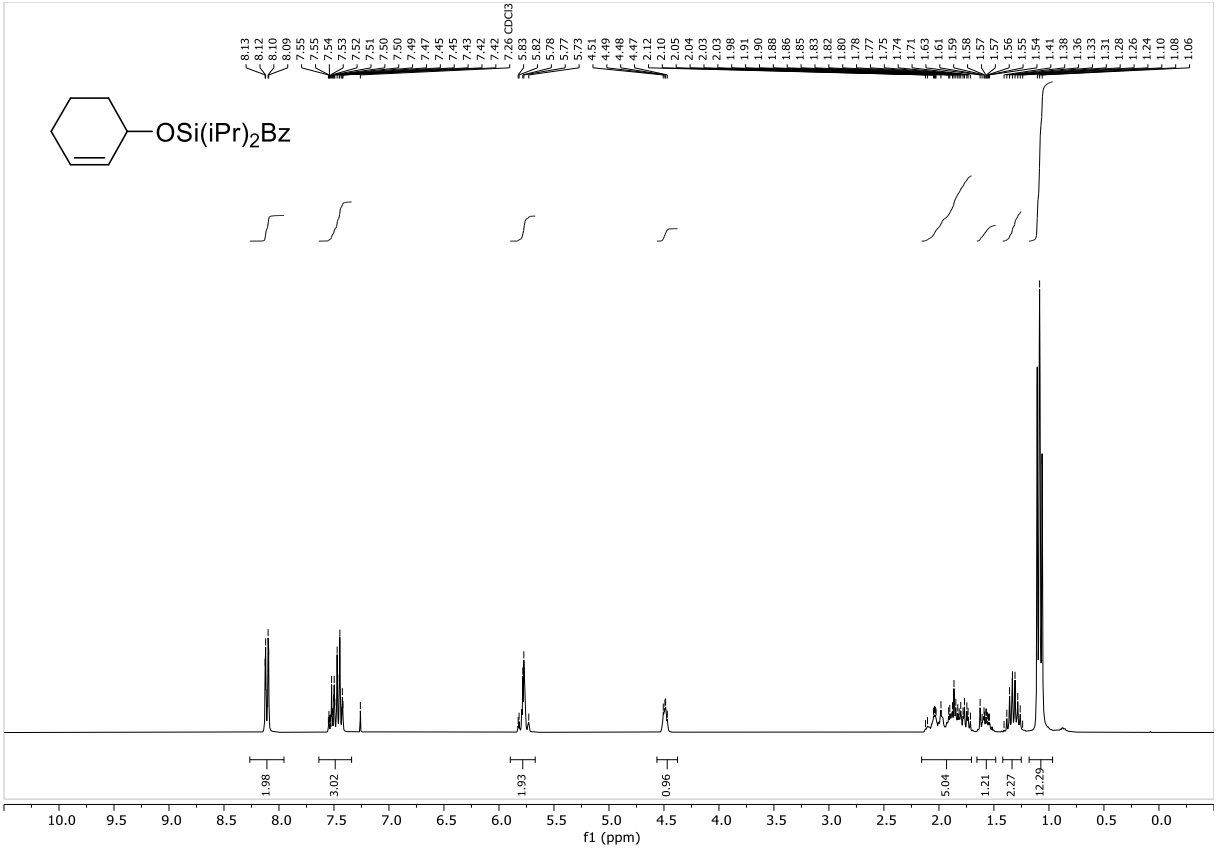


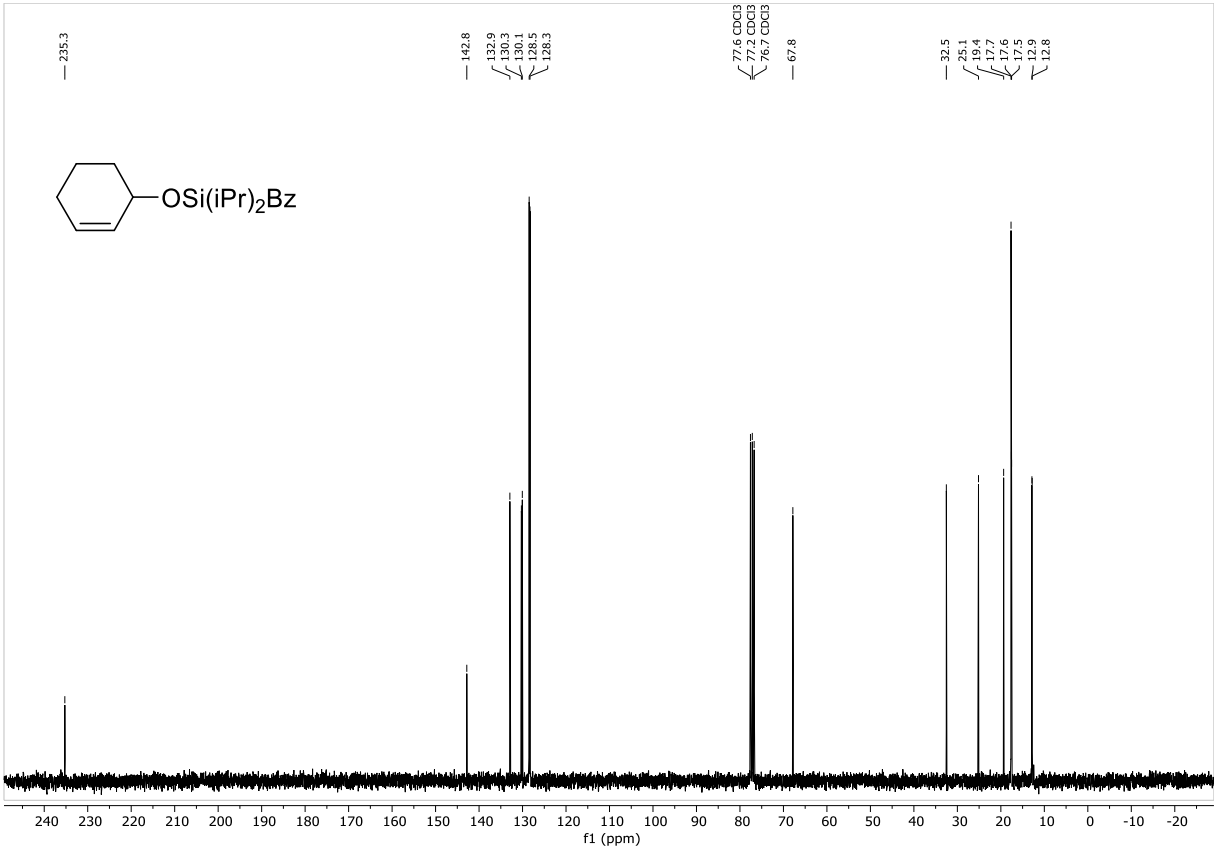
((((3S,8R,9S,10R,13S,14S)-10,13-Dimethyl-17-(pyridin-3-yl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)diisopropylsilyl)(phenyl)methanone 8z



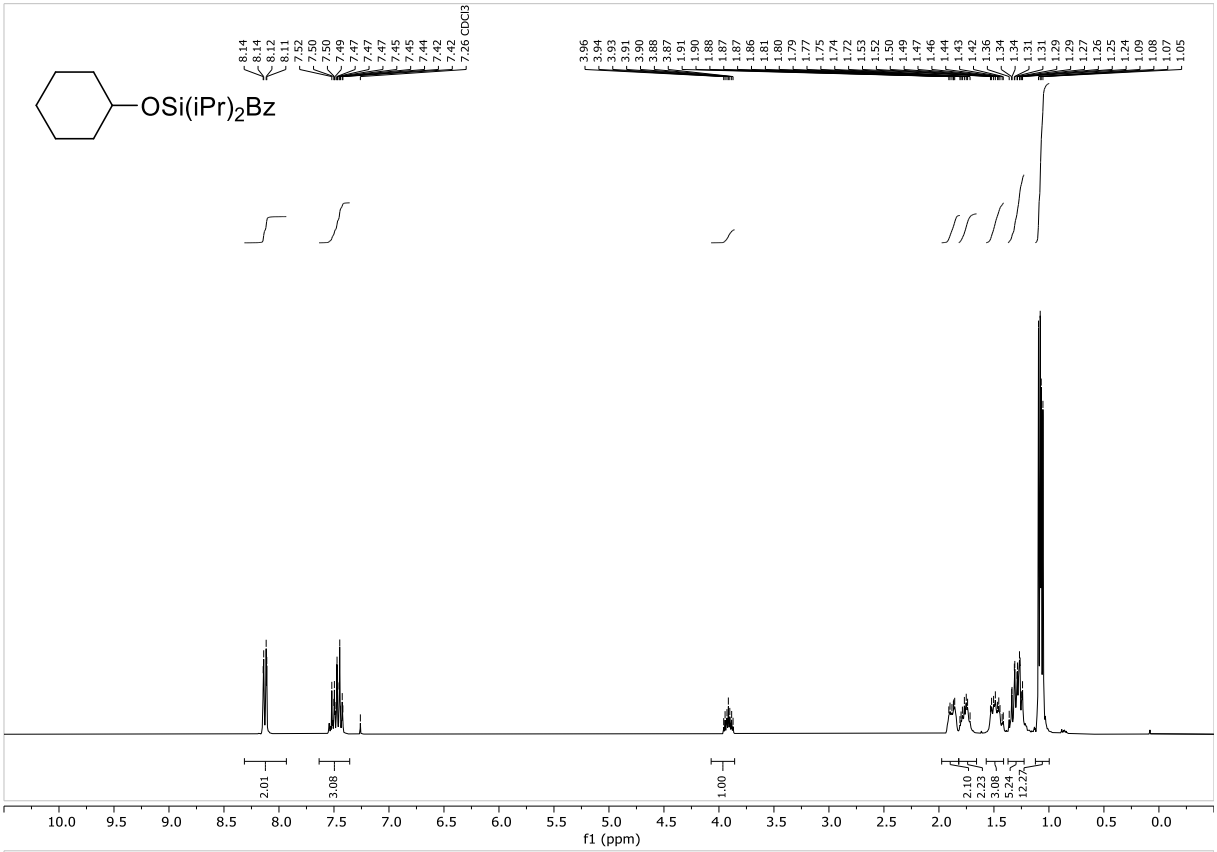


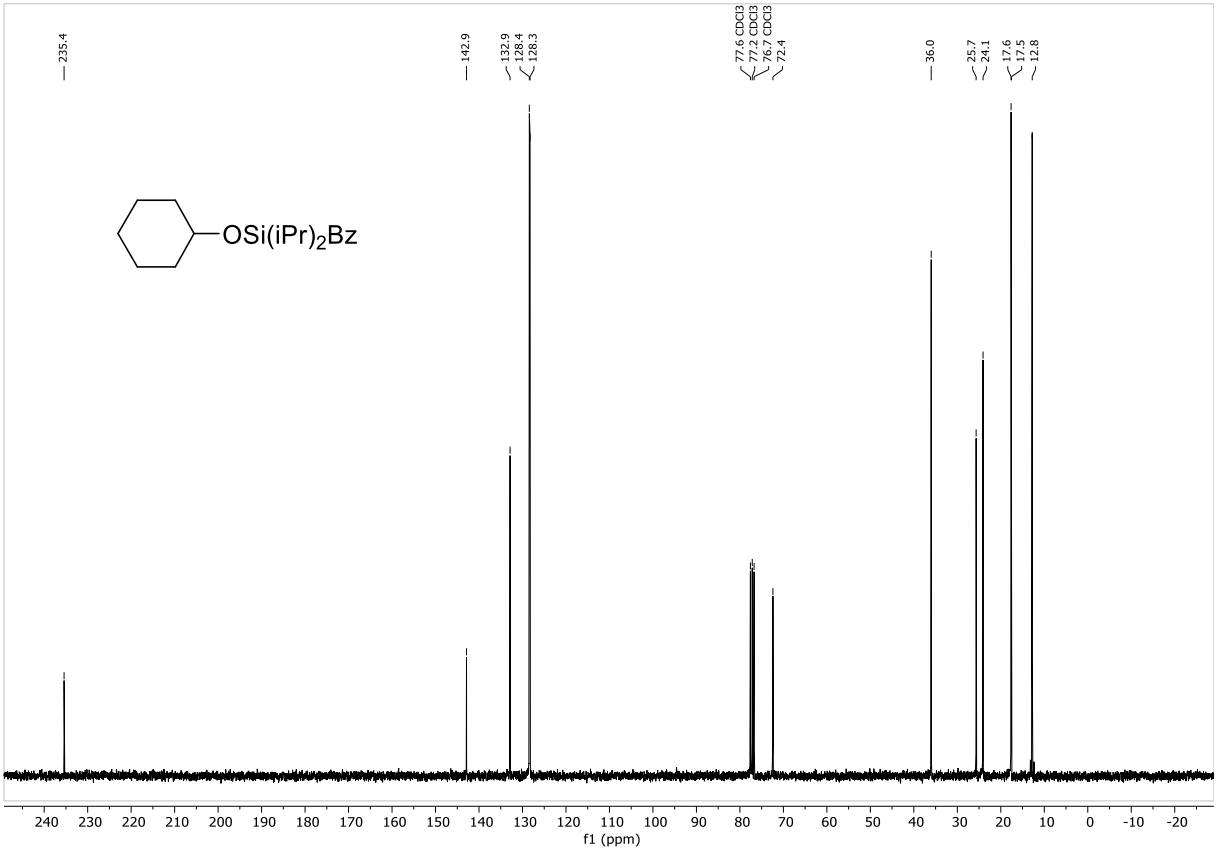
((Cyclohex-2-en-1-yloxy)diisopropylsilyl)(phenyl)methanone 8ab



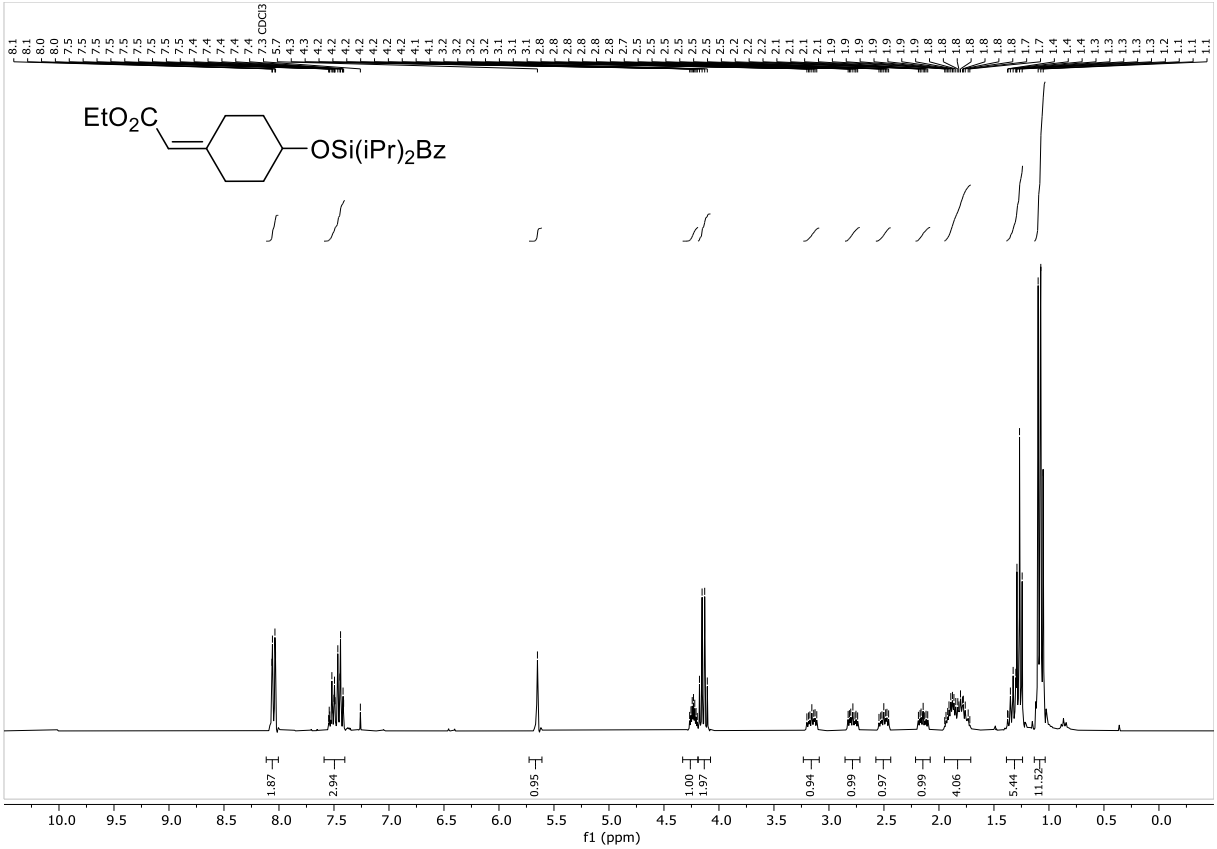


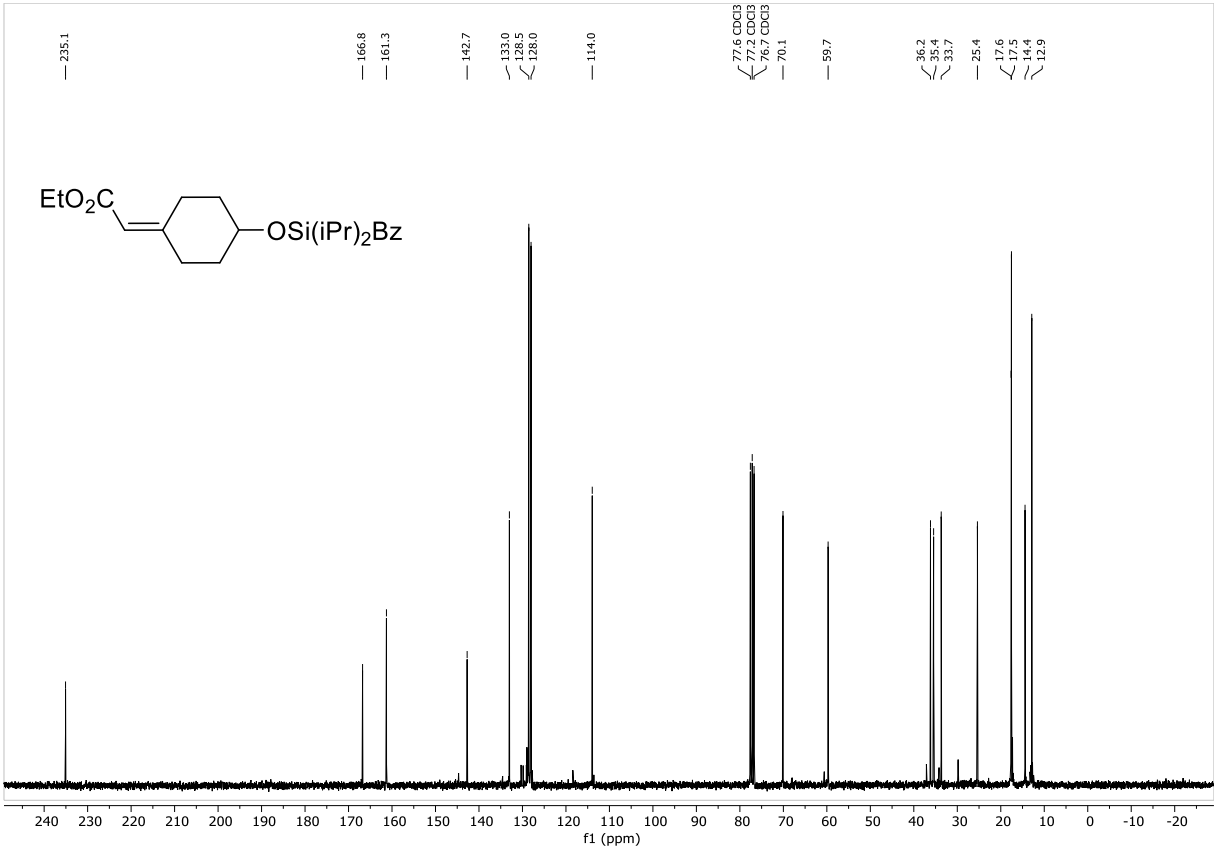
((Cyclohexyloxy)diisopropylsilyl)(phenyl)methanone 8ac



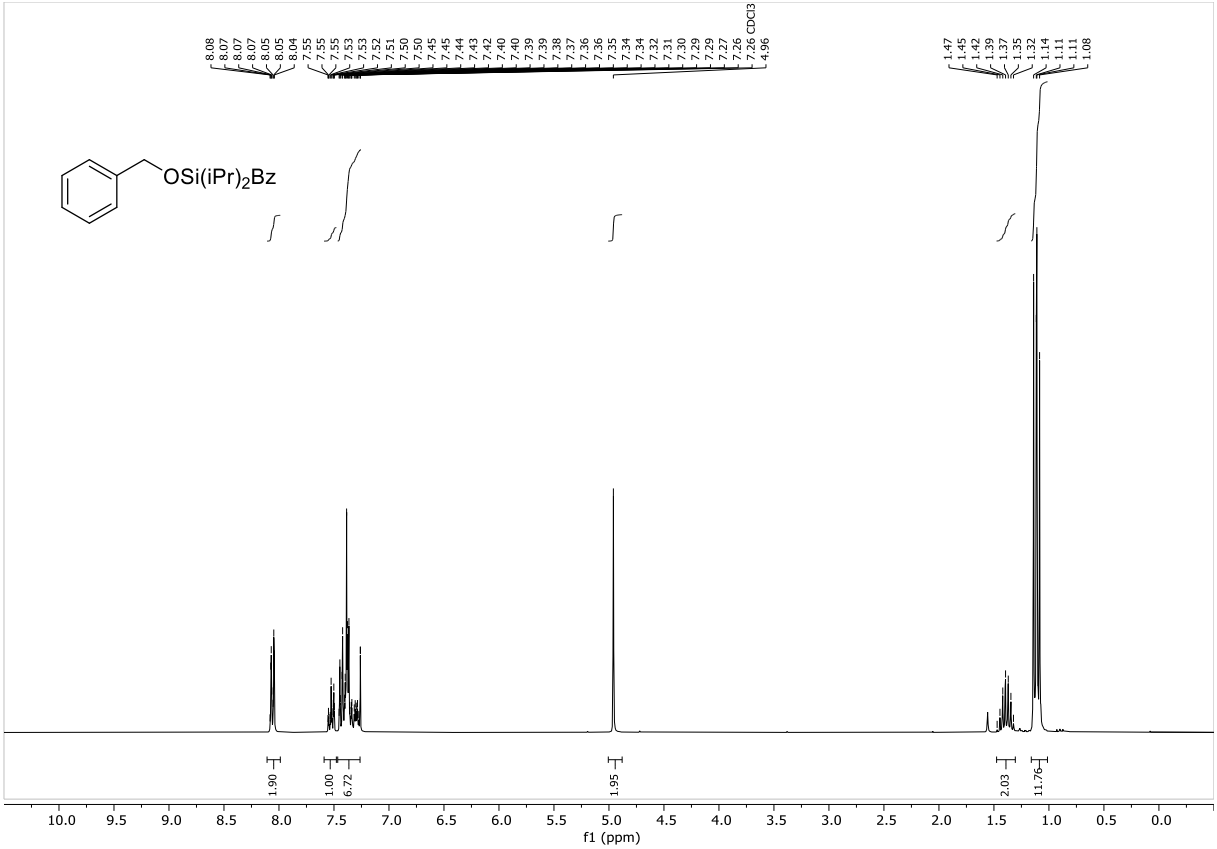


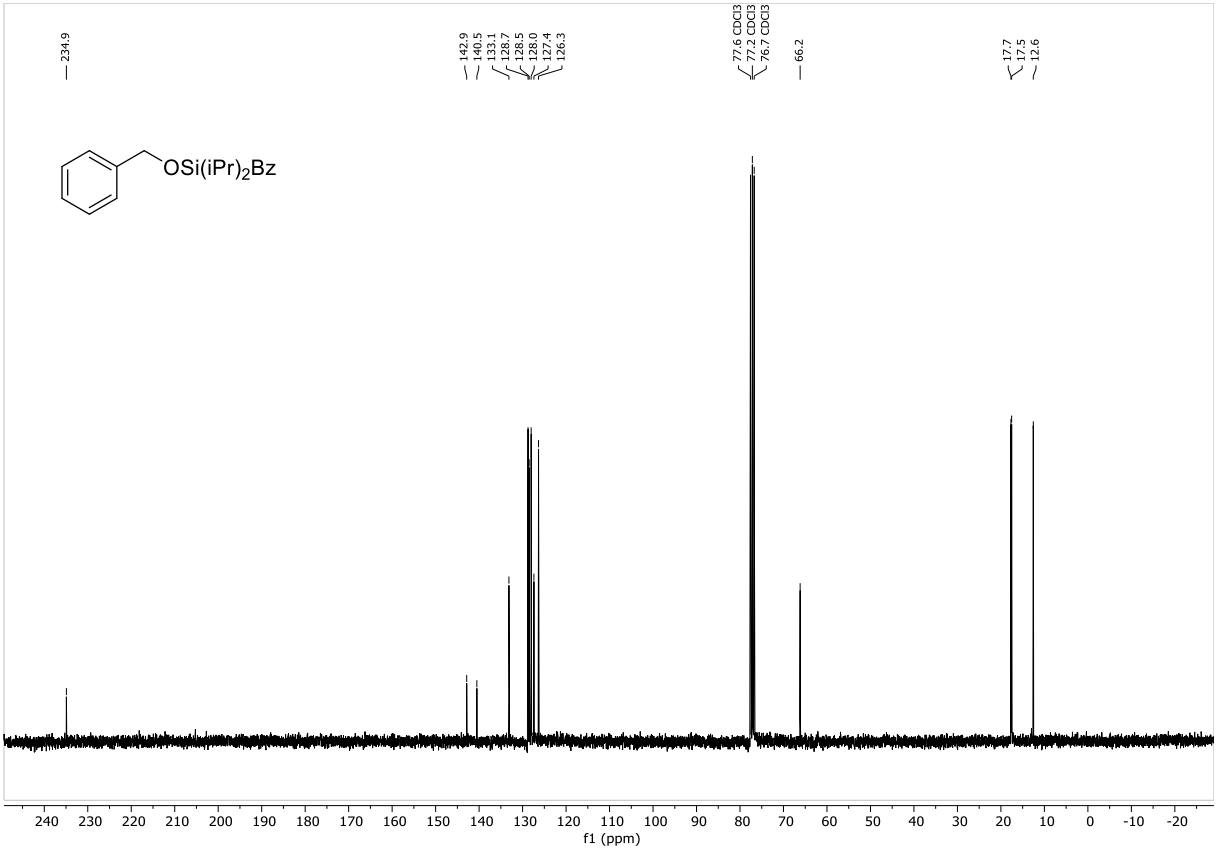
Ethyl 2-(4-((benzoyldiisopropylsilyl)oxy)cyclohexylidene)acetate 8aa



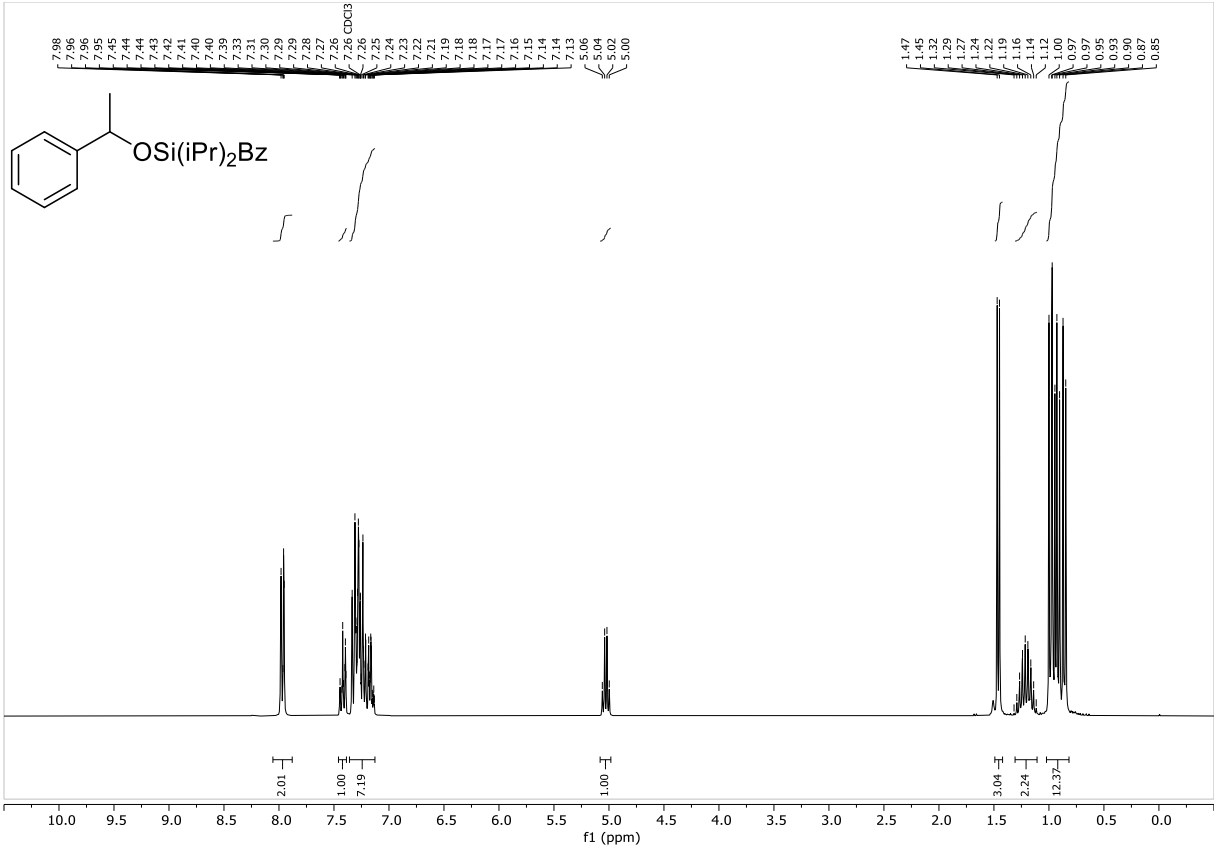


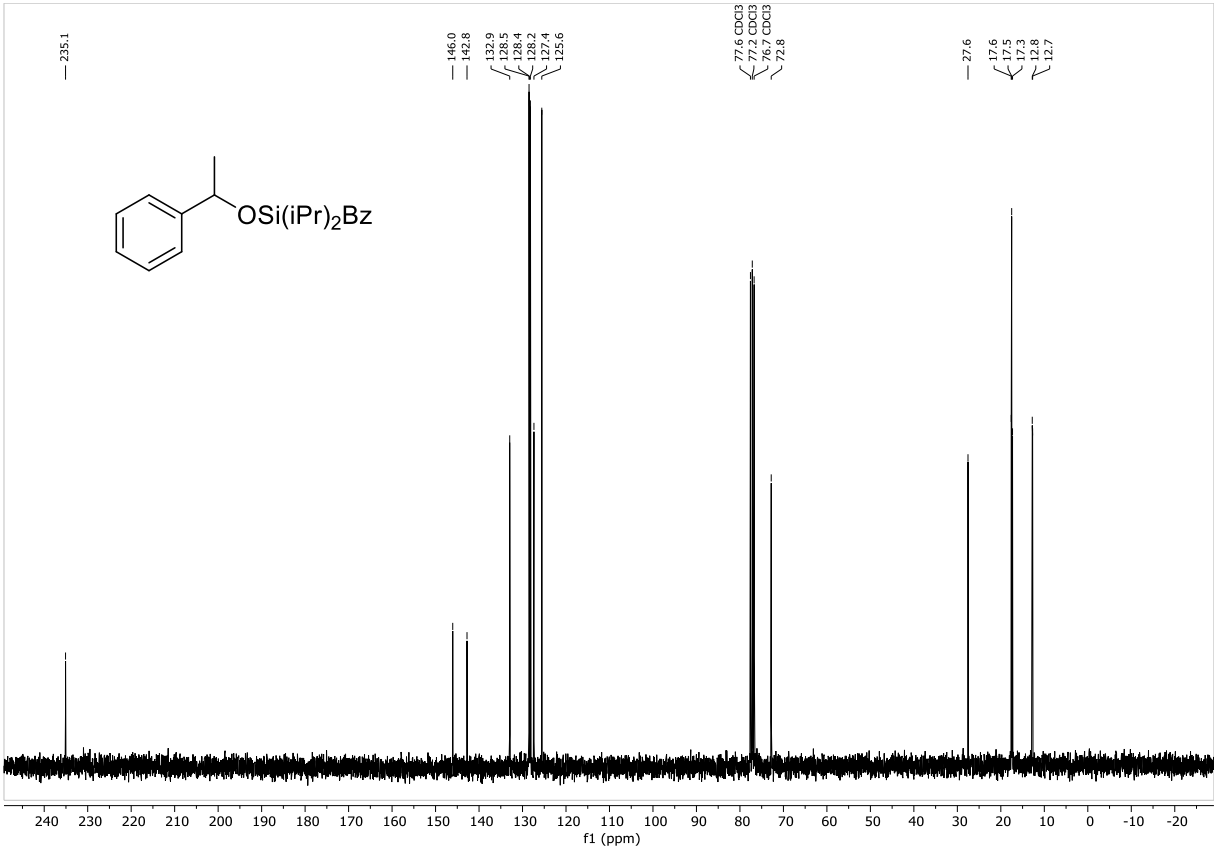
((Benzyloxy)diisopropylsilyl)(phenyl)methanone 8ae



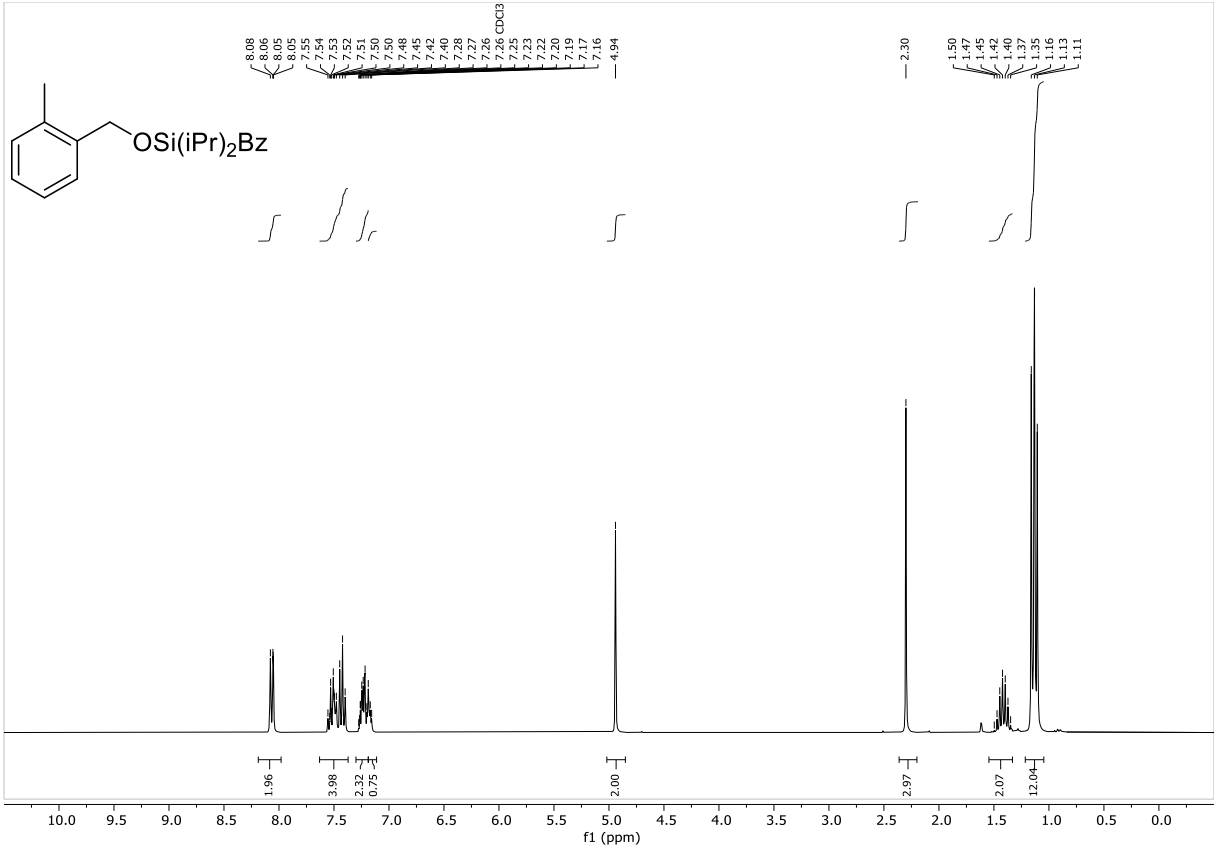


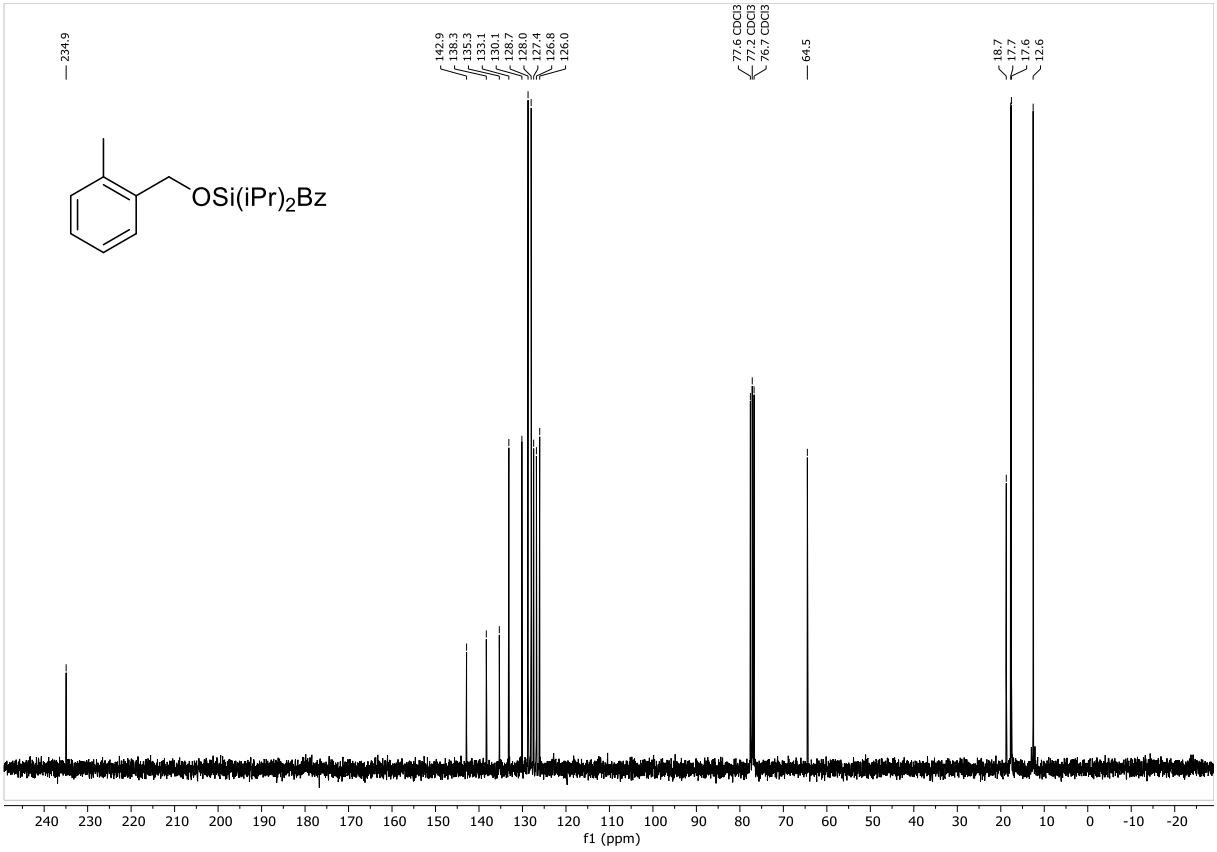
(Diisopropyl(1-phenylethoxy)silyl)(phenyl)methanone 8af



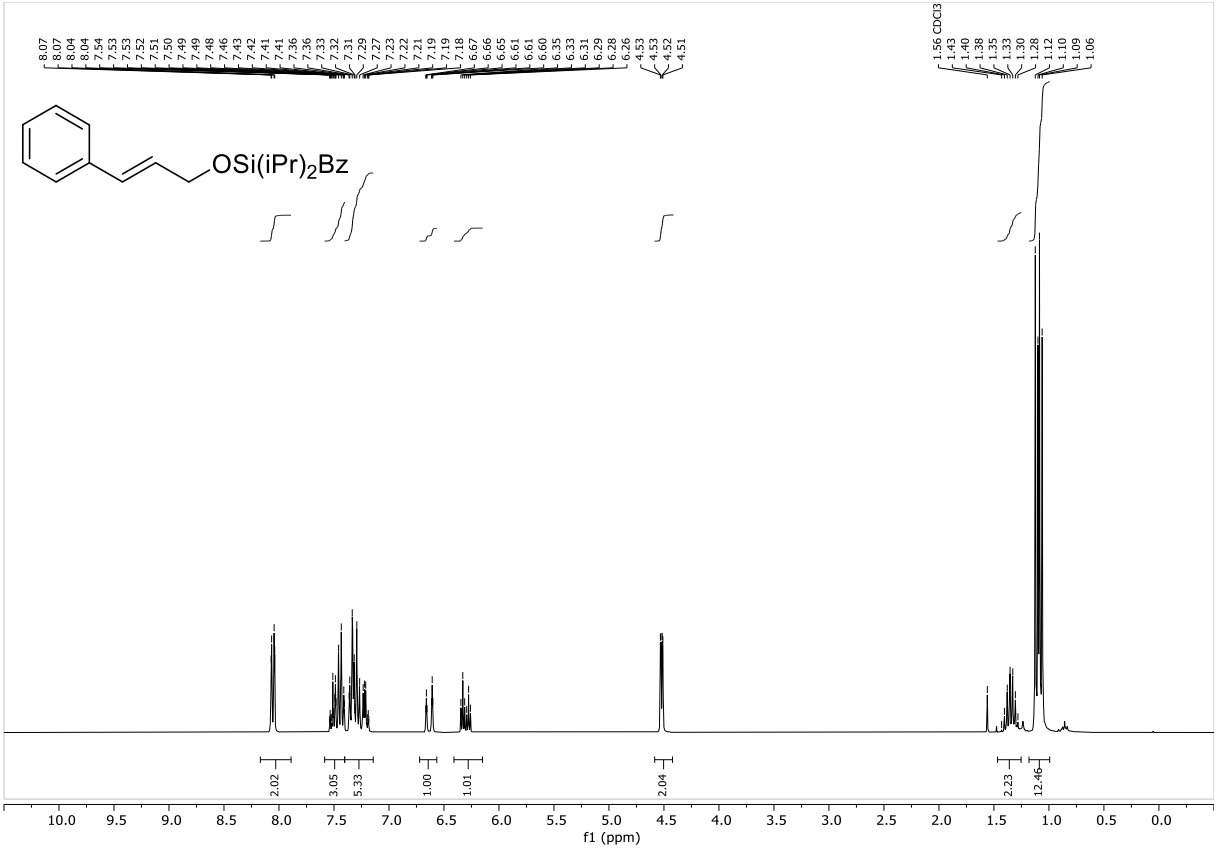


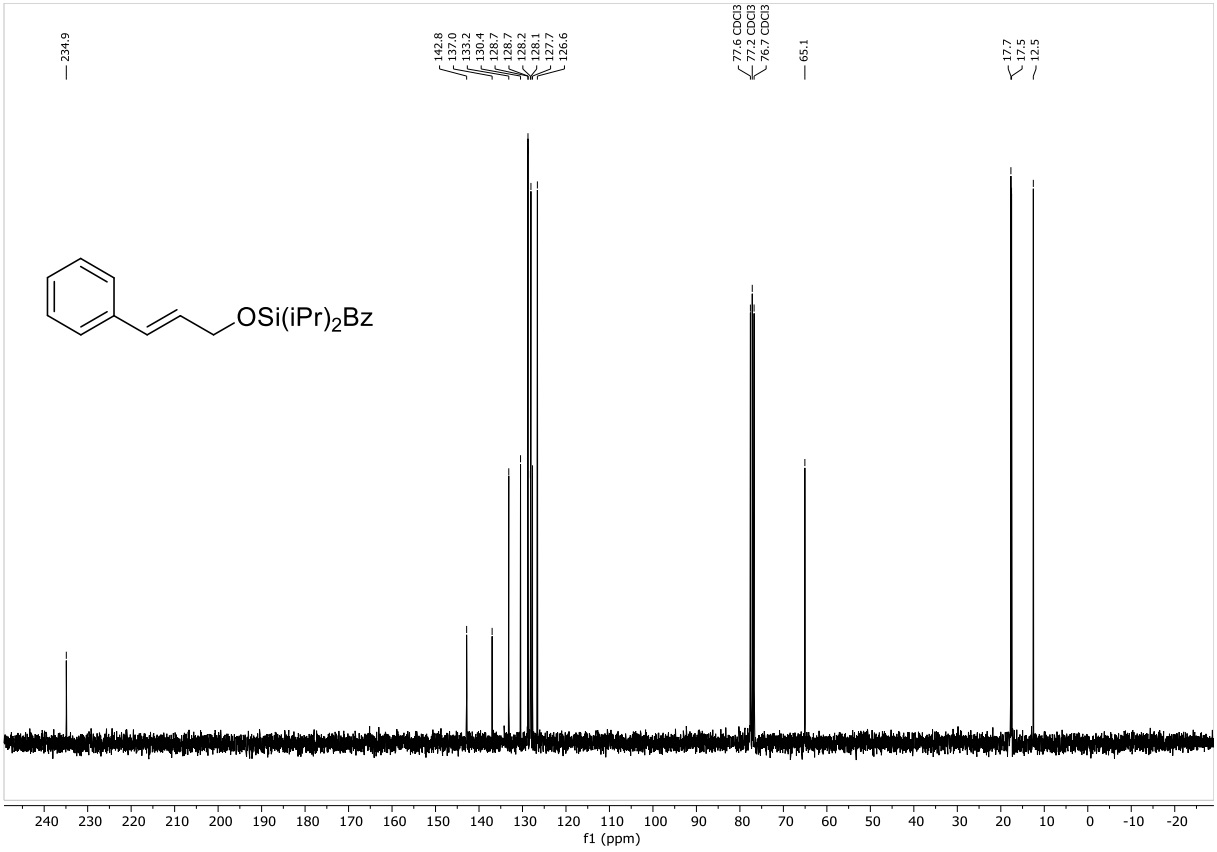
(Diisopropyl((2-methylbenzyl)oxy)silyl)(phenyl)methanone 8ag



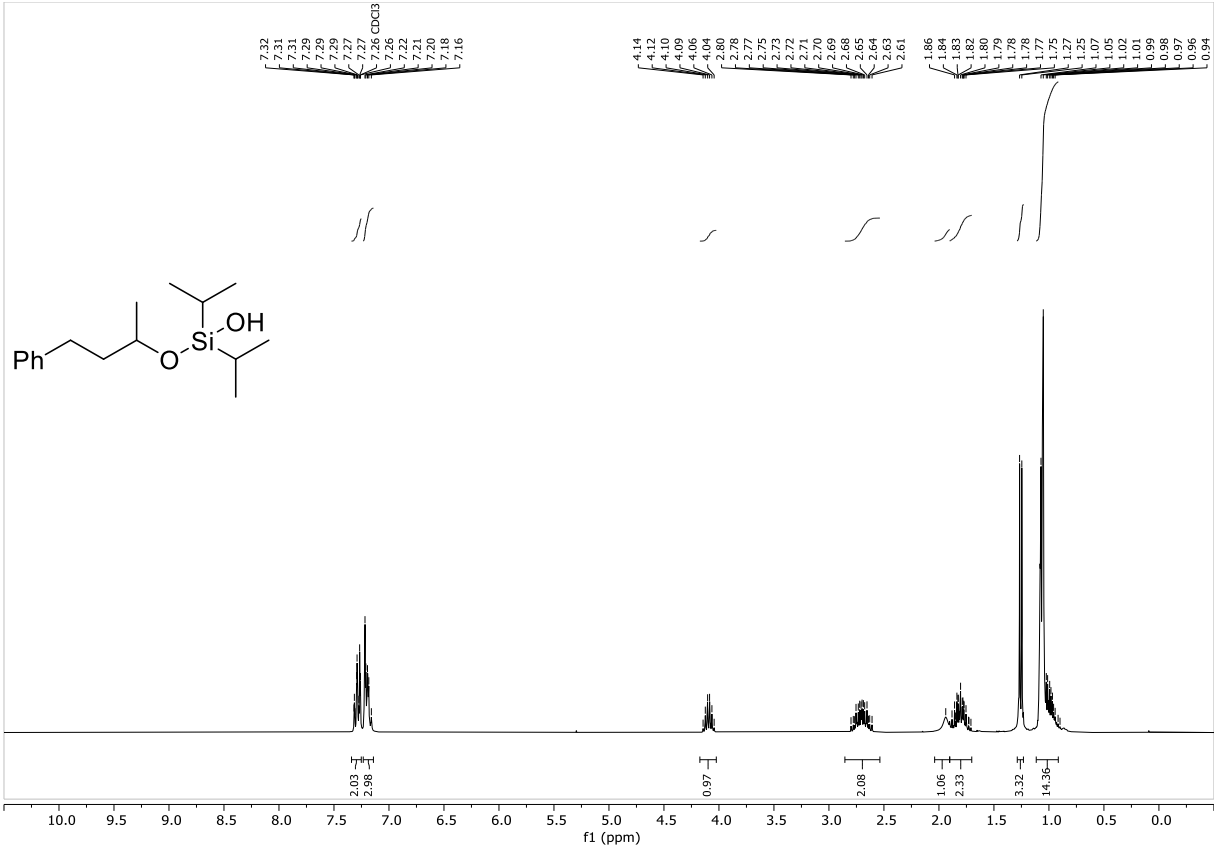


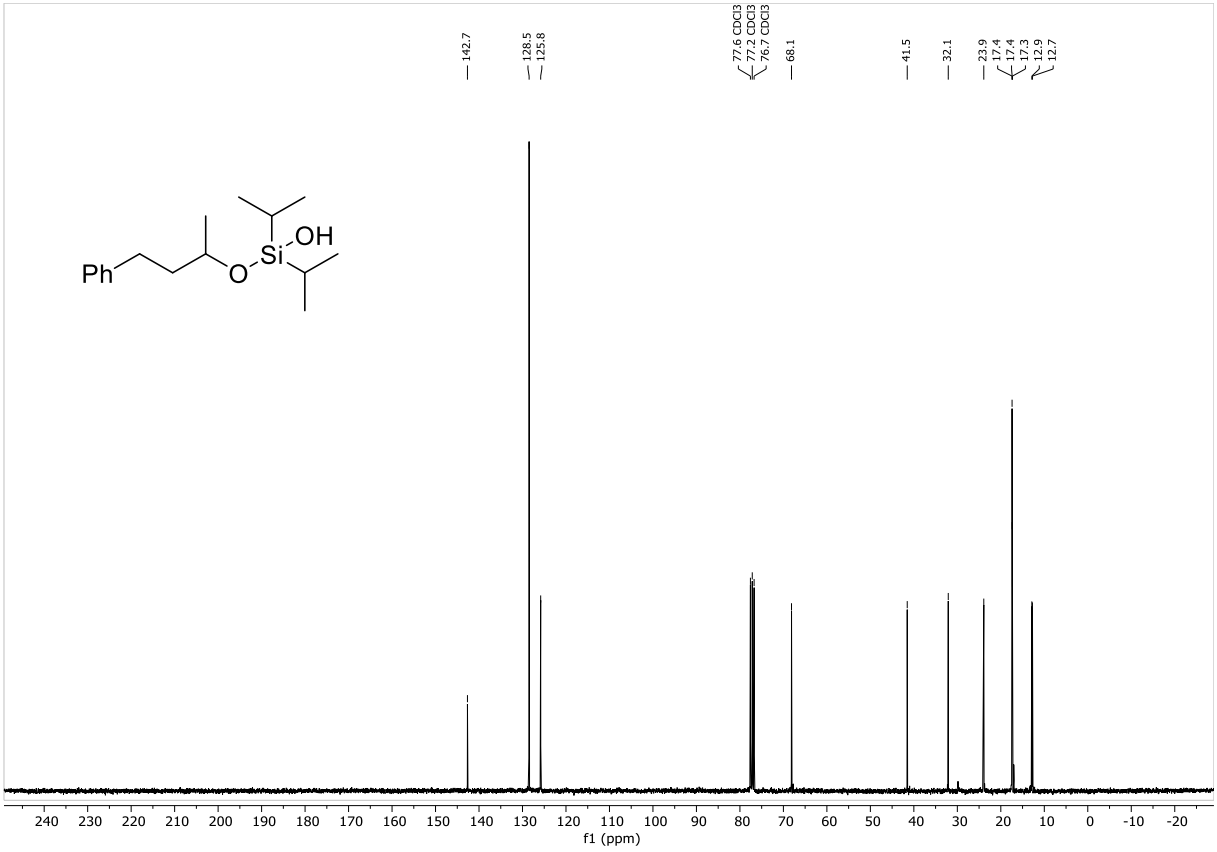
((Cinnamyloxy)diisopropylsilyl)(phenyl)methanone 8ah

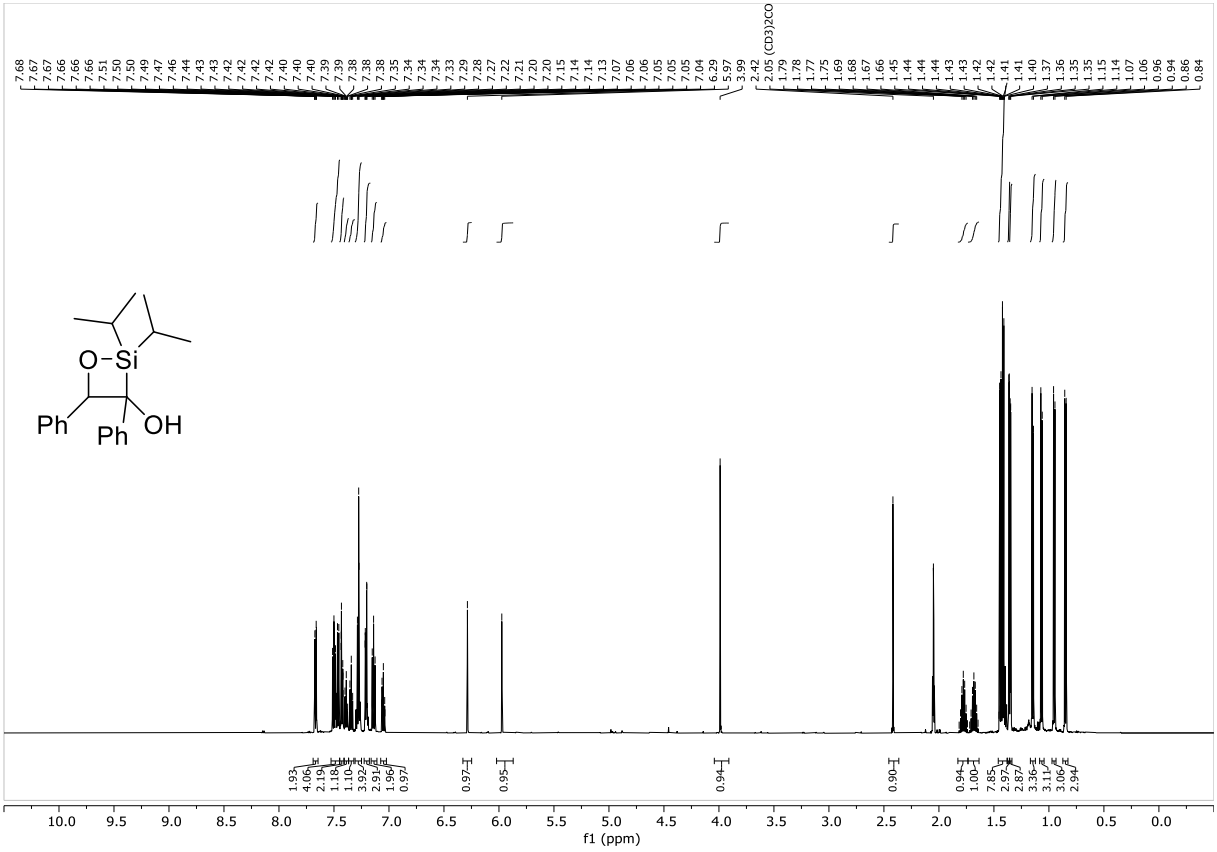


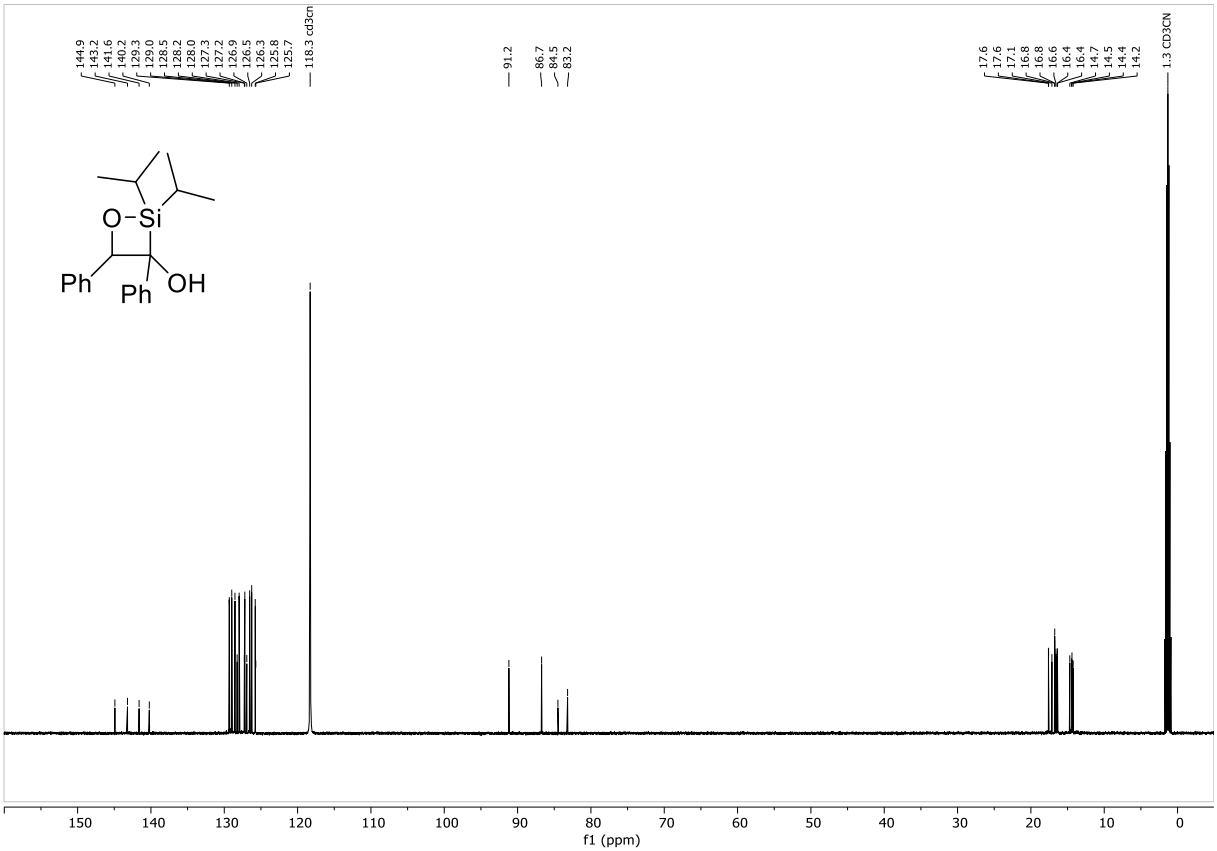


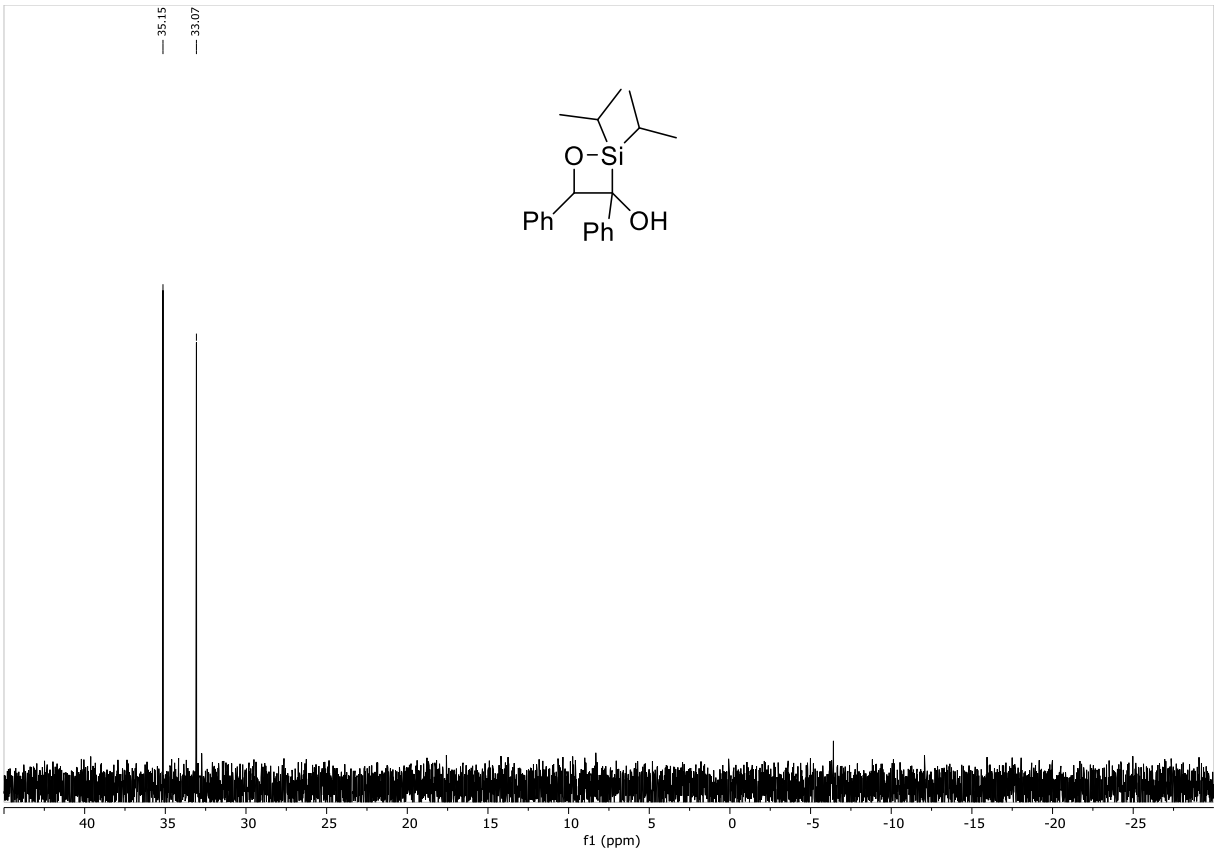
Diisopropyl((4-phenylbutan-2-yl)oxy)silanol 4a






7.68 7.67 7.67 7.66 7.66 7.66 7.51 7.50 7.50 7.49 7.47 7.46 7.44 7.43 7.43 7.42 7.42 7.42 7.42 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.35 7.34 7.34 7.34 7.33 7.29 7.28 7.27 7.22 7.21 7.20 7.20 7.15 7.14 7.14 7.13 7.07 7.06 7.06 7.05 7.05 7.05 7.04 6.29 5.97 3.99 2.42 2.05 (CD3)2CO 1.79 1.78 1.77 1.75 1.69 1.68 1.67 1.66 1.45 1.44 1.44 1.44 1.43 1.43 1.42 1.42 1.41 1.41 1.40 1.37 1.36 1.35 1.35 1.15 1.14 1.07 1.06 0.96 0.94 0.86 0.84
O−Si
Ph
Ph
OH
1.93 4.06 2.19 1.18 1.10 3.92 2.91 1.96 0.97 0.97 0.95 0.94 0.90 0.94 1.00 7.85 2.97 2.97 3.16 3.11 3.06 2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.9 143.2 141.6 140.2 129.3 129.0 128.5 128.2 128.0 127.3 127.2 126.9 126.5 126.3 125.8 125.7 118.3 cd3cn 91.2 86.7 84.5 83.2 17.6 17.6 17.1 16.8 16.8 16.6 16.4 16.4 14.7 14.5 14.4 14.2 1.3 CD3CN
O−Si
Ph
Ph
OH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


35.15
33.07
O
Si
Ph
Ph
OH
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

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