

Supporting Information

Direct Synthesis and Applications of Solid Silylzinc Reagents

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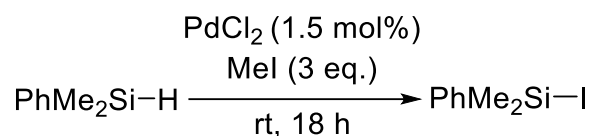
1. General considerations:

Reagents: Commercially purchased chemicals were taken to the reaction without any further purification. Ni(OAc)₂·4H₂O (product code: 379883) and dtbpy (product code: 515477) were purchased from Sigma Aldrich. PhMe₂SiH (product code: L04558) and Zn powder (100 mesh, product code: L13310) were purchased from Alfa Aesar. PdCl₂ (product code: 28439019) was purchased from Souvenir chemicals. MeI (product code: 011361), Me₃SiI (product code: I0308), PhMe₂SiCl (product code: 0104504) and Lithium (product code: 011235) were purchased from Spectrochem. Anhydrous Ni(OAc)₂ was prepared from Ni(OAc)₂·4H₂O according to the literature procedure.¹ PhMe₂SiLi and PhMe₂SiZnCl were prepared according to known literature procedures.^{2,3}

Solvents: Dichloromethane (DCM) was purchased from Merck was dried and distilled over CaH₂. Anhydrous diethyl ether, toluene, tetrahydrofuran (THF) and 1,2-dimethoxy ethane (DME) were purchased from Spectrochem and dried using sodium wire. The solvents were degassed for 1 h using a nitrogen balloon and stored in 4 Å molecular sieves for further use.

Analytical methods: All the NMR spectra were recorded in a 500 MHz Bruker Avance spectrometer at 23 °C with TMS as an internal standard. NMR spectra chemical shifts were reported in δ (ppm). ¹H NMR recorded in CDCl₃, C₆D₆ were reported with reference at 7.26 ppm, 7.16 ppm respectively, ¹³C NMR in CDCl₃ at 77.16 ppm, C₆D₆ at 128.06 ppm. CDCl₃ (Cat. No: 151823, 99.8 atom % D), C₆D₆ (Cat. No: 151815, 99.6 atom % D) were purchased from Sigma Aldrich and stored with 4 Å molecular sieves. Progress of the reactions was analyzed by GC-Agilent 7890B series (Mass detector G7077B series, EI-70 eV, quadrupole ion detector) with silica capillary column (9091S-433UI, HP-5MSUI, with 30 m x 0.25 mm dimension). Thin-layer chromatography was purchased from Merck (Cat. No. 1.05554.0007), aluminum sheets with TLC Silica gel 60 (F₂₅₄ coating). TLC was visualized using shortwave UV-254 nm or the stain made out of phosphomolybdic acid or potassium permanganate then heating as the developer. Silica gel 230-400 mesh (purchased from FINAR, Product Code: 11457S5K25) was used for the column chromatography. FT-IR Alpha E (Bruker) spectrometer was used to record IR Spectra, solid and liquid compounds were measured in neat condition. The wave numbers are given in [cm⁻¹]. HRMS (Q-Exactive benchtop) was used for the high-resolution mass analysis. Crystals were layered with paratone oil before mounting on the X-Ray diffractometer. X-ray diffraction data were collected on a Bruker Kappa Apex-II CCD diffractometer at 150 K, SHELXT and SHELXL-2014 were used for structure solution.

Preparation of PhMe₂SiI



A flame dried 100 mL Schlenk round bottom flask was equipped with a magnetic stir bar and the condenser. It was evacuated and back filled with nitrogen three times. PdCl₂ (1.5 mol%, 1.91 mmol) was added to the Schlenk round bottom flask from the glovebox. To this, the mixture of MeI (3 eq., 380 mmol) and PhMe₂SiH (1 eq., 127 mmol) was added dropwise and stirred for 18 h at room temperature. This reaction mixture was transferred to the round bottom flask connected to a short path distillation condenser with a fractional collector under the nitrogen atmosphere. The methyl iodide was removed at 40-50 °C under 50 mbar. The desired PhMe₂SiI was distilled out at 80-90 °C under 1 mbar- 0.5 mbar pressure. **¹H NMR (500 MHz, CDCl₃) δ:** 7.75 – 7.66 (m, 2H, 2 x ArCH), 7.51 – 7.44 (m, 3H, 3 x ArCH), 1.11 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃) δ:** 135.7 (ArC), 133.5 (2 x ArCH), 130.6 (ArCH), 128.2 (2 x ArCH), 4.5 (Si(CH₃)₂). NMR data matches with that of literature⁴

2. Optimization of direct synthesis of silylzinc reagent

General procedure for optimization

A flame dried Schlenk tube was evacuated and refilled with nitrogen three times. The Zn powder (2 eq., 10.62 mmol) was taken into the Schlenk tube from the glove box. The Zinc powder was heated with a heat gun for 5 min under the vacuum, evacuated and refilled with nitrogen three times. The additive or activator was added into the tube under the nitrogen atmosphere, followed by the addition of solvent (1.2 M, 4.4 mL) and PhMe₂SiI (1 eq., 5.31 mmol). Then the tube was closed and heated to the temperature mentioned in table S1. The formation of silylzinc reagent was confirmed by titration with iodine (Knochel's method)⁵. On successful titration, the formation of the reagent was further confirmed by copper-catalyzed 1,4-addition on 2-cyclohexen-1-one⁶.

Table S1: Screening of various parameters

$$\text{Ph-Si-I} \xrightarrow[\text{solvent (1.2 M)}]{\text{Zn powder (2 eq.) activator/additive}} \text{Ph-Si-Zn-I}$$

entry	activator (eq.)	additive (eq.)	solvent	temp	time (h)	2a (M)
1	TMSCl (0.12)	-	THF	60 °C	87	ND ^a
2	TMSCl (0.12)	-	toluene	60 °C	87	ND
3 ^d	-	-	THF	70 °C	87	ND ^a
4 ^d	iodine (0.05)	-	DMA	80 °C	87	ND
5 ^d	iodine (0.05)	-	THF	60 °C	87	ND ^a
6 ^d	iodine (0.05)	-	toluene	70 °C	87	ND
7 ^d	-	LiCl (1.0)	toluene	70 °C	87	ND
8 ^b	BrCH ₂ CH ₂ Br (0.03)	LiCl (1.0)	toluene	70 °C	36	ND
9 ^b	BrCH ₂ CH ₂ Br (0.03)	LiCl (1.0)	THF	60 °C	36	ND ^a
10 ^b	BrCH ₂ CH ₂ Br (0.03)	LiCl (1.0)	Et ₂ O	rt	87	ND
11 ^b	BrCH ₂ CH ₂ Br (0.03)	LiCl (1.0)	2-MeTHF	70 °C	87	ND ^a
12 ^b	BrCH ₂ CH ₂ Br (0.03)	LiCl (1.0)	1,4-dioxane	70 °C	36	ND
13 ^d	iodine (0.03)	TMEDA (1.1)	toluene	70 °C	63	0.21
14 ^d	iodine (0.03)	TMEDA (1.1)	toluene	70-90 °C	63	0.68 ^c
15	iodine (0.03)	NMP (1.5)	toluene	85 °C	87	ND
16	iodine (0.03)	DMA (1.5)	toluene	85 °C	87	ND

^aTHF cleaved product observed in GC-MS analysis; ^bTMSCl (1.5 mol%) was used; ^can average of 5 isolated runs; ^d1.5 eq. of Zn powder was used.

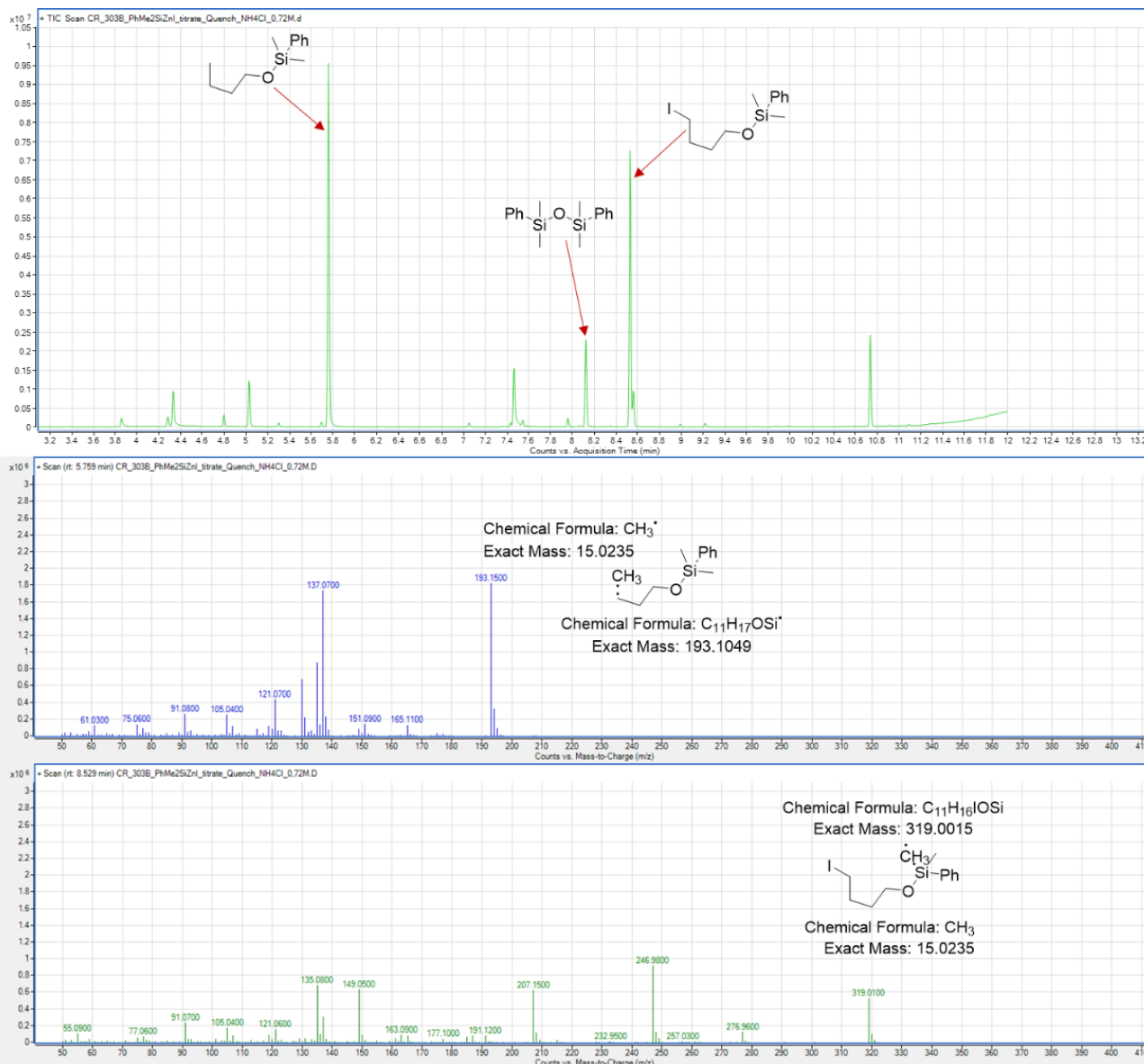


Figure 1a: GC-MS spectrum of entry 1, table S1 after titration with iodine

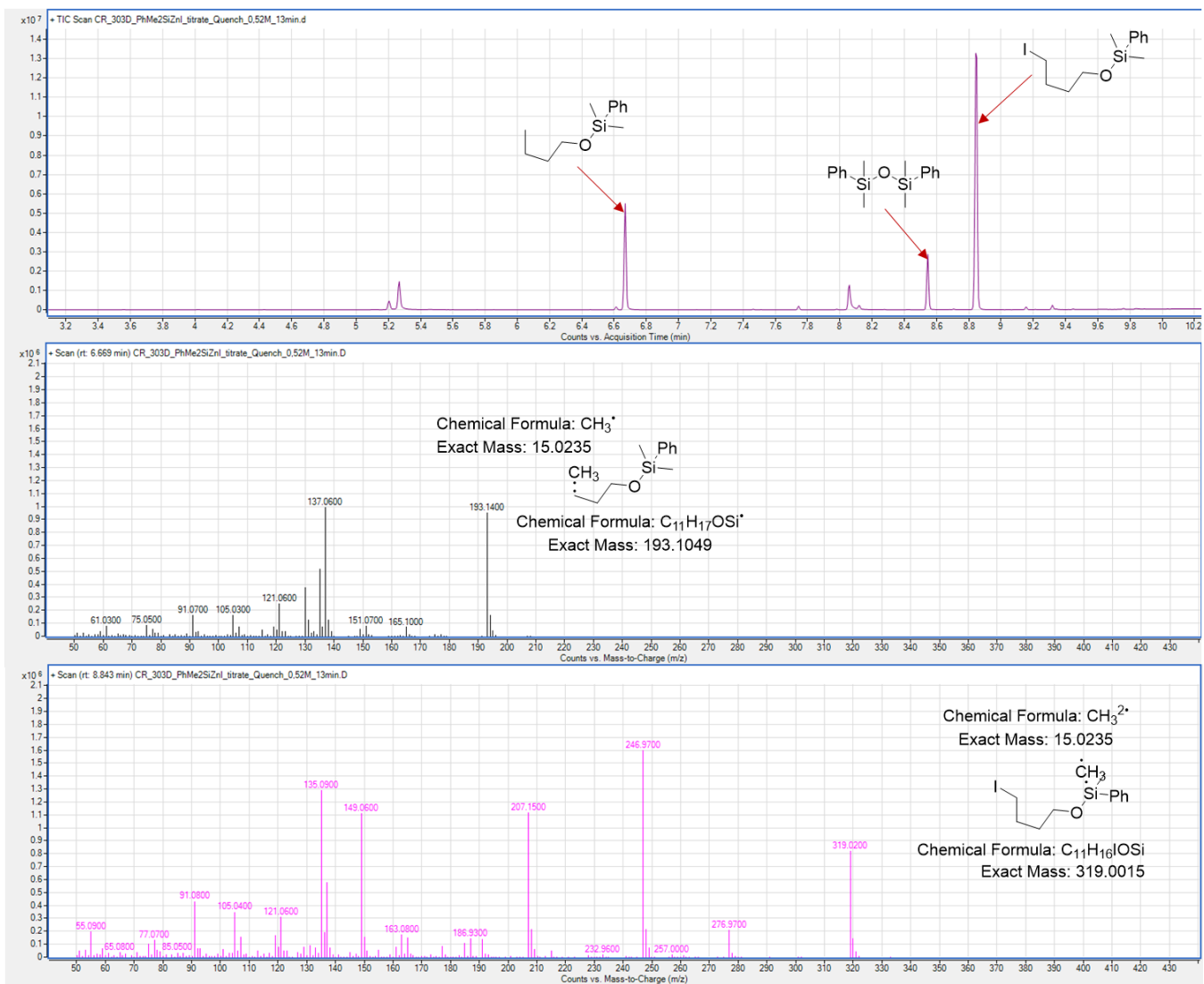


Figure 1b: GC-MS spectrum of entry 5, table S1 after titration with iodine

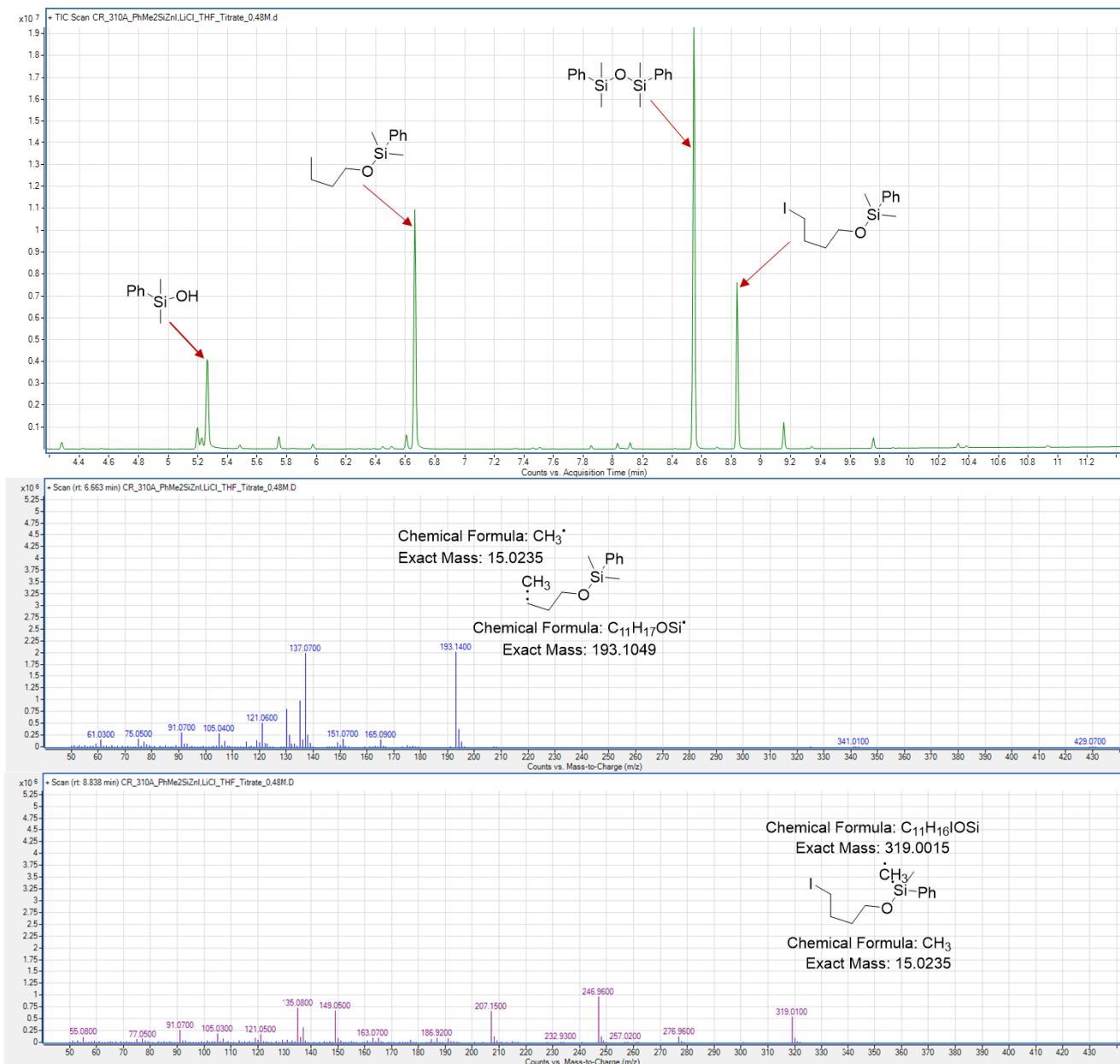
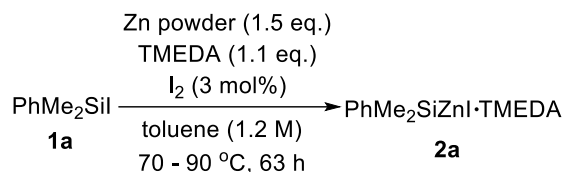


Figure 1c: GC-MS spectrum of entry 9, table S1 after titration with iodine

3. Direct synthesis of silylzinc reagent from silyl iodide

3.1 Preparation of PhMe₂SiZnI·TMEDA (2a)



A flame dried Schlenk tube was evacuated and backfilled with nitrogen three times, then zinc powder (1.5 eq., 39 mmol, 2.63 g) was added and heated with a heat gun under vacuum for 5 min, backfilled with nitrogen then iodine (0.03 eq., 0.78 mmol, 0.204 g) was added, and stirred vigorously for 20 min. After the zinc was activated with iodine, dry toluene (11 mL) and iodo(dimethylphenyl)silane (1 eq., 26 mmol, 7.25 g) were added. To this, a solution of N, N-tetramethylethylene diamine (1.1 eq., 28.6 mmol, 3.43 g, 4.42 mL) in toluene (11 mL) was added dropwise over 45 minutes. The reaction mixture was stirred vigorously at 70 °C for 24 h, then 90 °C for 39 h. After cooling down to rt, the reagent was filtered into the Schlenk tube through a filter paper tipped cannula under the nitrogen atmosphere. The formed PhMe₂SiZnI·TMEDA was titrated against iodine (Knochel's method)⁵ to afford silyl zinc reagent with titers typically ranging from 0.63 – 0.7 M. The silylzinc reagent exists without degradation for more than six months when it is stored at 4 °C.

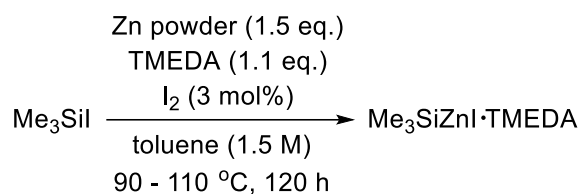
3.1.1 Solidification of PhMe₂SiZnI·TMEDA (2a)



The PhMe₂SiZnI·TMEDA in toluene was filtered into the Schlenk tube via filter paper tipped cannula under the nitrogen atmosphere. The toluene was removed under reduced pressure resulting in dense oil, to this dry hexane/pentane was added resulting in an off white solid (If the solid is not formed immediately after the addition of hexane, the Schlenk tube was cooled to -23 °C and kept undisturbed for 12 h). The formed solid was then washed with hexane three times and dried under reduced pressure. The solid PhMe₂SiZnI·TMEDA was stored at 4 °C under the nitrogen atmosphere. **Melting Point:** 89.6 – 96.1 °C. **¹H NMR** (500 MHz, C₆D₆) δ 7.83 (d, *J* = 6.4 Hz, 2H, 2 x ArCH), 7.30 (t, *J* = 7.5 Hz, 2H, 2 x ArCH), 7.21 – 7.17 (m, 1H, 1 x ArCH), 2.15 (brs, 7H, 7 x NCH₃), 2.00 (s, 1H, NCH₃ proton from partially dissociated/ uncomplexed TMEDA), 1.75 (brs, 9H, 5 x NCH₃ and 4 x N-CH₂), 1.60 (s, 1H, N-CH₂ proton from partially dissociated/ uncomplexed TMEDA), 1.52 (brs, 2H, 2 x N-CH₂ proton from partially dissociated/ uncomplexed TMEDA), 0.63 (s, 6H, Zn-Si(CH₂)₂). **¹³C NMR** (126 MHz, C₆D₆) δ 148.2 (ArC), 134.5 (2 x ArCH), 127.9 (2 x ArCH), 127.4 (1 x ArCH), 56.8 (N-CH₂),

56.2 (N-CH₂ from partially dissociated/ uncomplexed TMEDA), 49.8 (2 x NCH₃), 49.3 (NCH₃ from partially dissociated/ uncomplexed TMEDA), 47.6 (2 x NCH₃), 1.8 (Zn-Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 2995, 2929, 2902, 1468, 1293, 1028, 954, 834, 795.

3.2 Preparation of Me₃SiZnI·TMEDA (2b)



The trimethylsilyl zinc iodide reagent was synthesized from trimethylsilyl iodide (1 eq., 33.7 mmol, 7.03 g, 5 mL), N, N-tetramethylethylene diamine (1.1 eq., 37.1 mmol, 4.44 g, 5.73 mL) and Zn powder (1.5 eq., 50.6 mmol, 3.41 g) by following the above procedure with slight modification in temperature, initially 90 °C for 24 h and temperature was increased to 110 °C for 96 h, toluene (1.5 M). The formed Me₃SiZnI·TMEDA was titrated against iodine (Knochel's method)⁵, to afford silyl zinc reagent with titers typically ranging from 0.53 – 0.66 M. The silylzinc reagent exists without degradation for more than six months when it is stored at 4 °C.

Attempts to synthesize trimethylsilyl zinc bromide from trimethylsilyl bromide by following the above procedure resulted the desired reagent in a very poor concentration i.e., 0.04 M against iodine (Knochel's method)⁵.

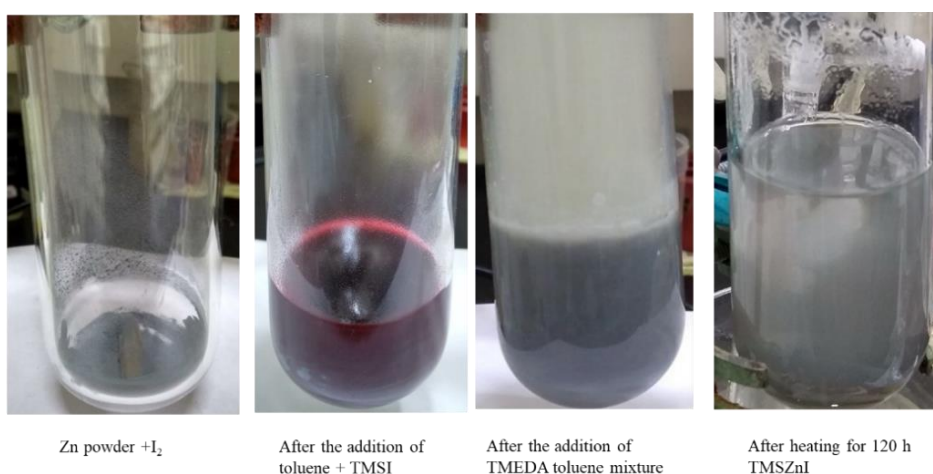


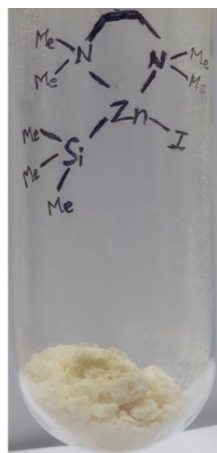
Figure 2: Preparation of Me₃SiZnI·TMEDA

3.2.1 Solidification of Me₃SiZnI·TMEDA (2b)

The Me₃SiZnI·TMEDA in toluene was transferred to the Schlenk tube via filter paper tipped cannula and the toluene was evaporated under reduced pressure giving a crystalline off-white solid which was washed with hexane/pentane three times and dried under reduced pressure. The solid Me₃SiZnI·TMEDA was stored at 4 °C under the nitrogen atmosphere. **Melting Point:** 100 – 108.7 °C. **¹H NMR** (500 MHz, C₆D₆) δ 2.20 (brs, 7H, 7 x NCH₃), 2.03 (s, 5H, NCH₃ proton from partially dissociated/ uncomplexed TMEDA), 1.89 (brs, 9H, 5 x NCH₃ and 4 x N-CH₂), 1.65 (s, 1H, 1 x N-CH₂ proton from partially dissociated/ uncomplexed TMEDA), 0.41 (s, 9H, Zn-Si(CH₃)₃). **¹³C NMR** (126 MHz, C₆D₆) δ 56.7 (N-CH₂), 56.2 (N-CH₂ from partially dissociated/ uncomplexed TMEDA), 49.7 (2 x NCH₃), 49.2 (NCH₃ from partially dissociated/ uncomplexed TMEDA), 47.5 (2 x NCH₃), 3.7 (Zn-Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν: 2945, 2897, 1467, 1293, 1238, 1059, 953, 849, 828, 796.



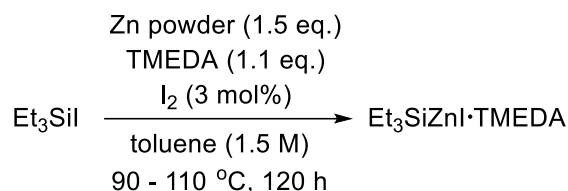
TMSZnI in toluene
after the reaction



Filtered TMSZnI after evaporation

Figure 3. Solidification of Me₃SiZnI·TMEDA

3.3 Preparation of Et₃SiZnI·TMEDA

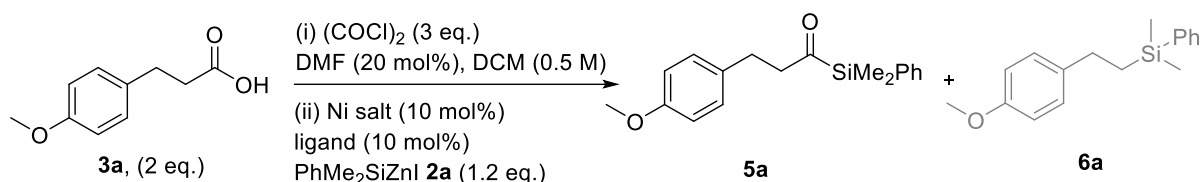


The triethylsilyl zinc iodide was prepared from triethylsilyl iodide⁴ (1 eq., 18.6 mmol, 4.7 g), zinc powder (1.5 eq., 27.9 mmol, 1.88 g), iodine (3 mol%, 0.56 mmol, 0.15 g) and TMEDA (1.1 eq., 20.5 mmol, 2.46 g) by following the procedure in the section 3.2. The formed Et₃SiZnI·TMEDA was titrated against iodine (Knochel's method)⁵ to afford silyl zinc reagent with 0.16 M. However, the reaction of triethylsilyl zinc iodide with 3-(4-

methoxyphenyl)propanoyl chloride (**4a**) was unsuccessful under the optimized condition (general procedure B).

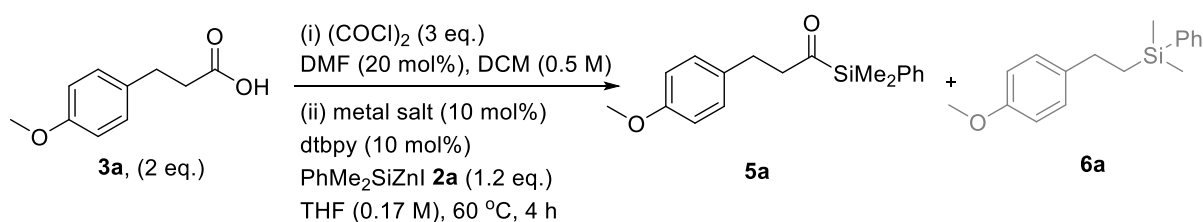
4. Optimization of acylsilane synthesis

General procedure for optimization



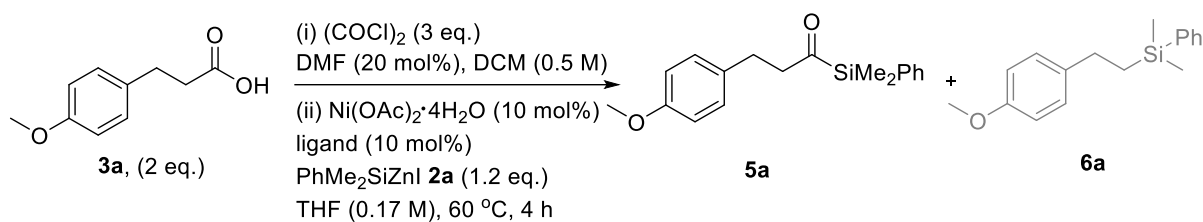
The 3-(4-methoxyphenyl)propanoic acid (**3a**, 2 eq., 0.394 mmol) was added into the flame dried, evacuated and nitrogen filled culture tube containing dry DCM (0.5 M). It was cooled in an ice bath and subsequently DMF (0.2 eq., 0.0394 mmol) and oxalyl chloride (3 eq., 0.591 mmol) were added dropwise and allowed to stir at room temperature. After 1 h, DCM and other volatiles were removed under reduced pressure from the reaction mixture. Thus, the obtained acid chloride was transferred into another flame dried culture tube containing the stirred (5-10 min) mixture of Ni salt (10 mol%, 0.0195 mmol), ligand (10 mol%, 0.0195 mmol) and solvent (0.5 mL). Following the dropwise addition of $\text{PhMe}_2\text{SiZnI}\cdot\text{TMEDA}$ [**2a**, 0.66 M in toluene, 1.2 eq. (0.2 eq. to activate the Ni (II) salt), 0.234 mmol], the remaining solvent (0.29 mL) was also added and stirred at the temperature as mentioned in the screening table. After the completion of the reaction, 1,3,5-trimethoxy benzene (0.195 mmol, 0.25 M in EtOAc, 0.78 mL) was added as an internal standard and diluted with ethyl acetate. An aliquot was taken from the reaction tube and analyzed using ^1H NMR.

Table S2: Screening of metal salt

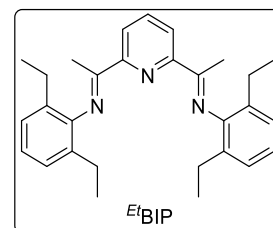


entry	metal salt	5a % ^a
1 ^{b, c}	Ni(COD) ₂	97 (90)
2 ^{b, c, d}	Ni(COD) ₂	95
3 ^{b, g}	NiBr ₂ ·diglyme	60
4	NiCl ₂	29
5	NiBr ₂ ·diglyme	92
6	NiBr ₂ ·glyme	85
7	Ni(acac) ₂	66
8	NiBr ₂	30
9	NiBr ₂ (PPh ₃) ₂	27
10	Ni(OAc) ₂ ·4H ₂ O	86
11	NiI ₂	58
12	NiBr ₂ bpy	21
13	anhydrous Ni(OAc) ₂	10
14	FeCl ₂	5
15	Fe(acac) ₃	10
16	FeBr ₂	3
17	CoBr ₂	ND
18	CoCl ₂	9
19	Co(acac) ₂	6
20 ^{e, f}	CuI	2
21 ^{e, f}	CuCN	3
22 ^f	Without catalyst and ligand	2

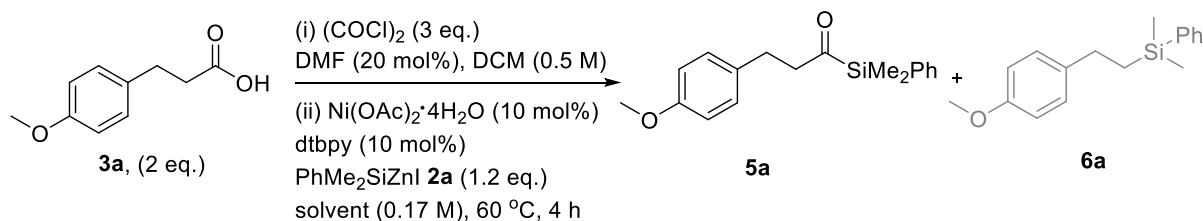
^ayields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard; ^b45 °C; ^c1 eq. of PhMe₂SiZnI; ^d1.5 eq. of carboxylic acid chloride (**4a**); ^e20 mol% of copper catalyst; ^frt, 12 h, 1,2-dimethoxyethane solvent; ^g1.3 eq. of PhMe₂SiZnI·TMEDA; yield in the parenthesis is isolated yield; ND: not detected. 0.17 M is the overall concentration of the reaction. The isolated acid chloride was used for entries 1-22.

Table S3: Screening of ligand

entry	ligand	5a % ^a
1	dtbpy	85
2	bpy	70
3	1,10-phenanthroline	70
4	TMEDA	28
5	^{Et} BIP	23
6	dppe	10
7	PPh_3	34
8	without ligand	17

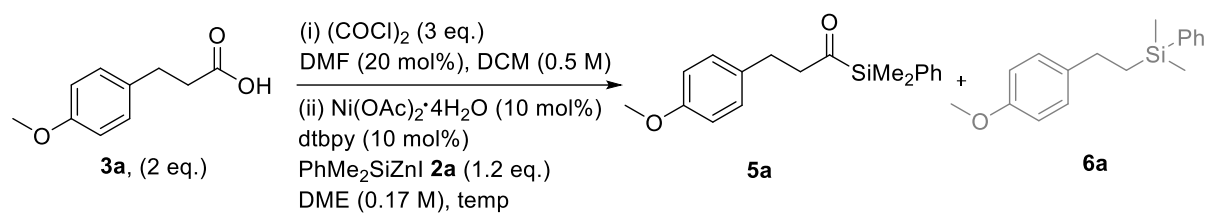


^ayields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Table S4: Screening of solvent

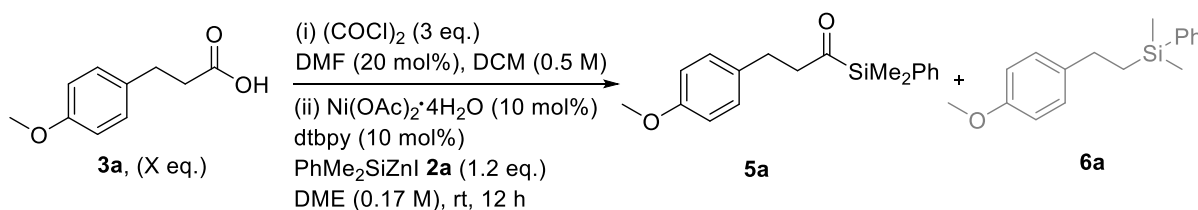
entry	solvent	5a % ^a
1	THF	85
2	2-Me-THF	77
3	toluene	38
4	Et_2O	36
5	1,2-dimethoxyethane	95
6	1,4-dioxane	56
7	1,2-dichloroethane	50

^ayields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard

Table S5: Screening of reaction temperature

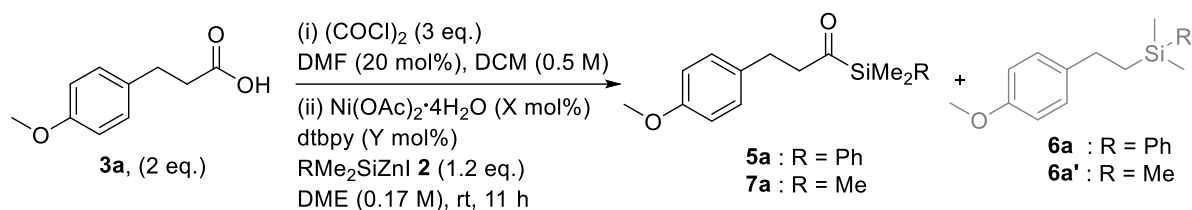
entry	temperature	time (h)	5a % ^a
1	rt	12 h	90 ^b
2	45 °C	8 h	93
3	60 °C	4 h	98

^ayields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard;
^bthe average of two runs. DME: 1,2-dimethoxyethane.

Table S6: Screening of acid chloride equivalence

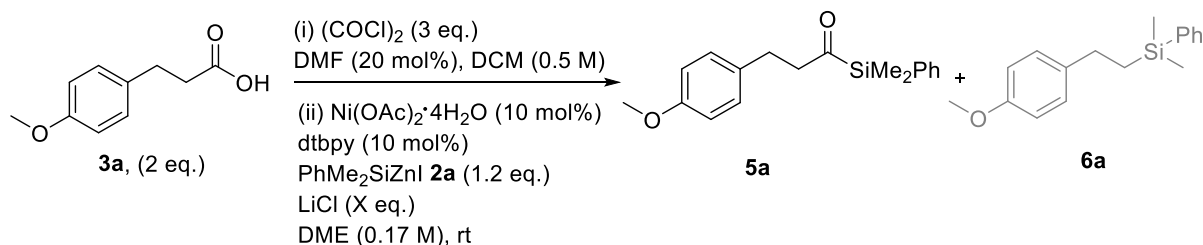
entry	acid chloride eq.	5a % ^a
1	2	91
2	1.5	56

^ayields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard.

Table S7: Screening of nickel salt and ligand equivalence

entry	$\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (X mol%)	dtbpy (Y mol%)	5a % ^a
1 ^b	10	10	89
2 ^{b, d}	5	5	94 (86)
3 ^{b, e}	2	2	52
4 ^{b, f}	1	1	21
5 ^c	10	10	87 (82)
6 ^{c, d}	5	5	58

^a yields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard; ^bR : Ph; ^cR : Me; ^d1.1 eq. of RMe_2SiZnI ; ^e1.04 eq. of $\text{PhMe}_2\text{SiZnI}$; ^f1.02 eq. of $\text{PhMe}_2\text{SiZnI}$; isolated yield in the parenthesis.

Table S8: Effect of LiCl in the standard reaction

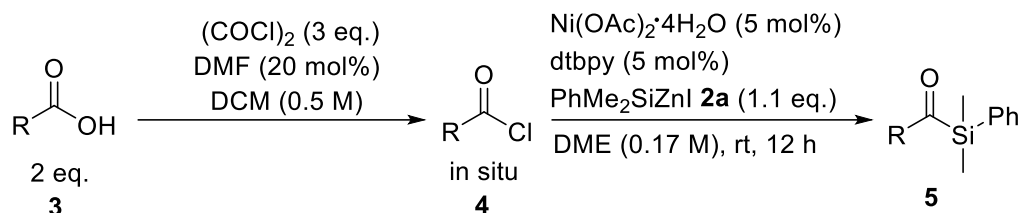
entry	LiCl (X eq.) ^b	5a % ^a
1	0.5 eq.	38 %
2	1 eq.	36 %
3	2 eq.	39 %
4 ^c	1 eq.	42 %

^a yields were determined by ¹H NMR using 1,3,5-trimethoxy benzene as an internal standard.

^b1 M LiCl in THF, ^c5 mol% of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and dtbpy; isolated acid chloride is used in entries 1-4.

5. Synthesis of acylsilane

General procedure A: Ni catalyzed cross-coupling of PhMe₂SiZnI·TMEDA reagent with acyl chloride generated in-situ from carboxylic acid



The oxalyl chloride (3 eq.) and dry DMF (0.2 eq.) was added dropwise to the solution of carboxylic acid (2 eq.) in dry DCM at 0 °C under the nitrogen atmosphere. Followed by stirring at room temperature for 2 h, all the volatiles were removed under reduced pressure.⁷ Then the crude acid chloride was transferred under the nitrogen into another flame dried, evacuated culture tube containing the stirred (5-10 min) mixture of Ni(OAc)₂·4H₂O (5 mol%), dtbpy (5 mol%) and 1,2-dimethoxyethane. The PhMe₂SiZnI·TMEDA [**2a**, 0.66 M in toluene, 1.1 eq (0.1 eq. to activate the Ni (II) salt)] was then added dropwise. Then remaining amount of 1,2-dimethoxyethane was added to make up the overall concentration of 0.17 M and stirred at room temperature for 12 h. The reaction crude was then diluted with EtOAc and quenched with saturated ammonium chloride (3 mL). The crude reaction mixture was extracted with EtOAc three times, then the combined organic layers were dried over Na₂SO₄, concentrated and purified through column chromatography.

General procedure B: Ni catalyzed cross-coupling of Me₃SiZnI·TMEDA reagent with acyl chloride generated in-situ from carboxylic acid

On a slight modification from the general procedure A, the in-situ prepared acyl chloride (**4**, 2 eq.) was transferred into the stirred (5-10 min) mixture of Ni(OAc)₂·4H₂O (10 mol%), dtbpy (10 mol%) and 1,2-dimethoxyethane. Then Me₃SiZnI·TMEDA [**2b**, 0.53 M in toluene, 1.2 eq. (0.2 eq. to activate the Ni (II) salt)] was added dropwise. Then remaining amount of 1,2-dimethoxyethane was added to make up the overall concentration to 0.17 M and stirred at rt for 12 h.

General procedure C: Ni catalyzed cross-coupling of PhMe₂SiZnI·TMEDA reagent with commercial acyl chlorides

The Ni(OAc)₂·4H₂O (5 mol%) and dtbpy (5 mol%) from the glovebox were taken into the flame dried, evacuated and nitrogen filled culture tube. Half of the required amount of 1,2-

dimethoxyethane solvent was added and stirred for 5-10 min. The commercial acyl chloride (**4**, 2 eq.) was added, followed by dropwise addition of PhMe₂SiZnI·TMEDA [**2a**, 0.66 M in toluene, 1.1 eq (0.1 eq. to activate the Ni (II) salt)]. The remaining amount of 1,2-dimethoxyethane was added to make up the overall reaction concentration to 0.17 M and stirred at room temperature for 12 h. The reaction crude was then diluted with EtOAc, quenched with saturated ammonium chloride (3 mL) and the compound was extracted with EtOAc three times. The organic layers were combined, dried over Na₂SO₄, concentrated and purified through column chromatography.

General procedure D: Ni catalyzed cross-coupling of Me₃SiZnI·TMEDA reagent with commercially available acyl chloride

A slight modification from general procedure C was followed, Ni(OAc)₂·4H₂O (10 mol%) and dtbpy (10 mol%) were weighed into the culture tube and about half of the required amount of 1,2-dimethoxyethane was added and stirred for 5-10 min. Then commercial acyl chloride (**4**, 2 eq.) was added, followed by dropwise addition of Me₃SiZnI·TMEDA [**2b**, 0.53 M in toluene, 1.2 eq. (0.2 eq. to activate the Ni (II) salt)] and the remaining amount of 1,2-dimethoxyethane was added to make up the overall concentration to 0.17 M. This was allowed to stir for 12 h at rt.

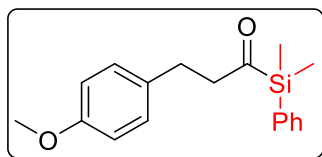
Modified procedure for poor performing substrate

General procedure E: Copper-catalyzed coupling of silylzinc reagent with acyl chloride

The oxalyl chloride (3 eq.) and dry DMF (0.2 eq.) was added dropwise to the solution of carboxylic acid (2 eq.) in dry DCM at 0 °C under the nitrogen atmosphere. Followed by stirring at room temperature for 2 h, all the volatiles were removed under reduced pressure⁷. Then the crude acid chloride was transferred into another flame dried, evacuated nitrogen filled culture tube containing the stirred (5 min) mixture of CuI (20 mol%), LiCl (1 eq.) and 1,2-dimethoxyethane, in an ice bath. The PhMe₂SiZnI·TMEDA [**2a**, 0.71 M in toluene, 1 eq.] or Me₃SiZnI·TMEDA [**2b**, 0.66 M in toluene, 1 eq.] was then added dropwise. Then remaining amount of 1,2-dimethoxyethane was added to make up the overall concentration to 0.15 M and slowly warmed to room temperature and continued the stirring for 12 h. Then 1,3,5-trimethoxybenzene (1 eq., internal standard for NMR measurement) was added to the crude reaction mixture and passed through a plug of silica using ethyl acetate as eluent. The solvent was removed under reduced pressure and yield was measured by ¹H NMR.

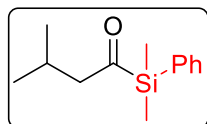
5.1 Substrate scope

1-(dimethyl(phenyl)silyl)-3-(4-methoxyphenyl)propan-1-one (**5a**)



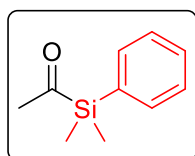
1-(dimethyl(phenyl)silyl)-3-(4-methoxyphenyl)propan-1-one (**5a**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.03mmol, 1.61mL) and in-situ 3-(4-methoxyphenyl)propanoyl chloride (**4a**, 2 eq., 1.87 mmol, 391 mg) by following the general procedure A. The crude was purified by column chromatography (2 % EtOAc/pet ether) to obtain pure product **5a** (240 mg, 86%). ¹H NMR (500 MHz, CDCl₃) δ: 7.57 – 7.50 (m, 2H, 2 x ArCH), 7.45 – 7.36 (m, 3H, 3 x ArCH), 6.99 (d, *J* = 8.7 Hz, 2H, 2 x ArCH), 6.78 (d, *J* = 8.6 Hz, 2H, 2 x ArCH), 3.77 (s, 3H, OCH₃), 2.87 (t, *J* = 7.7 Hz, 2H, -COCH₂-), 2.72 (t, *J* = 7.5 Hz, 2H, -COCH₂CH₂-), 0.48 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ: 245.4 (SiCO), 157.8 (ArC), 134.4 (ArC), 134.0 (2 x ArCH), 133.5 (ArC), 129.9 (ArCH), 129.2 (2 x ArCH), 128.2 (2 x ArCH), 113.8 (2 x ArCH), 55.3 (OCH₃), 50.6 (-COCH₂), 27.4 (COCH₂CH₂), -4.8 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 3028, 2973, 1648, 1518, 1250. LRMS (ESI) *m/z*: (M)⁺ calcd for C₁₈H₂₂O₂Si 298.1384, found 298.1396. Literature⁸

1-(dimethyl(phenyl)silyl)-3-methylbutan-1-one (**5b**)



1-(dimethyl(phenyl)silyl)-3-methylbutan-1-one (**5b**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.37 mmol, 2.1 mL) and in-situ 3-methylbutanoyl chloride (**4b**, 2 eq., 2.49 mmol, 313 mg) by following the general procedure A. The crude was purified by column chromatography (1.5 - 2 % EtOAc/pet ether) to obtain pure product **5b** (218 mg, 79 %). ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H, 2 x ArCH), 7.44 – 7.34 (m, 3H, 3 x ArCH), 2.45 (d, *J* = 6.7 Hz, 2H, -COCH₂-), 2.17 – 2.07 (m, 1H, -CH(CH₃)₂), 0.79 (d, *J* = 6.7 Hz, 6H, -CH(CH₃)₂), 0.48 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 246.9 (SiCO), 134.7 (ArC), 134.1 (2 x ArCH), 129.9 (ArCH), 128.3 (2 x ArCH), 57.8 (-COCH₂-), 23.1 (-CH(CH₃)₂), 22.8 (-CH(CH₃)₂), -4.6 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2971, 1649, 1435, 1115. LRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₃H₂₀OSi 221.1356, found 221.1385. Literature⁹

1-(dimethyl(phenyl)silyl)ethan-1-one (**5bc**)



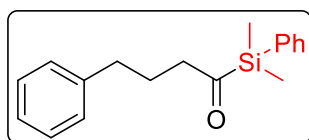
1-(dimethyl(phenyl)silyl)ethan-1-one (**5bc**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and acetyl chloride (**4bc**, 2 eq., 1.78 mmol, 140 mg) by following the general procedure C. The crude was purified through flash column chromatography [step gradient 1%

→2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5bc** (70 mg, 44%). **¹H NMR (500 MHz, CDCl₃)** δ : 7.60 – 7.51 (m, 2H, 2 x ArCH), 7.47 – 7.34 (m, 3H, 3 x ArCH), 2.24 (s, 3H COCH₃), 0.50 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃)** δ : 245.4 (SiCO), 134.4 (ArC), 134.1 (2 x ArCH), 130.0 (ArCH), 128.3 (2 x ArCH), 36.0 (COCH₃), -4.8 (Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 3084, 2982, 1650, 1435, 1346, 1256, 1115, 815, 782, 737, 701. **EI-MS (m/z)**: [M]⁺ for C₁₀H₁₄OSi 178.06. Literature¹⁰

With Ni(OAc)₂ anhydrous instead of Ni(OAc)₂·4H₂O:

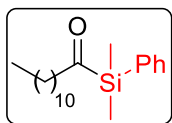
Ni(OAc)₂ anhydrous (5 mol%, 0.0222 mmol, 4 mg) instead of Ni(OAc)₂·4H₂O, dtbpy (5 mol%, 0.0222 mmol, 6.2 mg), (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.488 mmol, 0.79 mL) and acetyl chloride (**4bc**, 2 eq., 0.887 mmol, 71.8 mg) by following the general procedure C gives **5bc** in 10 % NMR yield (w.r.t internal standard 1,3,5-trimethoxybenzene).

1-(dimethyl(phenyl)silyl)-4-phenylbutan-1-one (**5c**)



1-(dimethyl(phenyl)silyl)-4-phenylbutan-1-one (**5c**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.29 mmol, 2.01 mL) and in-situ 4-phenylbutanoyl chloride (**4c**, 2 eq., 2.34 mmol, 489 mg) by following the general procedure A. The reaction crude was purified through column chromatography (2 % EtOAc/pet ether) to obtain pure product **5c** (325.2 mg, 98 %). **¹H NMR (500 MHz, CDCl₃)** δ 7.57 – 7.54 (m, 2H, 2 x ArCH), 7.44 – 7.38 (m, 3H, 3 x ArCH), 7.28 – 7.23 (m, 2H, 2 x ArCH), 7.20 – 7.16 (m, 1H, ArCH), 7.09 – 7.06 (m, 2H, 2 x ArCH), 2.61 (t, J = 7.1 Hz, 2H, COCH₂), 2.51 (t, J = 7.5 Hz, 2H, CH₂), 1.84 – 1.77 (m, 2H, CH₂), 0.49 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃)** δ 246.2 (SiCO), 141.9 (ArC), 134.6 (ArC), 134.1 (2 x ArCH), 130.0 (ArCH), 128.5 (2 x ArCH), 128.4 (2 x ArCH), 128.3 (2 x ArCH), 125.9 (ArCH), 48.0 (COCH₂), 35.2 (CH₂), 23.9 (CH₂), -4.6 (Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 3042, 2961, 1648, 1255. **LRMS (ESI) m/z**: [M+H]⁺ calcd for C₁₈H₂₂OSi 283.1513, found 283.1504. Literature¹¹

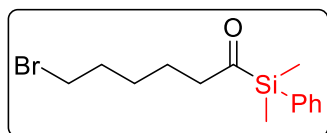
1-(dimethyl(phenyl)silyl)dodecan-1-one (**5d**)



1-(dimethyl(phenyl)silyl)dodecan-1-one (**5d**) was obtained as a colorless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ dodecanoyl chloride (**4d**, 2 eq., 1.78 mmol, 390 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure

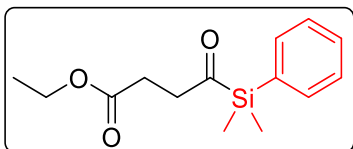
product **5d** (201 mg, 71%). ¹H NMR (500 MHz, CDCl₃) δ: 7.60 – 7.55 (m, 2H, 2 x ArCH), 7.47 – 7.37 (m, 3H, 3 x ArCH), 2.59 (t, *J* = 7.6 Hz, 2H, CH₃CH₂), 1.50 – 1.44 (m, 2H, CH₃CH₂CH₂), 1.38 – 1.16 (m, 16H, Alk-CH₂), 0.94 – 0.88 (m, 3H, Alk-CH₃), 0.52 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ: 246.7 (SiCO), 134.8 (ArC), 134.1 (2 x ArCH), 129.9 (ArCH), 128.3 (2 x ArCH), 49.0 (COCH₂), 32.0 (Alk-C), 29.8 (Alk-C), 29.7 (Alk-C), 29.6 (Alk-C), 29.5 (Alk-C), 29.4 (Alk-C), 22.8 (COCH₂CH₂), 22.3 (CH₃CH₂), 14.2 (CH₃), -4.6 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2970, 2938, 2868, 1650, 1469, 1435, 1257, 1117, 837, 821, 783, 736. EI-MS (*m/z*): [M]⁺ for C₂₀H₃₄OSi 318.16. Literature¹²

6-bromo-1-(dimethyl(phenyl)silyl)hexan-1-one (**5e**)



6-bromo-1-(dimethyl(phenyl)silyl)hexan-1-one (**5e**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.11 mmol, 1.69 mL) and in-situ 6-bromohexanoyl chloride (**4e**, 2 eq., 2.03 mmol, 451 mg) by following the general procedure A. The reaction crude was purified through column chromatography (3 % EtOAc/pet ether) to obtain pure product **5e** (266.5 mg, 84 %). ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H, 2 x ArCH), 7.45 – 7.36 (m, 3H, 3 x ArCH), 3.32 (t, *J* = 6.8 Hz, 2H, BrCH₂), 2.57 (td, *J* = 7.2, 2.4 Hz, 2H, Alk-CH₂), 1.81 – 1.69 (m, 2H, Alk-CH₂), 1.52 – 1.43 (m, 2H, Alk-CH₂), 1.35 – 1.23 (m, 2H, Alk-CH₂), 0.49 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 246.1 (SiCO), 134.6 (ArC), 134.1 (2 x ArCH), 130.0 (ArCH), 128.3 (2 x ArCH), 48.5 (COCH₂), 33.7 (BrCH₂), 32.7 (CH₂), 27.8 (CH₂), 21.3 (CH₂), -4.7 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2952, 1649, 1257, 651. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₁₄H₂₁BrOSi 335.0437, found 335.0436. Literature¹³

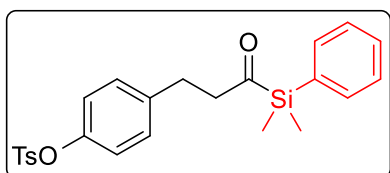
ethyl 4-(dimethyl(phenyl)silyl)-4-oxobutanoate (**5f**)



ethyl 4-(dimethyl(phenyl)silyl)-4-oxobutanoate (**5f**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and ethyl 4-chloro-4-oxobutanoate (**4f**, 2 eq., 1.78 mmol, 293 mg) by following the general procedure C. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f(DCM/pet ether 10:90): 0.5] to obtain pure product **5f** (150 mg, 64%). ¹H NMR (500 MHz, CDCl₃) δ: 7.58 (d, *J* = 6.4 Hz, 2H, 2 x ArCH), 7.41 (d, *J* = 7.5 Hz, 3H, 3 x ArCH), 4.14 – 4.06 (m, 2H, OCH₂CH₃), 2.94 – 2.87 (m, 2H, SiCOCH₂), 2.53 – 2.46 (m, 2H, COOCH₂CH₂), 1.28 – 1.20 (m, 3H, CH₂CH₃), 0.53 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz,

CDCl₃ δ : 243.1 (SiCO), 173.0 (CO₂Et), 134.2 (ArC), 134.1 (2 x ArCH), 130.1 (ArCH), 128.3 (2 x ArCH), 60.5 (OCH₂CH₃), 43.0 (Si-COCH₂CH₂), 26.7 (Si-COCH₂CH₂), 14.2 (CH₂CH₃), -4.8 (Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 3010, 2972, 1740, 1652, 1378, 1256, 1203, 1116, 1033, 838, 814, 738. **HRMS (ESI) *m/z***: [M+H]⁺ Calcd for C₁₄H₂₀O₃Si 265.1254; Found 265.1252.

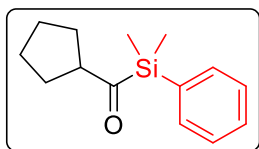
4-(3-(dimethyl(phenyl)silyl)-3-oxopropyl)phenyl 4-methylbenzenesulfonate (**5g**)



4-(3-(dimethyl(phenyl)silyl)-3-oxopropyl)phenyl 4-methylbenzenesulfonate (**5g**) was obtained as colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 4-(3-chloro-3-oxopropyl)phenyl 4-

methylbenzenesulfonate (**4g**, 2 eq., 1.78 mmol, 604 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5g** (160 mg, 41%). **¹H NMR (500 MHz, CDCl₃) δ** : 7.69 (d, *J* = 8.2 Hz, 2H, 2 x ArCH), 7.50 (d, *J* = 6.7 Hz, 2H, 2 x ArCH), 7.44 – 7.35 (m, 3H, 3 x ArCH), 7.30 (d, *J* = 8.1 Hz, 2H, 2 x ArCH), 6.96 (d, *J* = 8.4 Hz, 2H, 2 x ArCH), 6.82 (d, *J* = 8.4 Hz, 2H, 2 x ArCH), 2.84 (t, *J* = 7.4 Hz, 2H, COCH₂), 2.73 (t, *J* = 7.4 Hz, 2H, PhCH₂), 2.44 (s, 3H, Ar-CH₃), 0.46 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃) δ** : 244.8 (SiCO), 147.9 (ArC), 145.4 (ArC), 140.7 (ArC), 134.2 (ArC), 134.1 (2 x ArCH), 132.7 (ArC), 130.1 (ArCH), 129.9 (2 x ArCH), 129.5 (2 x ArCH), 128.6 (2 x ArCH), 128.4 (2 x ArCH), 122.3 (2 x ArCH), 50.0 (COCH₂), 27.6 (PhCH₂), 21.8 (Ar-CH₃), -4.8 (Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 3084, 1745, 1641, 1598, 1502, 1380, 1250, 1094, 833, 695. **HRMS (ESI) *m/z***: [M+H]⁺ Calcd for C₂₄H₂₆O₄SSi 439.1394; Found 439.1390.

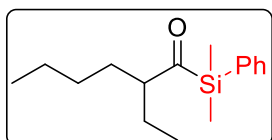
Cyclopentyl(dimethyl(phenyl)silyl)methanone (**5h**)



Cyclopentyl(dimethyl(phenyl)silyl)methanone (**5h**) was obtained as a bright yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ cyclopentanecarbonyl chloride (**4h**, 2 eq., 1.78 mmol, 236 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 05:95): 0.5] to obtain pure product **5h** (150 mg, 72 %). **¹H NMR (500 MHz, CDCl₃) δ** : 7.58 – 7.54 (m, 2H, 2 x ArCH), 7.42 – 7.33 (m, 3H, 3 x ArCH), 3.24 – 3.16 (m, 1H, COCH), 1.72 – 1.63 (m, 2H, Alk-CH₂), 1.59 – 1.44 (m, 6H, Alk-CH₂), 0.50 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃) δ** : 246.7 (CO), 135.2 (ArC), 134.2 (2 x ArCH), 129.9 (ArCH), 128.2 (2 x

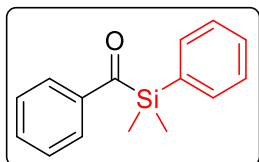
ArCH), 56.5 (Alk-CCO), 26.9 (2 x Alk-CH₂), 26.1 (2 x Alk-CH₂), -4.1(Si(CH₃)₂). **FT-IR** (neat, cm⁻¹) ν : 2970, 2884, 1751, 1735, 1643, 1257, 1118, 833, 783, 736, 702, 653. **EI-MS** (m/z): [M]⁺ for C₁₄H₂₀OSi 232.12. Literature¹¹

1-(dimethyl(phenyl)silyl)-2-ethylhexan-1-one (**5i**)



1-(dimethyl(phenyl)silyl)-2-ethylhexan-1-one (**5i**) was obtained as a colourless oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.11 mmol, 1.69 mL) and in-situ 2-ethylhexanoyl chloride (**4i**, 2 eq., 2.03 mmol, 343 mg) by following the general procedure A. The reaction crude was purified through column chromatography (2 % EtOAc/pet ether) to obtain pure product **5i** (187 mg, 71 %). **¹H NMR** (500 MHz, CDCl₃) δ : 7.59 – 7.54 (m, 2H, 2 x ArCH), 7.42 – 7.35 (m, 3H, 3 x ArCH), 2.78 – 2.70 (m, 1H, COCH₂Et), 1.58 – 1.45 (m, 2H, CH₂), 1.28 – 1.09 (m, 4H, CH₂CH₂), 1.06 – 0.97 (m, 2H, CH₂), 0.78 (t, J = 7.3 Hz, 3H, -CHCH₂CH₂CH₂CH₃), 0.69 (t, J = 7.5 Hz, 3H, -CHCH₂CH₃), 0.49 (s, 6H, Si(CH₃)₂). **¹³C NMR** (126 MHz, CDCl₃) δ : 249.9 (SiCO), 134.9 (ArC), 134.2 (2 x ArCH), 129.9 (ArCH), 128.2 (2 x ArCH), 58.1 (COCH), 29.7 (CHCH₂), 28.9 (CHCH₂CH₂), 22.9 (CHCH₂CH₃), 22.4 (CHCH₂CH₂CH₂CH₃), 13.9 (CHCH₂CH₂CH₂CH₃), 11.9 (CHCH₂CH₃), -4.3 (Si(CH₃)₂). **FT-IR** (neat, cm⁻¹) ν : 3066, 2974, 2942, 1644, 1116, 782. **HRMS** (ESI) m/z : [M+Na]⁺ calcd for C₁₆H₂₆OSi 285.1645, found 285.1644.

(dimethyl(phenyl)silyl)(phenyl)methanone (**5j**)

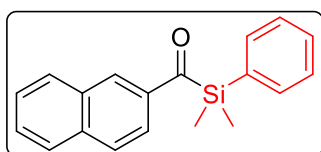


(dimethyl(phenyl)silyl)(phenyl)methanone (**5j**) was obtained as a yellow solid from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.07 mmol, 1.62 mL) and benzoyl chloride (**4j**, 2 eq., 1.94 mmol, 273 mg) by following the general procedure C. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5j** (145 mg, 62 %).

The title compound **5j** was synthesized in a modified procedure by using solid form of (dimethyl(phenyl)silyl)zinc(II) iodide. The copper(I) chloride (20 mol%, 0.0219 mmol, 2.23mg), LiO^tBu (1 eq., 0.109 mmol, 9.02 mg) was taken into the evacuated, nitrogen filled Schlenk tube, 1,2-dimethoxy ethane (0.5 mL) was added to this and cooled in an ice bath. To this mixture benzoyl chloride (**4j**, 2 eq., 0.219 mmol, 32.3 mg), (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1 eq., 0.109 mmol, 50 mg) were added in sequence. The reaction mixture was stirred

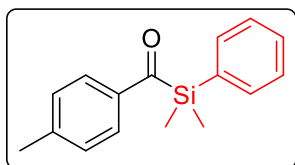
at room temperature for overnight. The 1,3,5-trimethoxy benzene (1 eq., 0.109 mmol, 18.6 mg) was added as an internal standard for NMR analysis. The sample was diluted with ethyl acetate and passed through a plug of silica, concentrated and analyzed by ^1H NMR gave 73 % yield of **5j**. **Melting point:** 57-60 °C. ^1H NMR (500 MHz, CDCl_3) δ : 7.78 – 7.74 (m, 2H, 2 x ArCH), 7.63 – 7.58 (m, 2H, 2 x ArCH), 7.50 – 7.45 (m, 1H, 1 x ArCH), 7.43 – 7.35 (m, 5H, 5 x ArCH), 0.64 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, CDCl_3) δ : 234.0 (SiCO), 141.5 (ArC(CO)), 135.8 (ArC), 134.1 (2 x ArCH), 132.9 (ArCH), 130.0 (ArCH), 128.7 (2 x ArCH), 128.4 (2 x ArCH), 128.0 (2 x ArCH), -2.8 ($\text{Si}(\text{CH}_3)_2$). **FT-IR (neat, cm^{-1})** ν : 3362, 3154, 2913, 2350, 1707, 1620, 1417, 1256, 1214, 1031. **EI-MS (m/z):** $[\text{M}]^+$ for $\text{C}_{15}\text{H}_{16}\text{OSi}$ 240.07. Literature¹⁴

(dimethyl(phenyl)silyl)(naphthalen-2-yl)methanone (**5k**)



(dimethyl(phenyl)silyl)(naphthalen-2-yl)methanone (**5k**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 2-naphthoyl chloride (**4k**, 2 eq., 1.78 mmol, 340 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% \rightarrow 2% \rightarrow 3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5k** (200 mg, 78%). ^1H NMR (500 MHz, CDCl_3) δ : 8.23 (s, 1H, 1 x ArCH), 7.86 – 7.80 (m, 3H, 3 x ArCH), 7.77 (d, $J = 8.2$ Hz, 1H, 1 x ArCH), 7.69-7.66 (m, 2H, 2 x ArCH), 7.58 – 7.53 (m, 1H, 1 x ArCH), 7.50-7.46 (m, 1H, ArCH), 7.45 – 7.39 (m, 3H, 3 x ArCH), 0.69 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, CDCl_3) δ : 233.47 (SiCO), 138.9 (ArC), 136.1 (ArC), 135.6 (ArC), 134.2 (2 x ArCH), 132.6 (ArCH), 131.8 (ArCH), 130.0 (ArCH), 129.8 (Ar-CH), 128.6 (ArCH), 128.5 (ArCH), 128.4 (2 x ArCH), 127.9 (ArCH), 126.7 (ArCH), 122.5 (ArCH), -2.73 ($\text{Si}(\text{CH}_3)_2$). **FT-IR (neat, cm^{-1})** ν : 3064, 2982, 1726, 1702, 1602, 1598, 1475, 1437, 1356, 1258, 1178, 1118, 830, 739. **EI-MS (m/z):** $[\text{M}]^+$ for $\text{C}_{19}\text{H}_{18}\text{OSi}$ 290.08. Literature¹⁵

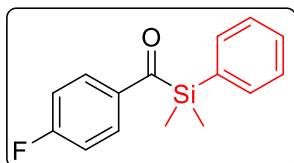
(dimethyl(phenyl)silyl)(*p*-tolyl)methanone (**5l**)



(dimethyl(phenyl)silyl)(*p*-tolyl)methanone (**5l**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.41 mL) and in-situ 4-methylbenzoyl chloride (**4l**, 2 eq., 1.78 mmol, 275 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% \rightarrow 2% \rightarrow 3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5l** (136 mg, 60 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.66 (d, $J = 7.1$ Hz, 2H, 2 x ArCH), 7.59 (d, $J = 6.4$ Hz, 2H, 2 x ArCH), 7.42 – 7.34 (m, 3H, 3 x ArCH), 7.17 (d, $J = 7.8$ Hz, 2H, 2 x ArCH), 2.35 (s, 3H, Ar-

CH_3), 0.61 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, CDCl_3) δ : 233.0 (SiCO), 143.7 (ArC), 139.3 (ArC), 136.1 (ArC), 134.1 (2 x ArCH), 129.9 (ArCH), 129.4 (2 x ArCH), 128.4 (2 x ArCH), 128.2 (2 x ArCH), 21.8 (PhCH_3), -2.7 ($\text{Si}(\text{CH}_3)_2$). FT-IR (neat, cm^{-1}) ν : 3083, 2965, 1593, 1499, 1217, 1111, 827, 785, 743, 655. EI-MS (m/z): $[\text{M}]^+$ for $\text{C}_{16}\text{H}_{18}\text{OSi}$ 254.07. Literature⁸

(dimethyl(phenyl)silyl)(4-fluorophenyl)methanone (5m)

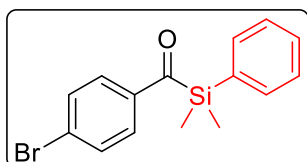


(dimethyl(phenyl)silyl)(4-fluorophenyl)methanone (**5m**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 4-fluorobenzoyl chloride (**4m**, 2 eq., 1.78 mmol, 283 mg) by following the general procedure

A. The reaction crude was purified through flash column chromatography [step gradient 1% \rightarrow 2% \rightarrow 3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5m** (120 mg, 52%).

The yield of compound **5m** was improved by following the general procedure E, CuI (20 mol%, 0.025 mmol, 5 mg), lithium chloride (1 eq., 0.127 mmol, 5.6 mg), in-situ 4-fluorobenzoyl chloride (**4m**, 2 eq., 0.255 mmol, 44 mg), cooled in an ice bath, (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1 eq., 0.127 mmol, 0.18 mL) stirred for 12 h at rt, gave 67 % NMR yield (w.r.t 1 eq., of internal standard 1,3,5-trimethoxybenzene) of **5m**. ^1H NMR (500 MHz, CDCl_3) δ : 7.80 – 7.72 (m, 2H, 2 x ArCH), 7.62 – 7.54 (m, 2H, 2 x ArCH), 7.45 – 7.34 (m, 3H, 3 x ArCH), 7.07 – 7.00 (m, 2H, 2 x ArCH), 0.62 (s, 6H, $\text{Si}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, CDCl_3) δ : 231.8 (SiCO), 165.5 (d, $J = 254.8$ Hz, ArCF), 138.1 (d, $J = 2.9$ Hz, ArC-CO), 135.6 (ArC), 134.1 (2 x ArCH), 130.5 (d, $J = 9.2$ Hz, 2 x ArCH), 130.1 (ArCH) 128.5 (2 x ArCH), 115.8 (d, $J = 22.0$ Hz, 2 x ArCH), -2.9 ($\text{Si}(\text{CH}_3)_2$). ^{19}F NMR (471 MHz, CDCl_3) δ : -105.4 (ArCF). FT-IR (neat, cm^{-1}) ν : 3083, 3038, 1717, 1619, 1587, 1434, 1258, 1210, 1116, 835, 784 EI-MS (m/z): $[\text{M}]^+$ for $\text{C}_{15}\text{H}_{15}\text{FOSi}$ 258.04. Literature¹⁵

(4-bromophenyl)(dimethyl(phenyl)silyl)methanone (5mn)

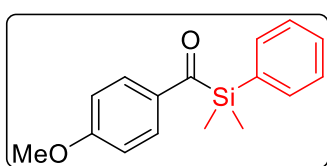


(4-bromophenyl)(dimethyl(phenyl)silyl)methanone (**5mn**) was obtained as a yellow solid from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 4-bromobenzoyl chloride (**4mn**, 2 eq., 1.78 mmol, 283 mg) by following the general

procedure A. The reaction crude was purified through flash column chromatography [step

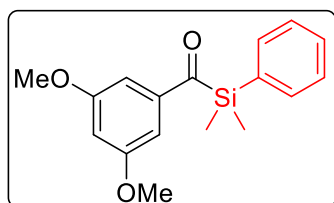
gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5mn** (179 mg, 63%). **Melting point:** 62-65 °C. **$^1\text{H NMR}$ (500 MHz, CDCl_3) δ :** 7.61 – 7.56 (m, 4H, 4 x ArCH), 7.53 – 7.49 (m, 2H, 2 x ArCH), 7.44 – 7.36 (m, 3H, 3 x ArCH), 0.61 (s, 6H, $\text{Si}(\text{CH}_3)_2$). **$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ :** 232.7 (SiCO), 139.9 (ArC), 135.4 (ArC), 134.1 (2 x ArCH), 132.0 (2 x ArCH), 130.1 (ArCH), 129.4 (2 x ArCH), 128.5 (2 x ArCH), 128.0 (ArC), -2.9 ($\text{Si}(\text{CH}_3)_2$). **FT-IR (neat, cm^{-1}) ν :** 3079, 3035, 2972, 1723, 1619, 1586, 1488, 1434, 1211, 1116, 1014, 836, 785. **EI-MS (m/z):** $[\text{M}]^+$ for $\text{C}_{15}\text{H}_{15}\text{BrOSi}$ 318.99. Literature¹⁵

(dimethyl(phenyl)silyl)(4-methoxyphenyl)methanone (**5n**)



(dimethyl(phenyl)silyl)(4-methoxyphenyl)methanone (**5n**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.4 mL) and in-situ 4-methoxybenzoyl chloride (**4n**, 2 eq., 1.78 mmol, 304 mg) by following the general procedure A. The reaction crude was purified through column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5n** (100 mg, 42 %). **$^1\text{H NMR}$ (500 MHz, CDCl_3) δ :** 7.75 (d, $J = 8.8$ Hz, 2H, 2 x ArCH), 7.61 – 7.57 (m, 2H, 2 x ArCH), 7.42 – 7.35 (m, 3H, 3 x ArCH), 6.85 (d, $J = 8.9$ Hz, 2H, 2 x ArCH), 3.82 (s, 3H, -OCH₃), 0.61 (s, 6H, $\text{Si}(\text{CH}_3)_2$). **$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ :** 231 (SiCO), 163.4 (ArC-OMe), 136.3 (ArC), 135.4 (ArC), 134.1 (2 x ArCH), 130.4 (2 x ArCH), 129.9 (ArCH), 128.4 (2 x ArCH), 113.9 (2 x ArCH), 55.6 (OCH₃), -2.6 ($\text{Si}(\text{CH}_3)_2$). **FT-IR (neat, cm^{-1}) ν :** 3085, 2974, 1717, 1619, 1574, 1514, 1314, 1260, 1167, 1114, 1033, 839, 783. **EI-MS (m/z):** $[\text{M}]^+$ for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Si}$ 270.08. Literature⁸

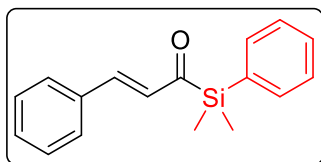
(3,5-dimethoxyphenyl)(dimethyl(phenyl)silyl)methanone (**5no**)



(3,5-dimethoxyphenyl)(dimethyl(phenyl)silyl)methanone (**5no**) was obtained as a bright yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 3,5-dimethoxybenzoyl chloride (**4no**, 2 eq., 1.78 mmol, 358 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5no** (110 mg, 41%). The yield of title compound **5no** was improved by modifying general procedure A. $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (10 mol%, 0.0159 mmol, 4 mg), 1,10-Phenanthroline (10 mol%, 0.0159 mmol, 2.93 mg), CuI (20 mol%, 0.0318 mmol, 6.25 mg), in-

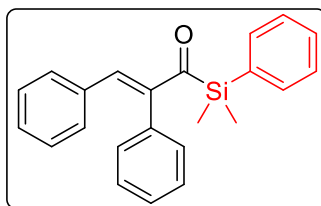
situ 3,5-dimethoxybenzoyl chloride (**4no**, 2 eq., 0.318 mmol, 67.2 mg), (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.2 eq., 0.191 mmol, 0.27 mL), 1,2-dimethoxy ethane (0.8 mL) as a modified general procedure A gave 54 % ¹H NMR yield (w.r.t 1 eq., of internal standard 1,3,5-trimethoxybenzene) of **5no**. ¹H NMR (500 MHz, CDCl₃) δ: 7.66 – 7.58 (m, 2H, 2 x ArCH), 7.43 – 7.37 (m, 3H, 3x ArCH), 6.90 (d, *J* = 2.3 Hz, 2H, 2 x ArCH), 6.57 (t, *J* = 2.4 Hz, 1H, 1 x ArCH), 3.68 (s, 6H, 2 x OCH₃), 0.62 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ: 233.2 (SiCO), 160.9 (2 x ArC), 143.3 (ArC), 136.0 (ArC), 134.1 (2 x ArCH), 130.0 (ArCH), 128.4 (2 x ArCH), 106.0 (ArCH), 105.5 (2 x ArCH), 55.5 (2 x ArOCH₃), -2.9 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2971, 2851, 1711, 1592, 1463, 1432, 1357, 1299, 1255, 1210, 1157, 1066, 842, 785, 758, 683, 626. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₀O₃Si 323.1074; Found 323.1073.

(E)-1-(dimethyl(phenyl)silyl)-3-phenylprop-2-en-1-one (**5o**)



(E)-1-(dimethyl(phenyl)silyl)-3-phenylprop-2-en-1-one (**5o**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ cinnamoyl chloride (**4o**, 2 eq., 1.78 mmol, 297 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/PET ether 10:90): 0.5] to obtain pure product **5o** (130 mg, 55%). ¹H NMR (500 MHz, CDCl₃) δ: 7.64 – 7.61 (m, 2H, 2 x ArCH), 7.45 – 7.33 (m, 8H, 8 x ArCH), 7.31 (d, *J* = 16.5 Hz, 1H, ArCH=CH-), 6.85 (d, *J* = 16.4 Hz, 1H, ArCH=CH-), 0.58 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ: 234.4 (SiCO), 144.3 (ArCH=CH), 135.7 (ArC), 134.9 (ArC), 134.2 (2 x ArCH), 131.5 (ArCH), 130.6 (ArCH), 130.0 (ArCH=CH), 129.0 (2 x ArCH), 128.4 (2 x ArCH), 128.4 (2 x ArCH), -3.6 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 3100, 3079, 1726, 1644, 1593, 987, 827, 742, 703. EI-MS (*m/z*): [M]⁺ for C₁₇H₁₈OSi 266.10. Literature¹⁶

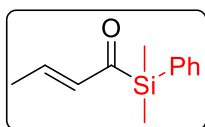
(E)-1-(dimethyl(phenyl)silyl)-2,3-diphenylprop-2-en-1-one (**5p**)



(E)-1-(dimethyl(phenyl)silyl)-2,3-diphenylprop-2-en-1-one (**5p**) was obtained as a yellow solid from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ (E)-2,3-diphenylacryloyl chloride (**4p**, 2 eq., 1.78 mmol, 432 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5]

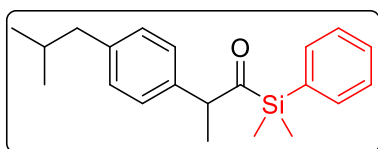
to obtain pure product **5p** (152 mg, 50%). **Melting point:** 133-137 °C. **¹H NMR (500 MHz, CDCl₃)** δ : 7.63 – 7.59 (m, 2H, 2 x ArCH), 7.45 – 7.40 (m, 3H, 3 x ArCH), 7.37 (s, 1H, HC=C), 7.35 – 7.31 (m, 3H, 3 x ArCH), 7.19 – 7.15 (m, 1H, 1 x ArCH), 7.11 (t, $J = 7.6$ Hz, 2H, 2 x ArCH), 7.05 – 7.01 (m, 2H, 2 x ArCH), 6.88 (d, $J = 8.1$ Hz, 2H, 2 x ArCH), 0.54 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃)** δ : 233.5 (SiCO), 146.3 (HC=CCO), 143.4 (ArC), 136.6 (ArCCO), 135.3 (ArC), 134.8 (ArCH), 134.0 (2 x ArCH), 130.7 (2 x ArCH), 129.9 (ArCH), 129.8 (2 x ArCH), 129.4 (ArCH), 128.7 (2 x ArCH), 128.4 (d, $J = 4.0$ Hz, 4 x ArCH), 127.9 (HC=CCO), -2.7 (Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 3081, 1745, 1647, 1631, 1586, 1570, 1251, 1170, 1116, 980, 838, 818, 785, 738, 693. **HRMS (ESI) m/z :** [M+H]⁺ Calcd for C₂₃H₂₂OSi 343.1513; Found 343.1510.

(E)-1-(dimethyl(phenyl)silyl)but-2-en-1-one (**5q**)



(E)-1-(dimethyl(phenyl)silyl)but-2-en-1-one (**5q**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 1.37 mmol, 2.1 mL) and in-situ (E)-but-2-enoyl chloride (**4q**, 2 eq., 2.49 mmol, 272 mg) by following the general procedure A. The reaction crude was purified through column chromatography (1.5 - 3 % EtOAc/pet ether) to obtain pure product **5q** (131 mg, 51 %). **¹H NMR (500 MHz, CDCl₃)** δ 7.57 – 7.51 (m, 2H, 2 x ArCH), 7.43 – 7.34 (m, 3H, 3 x ArCH), 6.70 – 6.60 (m, 1H, -COCH=CH-), 6.27 – 6.22 (m, 1H, -COCH=CH-), 1.82 (dd, $J = 6.8$, 1.6 Hz, 3H, -CH₃), 0.51 (s, 6H, Si(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃)** δ 234.4 (SiCO), 144.9 (ArC), 138.1 (ArC), 135.7 (ArCH), 134.1 (ArCH), 129.9 (-COCH=CH-), 128.3 (-COCH=CH-), 18.8 (-CH₃), -3.4 (Si(CH₃)₂). **FT-IR (neat, cm⁻¹)** ν : 3011, 1651, 1592, 1256. **EI-MS (m/z):** [M]⁺ for C₁₂H₁₆OSi 204.05. Literature¹⁶

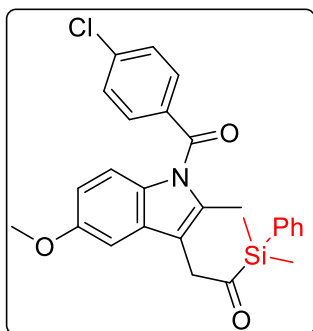
1-(dimethyl(phenyl)silyl)-2-(4-isobutylphenyl)propan-1-one (**5r**)



1-(dimethyl(phenyl)silyl)-2-(4-isobutylphenyl)propan-1-one (**5r**) was obtained as a yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 2-(4-isobutylphenyl)propanoyl chloride (**4r**, 2 eq., 1.78 mmol, 400 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% → 2% → 3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5r** (115 mg, 40%). The yield of title compound **5r** was improved by modifying general procedure A. Ni(OAc)₂•4H₂O (10 mol%, 0.0358 mmol, 9 mg), 1,10-Phenanthroline (10 mol%,

0.0358 mmol, 6.58 mg), CuI (20 mol%, 0.0716 mmol, 14.1 mg), in-situ 2-(4-isobutylphenyl)propanoyl chloride (**4r**, 2 eq., 0.716 mmol, 168 mg), (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.2 eq., 0.43 mmol, 0.61 mL), 1,2-dimethoxy ethane (1.8 mL) as a modified general procedure A gave 89 % (103 mg) of pure **5r** after column chromatography. ¹H NMR (500 MHz, CDCl₃) δ: 7.37 – 7.28 (m, 5H, 5 x ArCH), 7.00 (d, *J* = 7.8 Hz, 2H, 2 x ArCH), 6.83 (d, *J* = 7.8 Hz, 2H, 1 x ArCH), 3.92 (q, *J* = 6.9 Hz, 1H, PhCH), 2.43 (d, *J* = 7.3 Hz, 2H, PhCH₂), 1.87 – 1.81 (m, 1H, PhCH₂CH), 1.21 (d, *J* = 6.7 Hz, 3H, PhCHCH₃), 0.90 (d, *J* = 6.7 Hz, 6H, PhCH₂CH(CH₃)₂), 0.31 (s, 3H, SiCH₃), 0.18 (s, 3H, SiCH₃). ¹³C NMR (126 MHz, CDCl₃) δ: 243.4 (SiCO), 140.6 (ArC), 136.0 (ArC), 135.1 (ArC), 134.2 (2 x ArCH), 129.7 (ArCH), 129.6 (2 x ArCH), 129.0 (2 x ArCH), 128.0 (2 x ArCH), 57.5 (PhCH₂), 45.1 (PhCHCO), 30.4 (PhCH₂CH), 22.5 (PhCH₂CH(CH₃)₂), 16.5 (PhCHCH₃), -3.9 (d, *J* = 8.0 Hz, Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2972, 1683, 1592, 1491, 1431, 1403, 1256, 1209, 1178, 1113, 1071, 1014, 934, 836, 817, 757, 625, 598. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₁H₂₈OSi 347.1802; Found 347.1801.

2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-1-dimethyl(phenyl)silyl)ethan-1-one (**5s**)

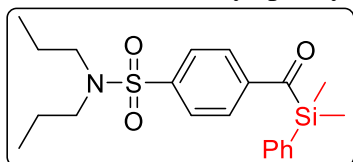


2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-1-(dimethyl(phenyl)silyl)ethanone (**5s**) was obtained as a pale yellow solid from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetyl chloride (**4s**, 2 eq., 1.78 mmol, 674 mg) by following the general procedure A. The reaction crude was purified through column chromatography [step gradient 1% →2%→3%, R_f(DCM/pet ether 20:80): 0.5] to obtain pure product **5s** (119 mg, 28%). **Melting point:** 195-198 °C. ¹H NMR (500 MHz, CDCl₃) δ: 7.61 – 7.58 (m, 2H, 2 x ArCH), 7.47 – 7.44 (m, 2H, 2 x ArCH), 7.42 – 7.40 (m, 2H, 2 x ArCH), 7.34 – 7.30 (m, 2H, 2 x ArCH), 6.83 (d, *J* = 9.0 Hz, 1H, 1 x ArCH), 6.62 (dd, *J* = 9.0, 2.6 Hz, 1H, 1 x ArCH), 6.56 (d, *J* = 2.5 Hz, 1H, 1 x ArCH), 3.78 (s, 2H, CH₂CO), 3.73 (s, 3H, OCH₃), 2.04 (s, 3H, ArCH₃), 0.43 (s, 6H, Si(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ: 241.9 (SiCO), 168.3 (ArCO), 156.1 (ArC), 139.3 (ArC), 136.3 (ArC), 134.3 (ArC), 134.1 (ArC), 134.0 (2 x ArCH), 131.2 (2 x ArCH), 131.1 (ArC), 131.0 (ArC), 130.1 (ArCH), 129.2 (2 x ArCH), 128.2 (2 x ArCH), 115.1 (ArCH), 111.8 (ArCH), 111.6 (ArC), 101.3 (ArCH), 55.7 (OCH₃), 44.9 (CH₂CO), 13.5 (ArCH₃), -4.4 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2957, 1748, 1669, 1616, 1480, 1458, 1372, 1336, 1254,

1231, 1153, 1091, 1069, 993, 840, 756. **HRMS (ESI) m/z :** $[M+H]^+$ Calcd for $C_{27}H_{26}ClNO_3Si$ 476.1443; Found 476.1447.

4-((dimethyl(phenyl)silyl)carbonyl)-N,N-dipropylbenzenesulfonamide (**5t**)

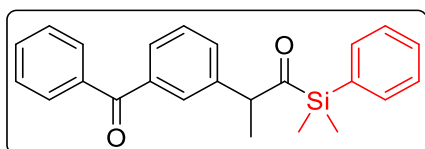
4-((dimethyl(phenyl)silyl)carbonyl)-N,N-dipropylbenzenesulfonamide (**5t**) was



obtained as a yellow solid from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98 mmol, 1.5 mL) and in-situ 4-(N,N-dipropylsulfamoyl)benzoyl chloride (**4t**, 2 eq., 1.78 mmol, 541

mg) by following the general procedure A. The reaction crude was purified through column chromatography [step gradient 1% \rightarrow 2% \rightarrow 3%, R_f (DCM/PET ether 10:90): 0.5] to obtain pure product **5t** (135 mg, 38%). **Melting point:** 126-129 °C. **1H NMR (500 MHz, $CDCl_3$) δ :** 7.79 (s, 4H, 4 x ArCH), 7.59 – 7.55 (m, 2H, 2 x ArCH), 7.47 – 7.37 (m, 3H, 3 x ArCH), 3.07 – 3.03 (m, 4H, N-CH₂), 1.54 – 1.48 (m, 4H, N-CH₂CH₂), 0.84 (t, J = 7.4 Hz, 6H, NCH₂CH₂CH₃), 0.63 (s, 6H, Si(CH₃)₂). **^{13}C NMR (126 MHz, $CDCl_3$) δ :** 233.8 (SiCO), 143.6 (ArC), 143.4 (ArC), 134.9 (ArC), 134.1 (2 x ArCH), 130.3 (ArCH), 128.6 (2 x ArCH), 128.2 (2 x ArCH), 127.4 (2 x ArCH), 50.1 (NCH₂), 22.1 (NCH₂CH₂), 11.2 (NCH₂CH₂CH₃), -3.4 (Si(CH₃)₂). **FT-IR (neat, cm^{-1}) ν :** 2984, 1745, 1625, 1598, 1474, 1352, 1166, 819, 709. **HRMS (ESI) m/z :** $[M+H]^+$ Calcd for $C_{21}H_{29}NO_3SSi$ 404.1710; Found 404.1709.

2-(3-benzoylphenyl)-1-(dimethyl(phenyl)silyl)propan-1-one (**5u**)

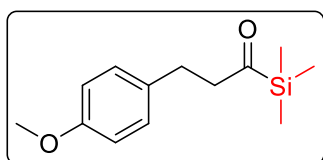


2-(3-benzoylphenyl)-1-(dimethyl(phenyl)silyl)propan-1-one (**5u**) was obtained as a very pale yellow oil from (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.1 eq., 0.98

mmol, 1.5 mL) and in-situ 2-(3-benzoylphenyl)propanoyl chloride (**4u**, 2 eq., 1.78 mmol, 486 mg) by following the general procedure A. The reaction crude was purified through flash column chromatography [step gradient 1% \rightarrow 2% \rightarrow 3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **5u** (83 mg, 25%). The yield of compound **5u** was improved by following the general procedure E, CuI (20 mol%, 0.025 mmol, 5 mg), lithium chloride (1 eq., 0.127 mmol, 5.6 mg), in-situ 2-(3-benzoylphenyl)propanoyl chloride (**4u**, 2 eq., 0.255 mmol, 72.3 mg), cooled in an ice bath, (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1 eq., 0.127 mmol, 0.18 mL) stirred for 12 h at rt, gave 69 % NMR yield of **5u** (w.r.t 1 eq., of internal standard 1,3,5-trimethoxybenzene) of **5u**. **1H NMR (500 MHz, $CDCl_3$) δ :** 7.67 – 7.63 (m, 2H, 2 x ArCH), 7.56 – 7.50 (m, 2H, 2 x ArCH), 7.43 – 7.38 (m, 2H, 2 x ArCH), 7.30 (t, J = 1.8 Hz, 1H, 1 x

ArCH), 7.28 – 7.23 (m, 4H, 4 x ArCH), 7.22 – 7.18 (m, 2H, 2 x ArCH), 7.10 – 7.07 (m, 1H, ArCH), 4.00 (q, $J = 6.9$ Hz, 1H, PhCH), 1.18 (d, $J = 7.0$ Hz, 3H, PhCHCH₃), 0.32 (s, 3H, SiCH₃), 0.20 (s, 3H, SiCH₃). ¹³C NMR (126 MHz, CDCl₃) δ : 243.2 (SiCO), 196.4 (ArCOAr), 139.4 (ArC), 138.1 (ArC), 138.1 (ArC), 134.5 (ArC), 134.1 (2 x ArCH), 132.9 (ArCH), 132.6 (ArCH), 130.8 (ArCH), 130.1 (2 x ArCH), 130.0 (ArCH), 128.9 (ArCH), 128.7 (ArCH), 128.4 (2 x ArCH), 128.1 (2 x ArCH), 57.4 (SiCOCH), 16.6 (SiCOCHCH₃), -4.0 (Si(CH₃)₂). FT-IR (neat, cm⁻¹) ν : 2953, 1659, 1640, 1597, 1280, 1110, 815, 780, 697, 646. HRMS (ESI) m/z : [M+H]⁺ Calcd for C₂₄H₂₄O₂Si 373.1618; Found 373.1616.

3-(4-methoxyphenyl)-1-(trimethylsilyl)propan-1-one (7a)

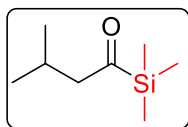


3-(4-methoxyphenyl)-1-(trimethylsilyl)propan-1-one (**7a**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.17 mL) and in-situ 3-(4-methoxyphenyl)propanoyl chloride (**4a**, 2 eq., 1.95 mmol, 408 mg) by following the general procedure B. The reaction crude was purified through column chromatography (1.5 % EtOAc/pet ether) to obtain pure product **7a** (189 mg, 82 %). ¹H NMR (500 MHz, CDCl₃) δ : 7.11 – 7.05 (m, 2H, 2 x ArCH), 6.84 – 6.79 (m, 2H, 2 x ArCH), 3.77 (s, 3H, OCH₃), 2.90 (t, $J = 7.4$ Hz, 2H, -COCH₂-), 2.78 (d, $J = 7.5$ Hz, 2H, -COCH₂CH₂-), 0.18 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ : 247.4 (SiCO), 158.0 (ArC), 133.8 (ArC), 129.3 (2 x ArCH), 113.9 (2 x ArCH), 55.4 (OCH₃), 50.4 (-COCH₂), 27.4 (COCH₂CH₂), -3.2 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν : 3015, 2970, 1649, 1519, 1250. LRMS (ESI) m/z : [M+H]⁺ calcd for C₁₃H₂₀O₂Si 237.1305, found 237.1330. Literature¹⁴

With anhydrous Ni(OAc)₂ instead of Ni(OAc)₂·4H₂O:

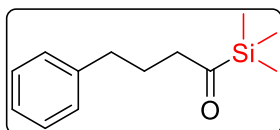
Anhydrous Ni(OAc)₂ (10 mol%, 0.0222 mmol, 4 mg) instead of Ni(OAc)₂·4H₂O, dtbpy (10 mol%, 0.0222 mmol, 6.2 mg), (trimethylsilyl)zinc(II) iodide (**2a**, 1.2 eq., 0.266 mmol, 0.42 mL) and in-situ 3-(4-methoxyphenyl)propanoyl chloride (**4a**, 2 eq., 0.443 mmol, 91.8 mg) by following the general procedure B gives **7a** in 12 % NMR yield (w.r.t internal standard 1,3,5-trimethoxybenzene).

3-methyl-1-(trimethylsilyl)butan-1-one (7b)



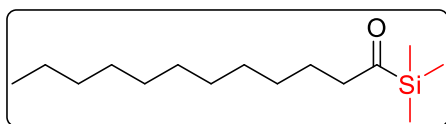
3-methyl-1-(trimethylsilyl)butan-1-one (**7b**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.19 mmol, 1.81 mL) and in-situ 3-methylbutanoyl chloride (**4b**, 2 eq., 1.99 mmol, 276 mg) by following the general procedure B. The reaction crude was purified through column chromatography (0-1 % EtOAc/pet ether) to obtain pure product **7b** (63 mg, 40 %). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 2.46 (d, $J = 6.8$ Hz, 2H, COCH_2), 2.21 – 2.14 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 0.86 (d, $J = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.17 (s, 9H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ : 249.2 (SiCO), 57.6 (CH_2), 23.2 ($\text{CH}(\text{CH}_3)_2$), 22.9 ($\text{CH}(\text{CH}_3)_2$), -3.07 ($\text{Si}(\text{CH}_3)_3$). FT-IR (neat, cm^{-1}) ν : 2973, 1736, 1656, 1597, 1255, 1186, 976, 840, 756. EI-MS (m/z): $[\text{M}]^+$ for $\text{C}_8\text{H}_{18}\text{OSi}$ 158.09. Literature¹⁷

4-phenyl-1-(trimethylsilyl)butan-1-one (7c)



4-phenyl-1-(trimethylsilyl)butan-1-one (**7c**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.17 mL) and in-situ 4-phenylbutanoyl chloride (**4c**, 2 eq., 1.95 mmol, 371 mg) by following the general procedure B. The reaction crude was purified through column chromatography (1.5 % EtOAc/pet ether) to obtain pure product **7c** (196 mg, 91 %). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.31 – 7.26 (m, 2H, 2 x ArCH), 7.21 – 7.15 (m, 3H, 3 x ArCH), 2.66 – 2.57 (m, 4H, CH_2CH_2), 1.91 – 1.82 (m, 2H, CH_2), 0.19 (s, 9H, $\text{Si}(\text{CH}_3)_3$). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ : 248.2 (SiCO), 141.9 (ArC), 128.6 (2 x ArCH), 128.4 (2 x ArCH), 125.9 (ArCH), 47.7 (CH_2), 35.3 (CH_2), 23.8 (CH_2), -3.1 ($\text{Si}(\text{CH}_3)_3$). FT-IR (neat, cm^{-1}) ν : 3041, 2967, 1649, 1255. LRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{20}\text{OSi}$ 243.1176, found 243.1164. Literature¹⁸

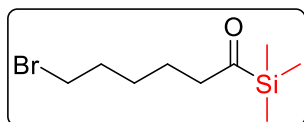
1-(trimethylsilyl)dodecan-1-one (7d)



1-(trimethylsilyl)dodecan-1-one (**7d**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 1.92 mL) and in-situ dodecanoyl chloride (**4d**, 2 eq., 1.95 mmol, 449 mg) by following the general procedure B. The reaction crude was purified through column chromatography (2 % EtOAc/pet ether) to obtain pure product **7d** (214.7 mg, 86 %). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 2.57 (t, $J = 7.3$ Hz, 2H, $-\text{COCH}_2-$), 1.53 – 1.46 (m, 2H, $-\text{COCH}_2\text{CH}_2-$), 1.24 (s, 16H – alkyl CH_2), 0.86 (t, $J = 6.9$ Hz, 3H, $-\text{CH}_3$), 0.18 (s,

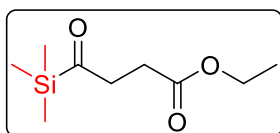
9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 248.8 (SiCO-), 48.7 (alkyl-CH₂), 32.1 (alkyl-CH₂), 29.8 (alkyl-CH₂), 29.6 (alkyl-CH₂), 29.5 (alkyl-CH₂), 29.5 (alkyl-CH₂), 22.8 (alkyl-CH₂), 22.3 (alkyl-CH₂), 14.2 (alkyl-CH₃), -3.0 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2938, 1651, 1255. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₅H₃₂OSi 257.2295; Found 257.2294.

6-bromo-1-(trimethylsilyl)hexan-1-one (7e)



6-bromo-1-(trimethylsilyl)hexan-1-one (**7e**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.17 mL) and in-situ 6-bromohexanoyl chloride (**4e**, 2 eq., 1.95 mmol, 433 mg) by following the general procedure B. The reaction crude was purified through column chromatography (2.5 % EtOAc/pet ether) to obtain pure product **7e** (190 mg, 77 %). ¹H NMR (500 MHz, CDCl₃) δ: 3.37 (t, *J* = 6.8 Hz, 2H, COCH₂), 2.59 (td, *J* = 7.2, 2.3 Hz, 2H, CH₂), 1.87 – 1.75 (m, 2H, CH₂), 1.57 – 1.48 (m, 2H, CH₂), 1.41 – 1.31 (m, 2H, CH₂), 0.18 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 248.1 (SiCO), 48.2 (CH₂), 33.7 (CH₂), 32.8 (CH₂), 27.9 (CH₂), 21.3 (CH₂), -3.1 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2956, 1649, 1256, 650. HRMS (ESI) *m/z*: [M+Na]⁺ calcd for C₉H₁₉BrOSi 273.0281, found 273.0281.

ethyl 4-oxo-4-(trimethylsilyl)butanoate (7f)



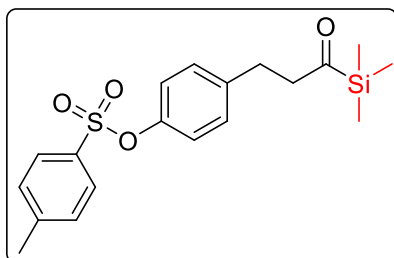
ethyl 4-oxo-4-(trimethylsilyl)butanoate (**7f**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.4 mmol, 2.63 mL) and Ethyl-4-chloro-4-oxobutyrate (**4f**, 2 eq., 2.34 mmol, 401 mg) by following the general procedure D. The reaction crude was purified through column chromatography (2-4 % EtOAc/pet ether) to obtain pure product **7f** (83 mg, 35 %). ¹H NMR (500 MHz, CDCl₃) δ: 4.11 (q, *J* = 7.2 Hz, 2H, CO₂CH₂), 2.92 (t, *J* = 6.6 Hz, 2H, COCH₂), 2.52 (t, *J* = 6.6 Hz, 2H, COCH₂CH₂), 1.24 (t, *J* = 7.1 Hz, 3H, CO₂CH₂CH₃), 0.22 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 245.2 (SiCO), 173.2 (OCO), 60.7 (CH₂), 42.6 (CH₂), 26.7 (CH₂), 14.3 (CH₃), -3.2 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2921, 1741, 1654, 1203, 1163. HRMS (ESI) *m/z*: (M+Na)⁺ calcd for C₉H₁₈O₃Si 225.0917, found 225.0917.

With anhydrous Ni(OAc)₂ instead of Ni(OAc)₂·4H₂O:

anhydrous Ni(OAc)₂ (10 mol%, 0.0277 mmol, 5 mg) instead of Ni(OAc)₂·4H₂O, dtbpy (10 mol%, 0.0277 mmol, 7.7 mg), (trimethylsilyl)zinc(II) iodide (**2a**, 1.2 eq., 0.333 mmol, 0.53 mL) and Ethyl-4-chloro-4-oxobutyrate (**4f**, 2 eq., 0.554 mmol, 94.1 mg) by following the

general procedure D gives **7f** in 21 % NMR yield (w.r.t internal standard 1,3,5-trimethoxybenzene).

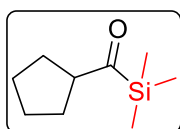
4-(3-oxo-3-(trimethylsilyl)propyl)phenyl 4-methylbenzenesulfonate (**7g**)



4-(3-oxo-3-(trimethylsilyl)propyl)phenyl 4-methylbenzenesulfonate (**7g**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.21 mL) and in-situ 4-(3-chloro-3-oxopropyl)phenyl 4-methylbenzenesulfonate (**4g**, 2 eq., 1.95 mmol, 688 mg) by

following the general procedure B. The reaction crude was purified through column chromatography (6-7 % EtOAc/pet ether) to obtain pure product **7g** (254 mg, 69 %). **¹H NMR (500 MHz, CDCl₃)** δ : 7.69 (d, J = 8.3 Hz, 2H, 2 x ArCH), 7.29 (d, J = 8.3 Hz, 2H, 2 x ArCH), 7.05 (d, J = 8.6 Hz, 2H, 2 x ArCH), 6.86 (d, J = 8.6 Hz, 2H, 2 x ArCH), 2.90 – 2.85 (m, 2H, COCH₂), 2.78 (t, J = 7.3 Hz, 2H, COCH₂CH₂), 2.44 (s, 3H, Ar-CH₃), 0.16 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃)** δ : 246.7 (SiCO), 147.9 (ArC), 145.4 (ArC), 140.8 (ArC), 132.6 (ArC), 129.8 (2 x ArCH), 129.6 (2 x ArCH), 128.6 (2 x ArCH), 122.4 (2 x ArCH), 49.7 (COCH₂), 27.6 (COCH₂CH₂), 21.8 (Ar-CH₃), -3.2 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν : 3065, 2611, 1650, 1377, 1182, 841. **HRMS (ESI) m/z** : [M+Na]⁺ calcd for C₁₉H₂₄O₄SSi 399.1057, found 399.1056.

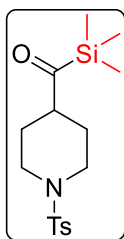
cyclopentyl(trimethylsilyl)methanone (**7h**)



cyclopentyl(trimethylsilyl)methanone (**7h**) was obtained as a pale yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 1.85 mL) and in-situ cyclopentanecarbonyl chloride (**4h**, 2 eq., 1.95 mmol, 641 mg) by

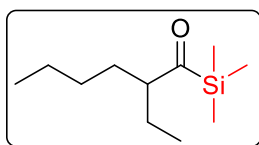
following the general procedure B. The reaction crude was purified through column chromatography (0.8 % EtOAc/pet ether) to obtain pure product **7h** (132 mg, 80 %). **¹H NMR (500 MHz, CDCl₃)** δ : 3.25 – 3.17 (m, 1H, COCH), 1.73 – 1.64 (m, 4H, COCH(CH₂)₂), 1.56 – 1.53 (m, 4H, COCHCH₂(CH₂)₂), 0.19 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃)** δ : 248.5 (SiCO), 56.1 (COCH), 26.8 (COCH(CH₂)₂), 26.1 (COCHCH₂(CH₂)₂), -2.5 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν : 2970, 1645, 1254, 843. **HRMS (ESI) m/z** : [M + H]⁺ Calcd for C₉H₁₈OSi 171.1200; Found 171.1199.

(1-tosylpiperidin-4-yl)(trimethylsilyl)methanone (**7hi**)



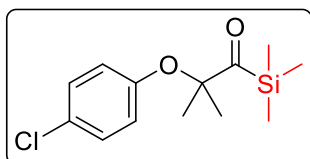
(1-tosylpiperidin-4-yl)(trimethylsilyl)methanone (**7hi**) was obtained as a white solid from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 1.92 mL) and in-situ 1-tosylpiperidine-4-carbonyl chloride (**4hi**, 2 eq., 1.95 mmol, 619 mg) by following the general procedure B. The reaction crude was purified through column chromatography (20-50 % EtOAc/pet ether) to obtain pure product **7hi** (192.1 mg, 58 %). **Melting point:** 111 -114 °C. **¹H NMR (500 MHz, CDCl₃) δ:** 7.62 (d, *J* = 8.2 Hz, 2H, 2 x ArCH), 7.31 (d, *J* = 8.0 Hz, 2H, 2 x ArCH), 3.68 (dt, *J* = 12.1, 3.9 Hz, 2H, -CH₂-), 2.57 (tt, *J* = 10.9, 3.8 Hz, 1H, -CHCO-), 2.42 (s, 3H, Ar-CH₃), 2.40 (d, *J* = 2.9 Hz, 1H, -CH₂-), 2.38 (d, *J* = 2.9 Hz, 1H, -CH₂-), 1.80 (dd, *J* = 13.7, 3.7 Hz, 2H, -CH₂-), 1.67 – 1.56 (m, 2H, -CH₂-), 0.16 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃) δ:** 248.0 (SiCO), 143.7 (ArC), 133.3 (ArC), 129.8 (2 x ArCH), 127.8 (2 x ArCH), 51.9 (2 x -CH₂N-), 45.7 (-CHCO), 25.6 (2 x -CH₂-), 21.6 (Ar-CH₃), -2.5 ((Si(CH₃)₃). **FT-IR (neat, cm⁻¹) ν:** 2944, 2865, 1640, 1339, 1164, 1096. **HRMS (ESI) *m/z*:** [M + H]⁺ Calcd for C₁₆H₂₅NO₃SSi 340.1397; Found 340.1397.

2-ethyl-1-(trimethylsilyl)hexan-1-one (**7i**)



2-ethyl-1-(trimethylsilyl)hexan-1-one (**7i**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.17 mL) and in-situ 2-ethylhexanoyl chloride (**4i**, 2 eq., 1.95 mmol, 330 mg) by following the general procedure B. The reaction crude was purified through column chromatography (1.4 % EtOAc/pet ether) to obtain pure product **7i** (120.8 mg, 62 %). **¹H NMR (500 MHz, CDCl₃) δ:** 2.81 – 2.71 (m, 1H, COCH₂Et), 1.64 – 1.57 (m, 2H, CH₂), 1.30 – 1.22 (m, 4H, CH₂CH₂), 1.20 – 1.10 (m, 2H, CH₂), 0.86 (t, *J* = 7.4 Hz, 3H, -CHCH₂CH₂CH₂CH₃), 0.81 (t, *J* = 7.5 Hz, 3H, -CHCH₂CH₃), 0.19 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃) δ:** 252.3 (SiCO-), 57.9 (-COCH-), 29.9 (-CHCH₂-), 28.9 (-CHCH₂CH₂-), 23.1 (-CHCH₂CH₃), 22.6 (-CHCH₂CH₂CH₂CH₃), 14.1 (-CHCH₂CH₂CH₂CH₃), 12.1 (-CHCH₂CH₃), -2.6 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹) ν:** 2975, 2947, 1644, 1116, 782. **HRMS (ESI) *m/z*:** [M+H]⁺ calcd for C₁₁H₂₄OSi 201.1669, found 201.1666.

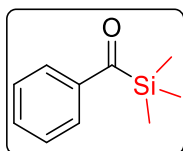
2-(4-chlorophenoxy)-2-methyl-1-(trimethylsilyl)propan-1-one (**7ij**)



2-(4-chlorophenoxy)-2-methyl-1-(trimethylsilyl)propan-1-one (**7ij**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 1.85 mL) and in-situ 2-(4-chlorophenoxy)-

2-methylpropanoyl chloride (**4ij**, 2 eq., 1.95 mmol, 473 mg) by following the general procedure B. The reaction crude was purified through column chromatography (2 % EtOAc/pet ether) to obtain pure product **7ij** (42 mg, 16 %). The title compound **7ij** was synthesized in an alternative method, Ni(COD)₂ (10 mol%, 0.0952 mmol, 27 mg), dtbpy (10 mol%, 0.0952 mmol, 26.3 mg), in-situ 2-(4-chlorophenoxy)-2-methylpropanoyl chloride (**4ij**, 1.5 eq., 1.43 mmol, 347mg), (trimethylsilyl)zinc(II) iodide (**2b**, 1 eq., 0.952 mmol, 1.51 mL), THF (4.1 mL) at rt gives the **7ij** in 22 % yield (56 mg). ¹H NMR (500 MHz, CDCl₃) δ: 7.21 (d, *J* = 8.8 Hz, 2H, 2 x ArCH), 6.80 (d, *J* = 8.9 Hz, 2H, 2 x ArCH), 1.30 (s, 6H, 2 x CH₃), 0.22 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 247.9 (SiCO), 153.7 (ArC), 129.4 (2 x ArCH), 127.8 (ArC), 121.8 (2 x ArCH), 90.0 (C(CH₃)₂), 22.4 (C(CH₃)₂), -1.4 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 3097, 2998, 1661, 1494, 1241, 829. HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₉ClO₂Si 293.0735; Found 293.0727.

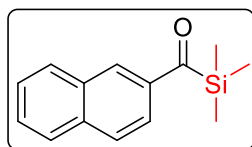
phenyl(trimethylsilyl)methanone (**7j**)



Phenyl(trimethylsilyl)methanone (**7j**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.16 mL) and benzoyl chloride (**4j**, 2 eq., 1.94 mmol, 273 mg) by following the general procedure D.

The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f(DCM/pet ether 10:90): 0.5] to obtain pure product **7j** (75 mg, 43%). ¹H NMR (500 MHz, CDCl₃) δ: 7.86 – 7.81 (m, 2H, 2 x ArCH), 7.57 – 7.52 (m, 1H, 1 x ArCH), 7.51 – 7.44 (m, 2H, 2 x ArCH), 0.38 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 235.9 (SiCO), 141.5 (ArC), 132.8 (ArCH), 128.8 (2 x ArCH), 127.6 (2 x ArCH), -1.2 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 3043, 2967, 1748, 1623, 1586, 1259, 848, 786, 700. EI-MS (*m/z*): [M]⁺ for C₁₀H₁₄OSi 178.07. Literature¹⁹

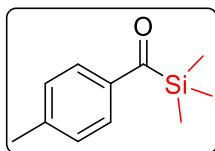
naphthalen-2-yl(trimethylsilyl)methanone (**7k**)



naphthalen-2-yl(trimethylsilyl)methanone (**7k**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.21 mL) and in-situ 2-naphthoyl chloride (**4k**, 2 eq., 1.95 mmol, 383 mg) by following the general procedure B. The reaction crude was purified through column chromatography (1.5 % EtOAc/pet ether) to obtain pure product **7k** (114 mg, 51 %). ¹H NMR (500 MHz, CDCl₃) δ: 8.37 (s, 1H, ArCH), 7.99 (d, *J* = 8.5 Hz, 1H, ArCH), 7.90 (s, 2H, 2 x ArCH), 7.87 (d, *J* = 8.7 Hz, 1H, ArCH), 7.62 – 7.53 (m, 2H, 2 x ArCH), 0.45 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 235.5 (SiCO), 138.9 (ArC), 135.6 (ArC), 132.8 (ArC), 130.9

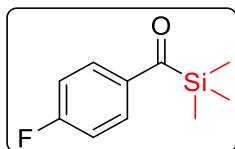
(ArCH), 129.8 (ArCH), 128.8 (ArCH), 128.5 (ArCH), 128.0 (ArCH), 126.8 (ArCH), 122.5 (ArCH), -1.0 (Si(CH₃)₃). **FT-IR** (neat, cm⁻¹) ν : 3070, 2975, 1702, 1254. **EI-MS** m/z : [M]⁺ for C₁₄H₁₆OSi 228.11. Literature²⁰

***p*-tolyl(trimethylsilyl)methanone (7l)**



p-tolyl(trimethylsilyl)methanone (**7l**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.07 mmol, 1.7 mL) and in-situ 4-methylbenzoyl chloride (**4l**, 2 eq., 1.78 mmol, 275 mg) by following the general procedure B. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **7l** (60 mg, 35%). **¹H NMR** (500 MHz, CDCl₃) δ 7.59 (d, J = 7.8 Hz, 2H, 2 x ArCH), 7.12 (d, J = 8.0 Hz, 2H, 2 x ArCH), 2.25 (s, 3H, ArCH₃), 0.21 (s, 9H, Si(CH₃)₃). **¹³C NMR** (126 MHz, CDCl₃) δ : 235.0 (SiCO), 143.6 (ArC), 139.3 (ArC), 129.5 (2 x ArCH), 127.8 (2 x ArCH), 21.8 (ArCH₃), -1.2 (Si(CH₃)₃). **FT-IR** (neat, cm⁻¹) ν : 3085, 2975, 1624, 1601, 1575, 1256, 1226, 1111, 840. **EI-MS** (m/z): [M]⁺ for C₁₁H₁₆OSi 192.09. Literature²¹

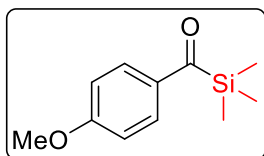
(4-fluorophenyl)(trimethylsilyl)methanone (7m)



(4-fluorophenyl)(trimethylsilyl)methanone (**7m**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.07 mmol, 2.2 mL) and in-situ 4-fluorobenzoyl chloride (**4m**, 2 eq., 1.78 mmol, 283 mg) by following the general procedure B. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **7m** (61 mg, 35%). The yield of compound **7m** was improved by following the general procedure E, CuI (20 mol%, 0.025 mmol, 5 mg), lithium chloride (1 eq., 0.127 mmol, 5.6 mg), in-situ 4-fluorobenzoyl chloride (**4m**, 2 eq., 0.255 mmol, 42.5 mg), cooled in an ice bath, (trimethylsilyl)zinc(II) iodide (**2b**, 1 eq., 0.127 mmol, 0.19 mL) stirred for 12 h at rt, gave 51 % NMR yield (w.r.t 1 eq., of internal standard 1,3,5-trimethoxybenzene) of **7m**. **¹H NMR** (500 MHz, CDCl₃) δ : 7.91 – 7.82 (m, 2H, 2 x *o*ArCH), 7.18 – 7.10 (m, 2H, 2 x *m*ArCH), 0.37 (s, 9H, Si(CH₃)₃). **¹³C NMR** (126 MHz, CDCl₃) δ : 233.7 (SiCO), 165.6 (d, J = 254.3 Hz, ArC), 138.1 (d, J = 2.9 Hz, ArC), 130.2 (d, J = 9.2 Hz, 2 x ArCH), 115.9 (d, J = 22.0 Hz, 2 x ArCH), -1.3 (Si(CH₃)₃). **¹⁹F NMR** (471 MHz, CDCl₃) δ : -105.6 (ArC-F). **FT-IR** (neat, cm⁻¹) ν : 3064,

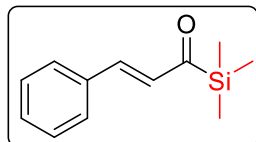
2976, 1621, 1583, 1435, 1257, 1214, 1115, 815, 787, 736, 692, 650. **EI-MS** (m/z): $[M]^+$ for $C_{10}H_{13}FOSi$ 196.08. Literature²¹

(4-methoxyphenyl)(trimethylsilyl)methanone (7n)



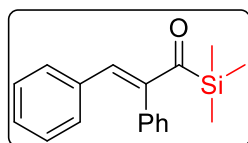
(4-methoxyphenyl)(trimethylsilyl)methanone (**7n**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.07 mmol, 1.62 mL) and in-situ 4-methoxybenzoyl chloride (**4n**, 2 eq., 1.78 mmol, 304 mg) by following the general procedure B. The reaction crude was purified through flash column chromatography [step gradient 1% →2%→3%, R_f (DCM/pet ether 10:90): 0.5] to obtain pure product **7n** (175 mg, 94 %). **¹H NMR (500 MHz, CDCl₃)** δ : 7.83 (d, $J = 8.8$ Hz, 2H, 2 x ArCH), 6.94 (d, $J = 8.8$ Hz, 2H, 2 x ArCH), 3.84 (s, 3H, OCH₃), 0.35 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃)** δ : 232.9 (SiCO), 163.3 (ArC), 135.4 (ArC), 129.9 (2 x ArCH), 113.9 (2 x ArCH), 55.5 (OCH₃), -1.2 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν : 3035, 2974, 1620, 1592, 1573, 1513, 1470, 1313, 1258, 1167, 1034, 836. **EI-MS** (m/z): $[M]^+$ for $C_{11}H_{16}O_2Si$ 208.07. Literature.^{19, 22}

(E)-3-phenyl-1-(trimethylsilyl)prop-2-en-1-one (7o)



(E)-3-phenyl-1-(trimethylsilyl)prop-2-en-1-one (**7o**) was obtained as an orange oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 6 mmol, 9.5 mL) and in-situ cinnamoyl chloride (**4o**, 2 eq., 10 mmol, 1754 mg) by following the general procedure B. The reaction crude was purified through column chromatography (1 % EtOAc/pet ether) to obtain pure product **7o** (633 mg, 62 %). **¹H NMR (500 MHz, CDCl₃)** δ : 7.58 – 7.54 (m, 2H, 2 x ArCH), 7.44 (d, $J = 16.5$ Hz, 1H, ArCH=CH-), 7.42 – 7.38 (m, 3H, 3 x ArCH), 6.90 (d, $J = 16.4$ Hz, 1H, ArCH=CH-), 0.33 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃)** δ : 236.4 (SiCO-), 143.0 (Ar-CH=CH-), 135.0 (ArC), 131.4 (ArCH), 130.6 (Ar-CH=CH-), 129.1 (2 x ArCH), 128.3 (2 x ArCH), -1.9 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν : 3045, 2970, 1648, 1586, 1570, 1456, 1254, 1165, 979, 839, 744, 690. **EI-MS** (m/z): $[M]^+$ for $C_{12}H_{16}OSi$ 204.07. Literature¹⁶

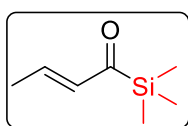
(E)-2,3-diphenyl-1-(trimethylsilyl)prop-2-en-1-one (7p)



2,3-diphenyl-1-(trimethylsilyl)prop-2-en-1-one (**7p**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 2.18 mL) and in-situ (E)-2,3-diphenylacryloyl chloride (**4p**, 2 eq., 1.95 mmol, 498 mg) by following the general procedure B. The reaction crude was purified through

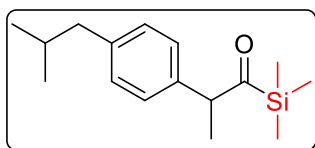
column chromatography (3% EtOAc/pet ether) to obtain pure product **7p** (115 mg, 42 %). **¹H NMR (500 MHz, CDCl₃) δ:** 7.67 (s, 1H, HC=C), 7.63 – 7.58 (m, 3H, 3 x ArCH), 7.50 – 7.46 (m, 1H, 1 x ArCH), 7.45 – 7.41 (m, 2H, 2 x ArCH), 7.38 – 7.34 (m, 4H, 4 x ArCH), 0.53 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃) δ:** 235.5 (SiCO), 146.6 (HC=CCO), 141.5 (ArCH), 135.7 (ArC), 134.9 (ArC), 130.8 (2 x ArCH), 129.8 (2 x ArCH), 129.4 (ArCH), 128.8 (2 x ArCH), 128.4 (2 x ArCH), 127.9 (HC=CCO), -0.88 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹) ν:** 3094, 2983, 1634, 1596, 1499. **HRMS (ESI) m/z:** [M + H]⁺ Calcd for C₁₈H₂₀OSi 281.1356; Found 281.1356.

(E)-1-(trimethylsilyl)but-2-en-1-one (**7q**)



(E)-1-(trimethylsilyl)but-2-en-1-one (**7q**) was obtained as a pale yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.19 mmol, 1.81 mL) and in-situ (E)-but-2-enoyl chloride (**4q**, 2 eq., 1.99 mmol, 226 mg) by following the general procedure B. The reaction crude was purified through column chromatography (1% EtOAc/pet ether) to obtain pure product **7q** (56 mg, 40 %, the yield corresponds to the compound with solvent). **¹H NMR (500 MHz, CDCl₃) δ:** 6.81 – 6.72 (m, 1H, CH₃HC=CH), 6.26 – 6.21 (m, 1H, CH₃HC=CH), 1.92 (dd, *J* = 6.7, 1.7 Hz, 3H, CH₃HC=CH), 0.23 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃) δ:** 236.6 (SiCO), 143.9 (CH₃HC=CH), 138.3 (CH₃HC=CH), 18.8 (CH₃HC=CH), -1.9 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹) ν:** 2973, 1736, 1656, 1597, 1449, 1255, 1186, 976, 840, 756, 697. **EI-MS m/z:** [M]⁺ for C₇H₁₄OSi 142.06. literature²³

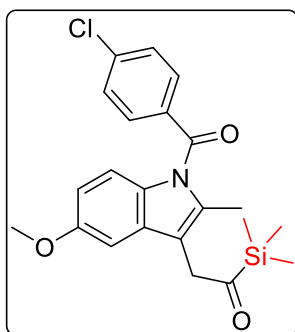
2-(4-isobutylphenyl)-1-(trimethylsilyl)propan-1-one (**7r**)



2-(4-isobutylphenyl)-1-(trimethylsilyl)propan-1-one (**7r**) was obtained as a colourless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.22 mmol, 2.3 mL) and in-situ 2-(4-isobutylphenyl)propanoyl chloride (**4r**, 2 eq., 2.03 mmol, 480 mg) by following the general procedure B. The reaction crude was purified through column chromatography (2.5-4 % EtOAc/pet ether) to obtain pure product **7r** (122mg, 46 %). The yield of title compound **7r** was improved by modifying general procedure A. Ni(OAc)₂·4H₂O (10 mol%, 0.0398 mmol, 10 mg), 1,10-Phenanthroline (10 mol%, 0.0398 mmol, 7.32 mg), CuI (20 mol%, 0.0796 mmol, 15.6 mg), in-situ 2-(4-isobutylphenyl)propanoyl chloride (**4r**, 2 eq., 0.716 mmol, 168 mg), (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 0.477 mmol, 0.76 mL), 1,2-dimethoxy ethane (1.9 mL) as a modified general procedure A gave 71 % (74.4 mg) of pure **7r** after column

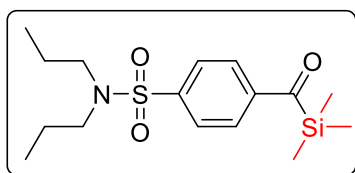
chromatography. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.10 (d, $J = 8.1$ Hz, 2H, 2 x ArCH), 7.02 (d, $J = 8.1$ Hz, 2H, 2 x ArCH), 3.97 (q, $J = 6.8$ Hz, 1H, COCH-), 2.45 (d, $J = 7.2$ Hz, 2H, Ar-CH₂), 1.84 (hept, $J = 13.3, 6.6$ Hz, 1H, -CH(CH₃)₂), 1.27 (d, $J = 6.9$ Hz, 3H, -COCHCH₃), 0.89 (d, $J = 1.3$ Hz, 3H, -CH(CH₃)₂), 0.87 (d, $J = 1.2$ Hz, 3H, -CH(CH₃)₂), -0.03 (s, 9H, Si(CH₃)₃). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ : 245.1 (SiCO), 140.7 (ArC), 136.4 (ArC), 129.7 (2 x ArCH), 128.9 (2 x ArCH), 57.4 (Ar-CH₂-), 45.2 (COCH-), 30.4 (-CH(CH₃)₂), 22.4 (-CH(CH₃)₂), 22.4 -CH(CH₃)₂, 16.4 (COCHCH₃), -2.3 ((Si(CH₃)₃). **FT-IR** (neat, cm^{-1}) ν : 2981, 2891, 1625, 1347. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for C₁₆H₂₆OSi 263.1826; Found 263.1825.

2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-1-(trimethylsilyl)ethan-1-one (7s)



2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)-1-(trimethylsilyl)ethan-1-one (**7s**) was obtained as a pale yellow solid from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 1.92 mL) and in-situ 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetyl chloride (**4s**, 2 eq., 1.95 mmol, 764 mg) by following the general procedure B. The reaction crude was purified through column chromatography (8-12% EtOAc/pet ether) to obtain pure product **7s** (94 mg, 23 %). **Melting point**: 150 – 152 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.66 – 7.64 (m, 2H, 2 x ArCH), 7.46 (d, $J = 8.5$ Hz, 2H, 2 x ArCH), 6.85 (d, $J = 9.0$ Hz, 1H, ArCH), 6.76 (d, $J = 2.5$ Hz, 1H, ArCH), 6.65 (dd, $J = 9.0, 2.6$ Hz, 1H, ArCH), 3.84 (s, 2H, -CH₂CO-), 3.80 (s, 3H, -OCH₃), 2.32 (s, 3H, Ar-CH₃), 0.16 (s, 9H, Si(CH₃)₃). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ : 243.5 (SiCO-), 168.3 (-NCO-Ar), 156.1 (ArC), 139.4 (ArC), 136.1 (ArC), 134.1 (ArC), 131.3 (2 x ArCH), 131.2 (ArC), 131.0 (ArC), 129.2 (2 x ArCH), 115.1 (ArCH), 112.0 (ArC), 111.7 (ArCH), 101.5 (ArCH), 55.8 (-OCH₃), 44.6 (-CH₂CO-), 13.8 (Ar-CH₃), -2.68 ((Si(CH₃)₃). **FT-IR** (neat, cm^{-1}) ν : 3081, 2965, 1671, 1615, 1481, 1371, 1336, 1230, 1068, 841. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for C₂₂H₂₄ClNO₃Si 414.1287; Found 414.1282.

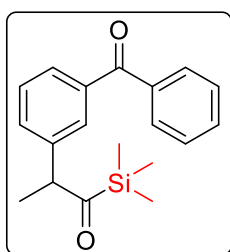
N,N-dipropyl-4-((trimethylsilyl)carbonyl)benzenesulfonamide (7t)



N, N-dipropyl-4-((trimethylsilyl)carbonyl)benzenesulfonamide (**7t**) was obtained as a yellow oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.22 mmol, 2.29 mL) and in-situ 4-(N,N-dipropylsulfamoyl)benzoyl chloride (**4t**, 2 eq., 2.03 mmol, 641

mg) by following the general procedure B. The reaction crude was purified through column chromatography (5 % EtOAc/pet ether) to obtain pure product **7t** (66 mg, 19 %). ¹H NMR (500 MHz, CDCl₃) δ: 7.89 (s, 4H, 4 x ArCH), 3.11 – 3.06 (m, 4H, N-(CH₂CH₂CH₃)₂), 1.58 – 1.50 (m, 4H, N-(CH₂CH₂CH₃)₂), 0.85 (t, *J* = 7.4 Hz, 6H, N-(CH₂CH₂CH₃)₂), 0.37 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 235.6 (SiCO), 143.6 (ArC), 143.4 (ArC), 127.9 (2 x ArCH), 127.5 (2 x ArCH), 50.1 (N-(CH₂CH₂CH₃)₂), 22.1 (N-(CH₂CH₂CH₃)₂), 11.2 (N-(CH₂CH₂CH₃)₂), -1.5 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2981, 1625, 1347, 1257, 1160, 841. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₂₇NO₃SSi 342.1554; Found 342.1551.

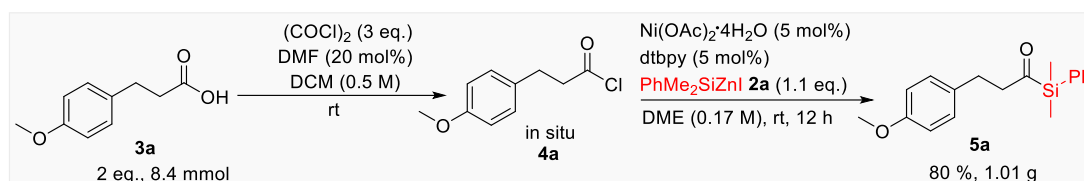
2-(3-benzoylphenyl)-1-(trimethylsilyl)propan-1-one (**7u**)



2-(3-benzoylphenyl)-1-(trimethylsilyl)propan-1-one (**7u**) was obtained as a colorless oil from (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 1.17 mmol, 1.92 mL) and in-situ 2-(3-benzoylphenyl)propanoyl chloride (**4u**, 2 eq., 1.95 mmol, 554 mg) by following the general procedure B. The reaction crude was purified through column chromatography (3-6% EtOAc/pet ether) to obtain pure product **7u** (53 mg, 17 %). The yield of title compound **7u** was improved by modifying general procedure A. Ni(OAc)₂·4H₂O (10 mol%, 0.0159 mmol, 4 mg), 1,10-Phenanthroline (10 mol%, 0.0159 mmol, 2.93 mg), CuI (20 mol%, 0.0318 mmol, 6.25 mg), in-situ 2-(3-benzoylphenyl)propanoyl chloride (**4u**, 2 eq., 0.318 mmol, 91.4 mg), (trimethylsilyl)zinc(II) iodide (**2b**, 1.2 eq., 0.191 mmol, 0.29 mL), 1,2-dimethoxy ethane (1.9 mL) as a modified general procedure A gave 41 % (w.r.t 1 eq., of internal standard 1,3,5-trimethoxybenzene) of **7u**. ¹H NMR (500 MHz, CDCl₃) δ: 7.79 – 7.76 (m, 2H, 2 x ArCH), 7.66 (dt, *J* = 7.7, 1.4 Hz, 1H, ArCH), 7.63 – 7.57 (m, 2H, 2 x ArCH), 7.50 – 7.42 (m, 3H, 3 x ArCH), 7.34 (dt, *J* = 7.7, 1.5 Hz, 1H, ArCH), 4.13 (q, *J* = 6.9 Hz, 1H, -CHCH₃), 1.32 (d, *J* = 6.9 Hz, 3H, -CHCH₃), 0.04 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 244.8 (SiCO), 196.6 (PhCO-), 139.9 (ArC), 138.3 (ArC), 137.6 (ArC), 132.8 (ArCH), 132.7 (ArCH), 130.6 (ArCH), 130.1 (2 x ArCH), 129.0 (ArCH), 128.8 (ArCH), 128.5 (2 x ArCH), 57.3 (-CHCH₃), 16.6 (-CHCH₃), -2.3 ((Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2970, 1720, 1647, 1458, 1254. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₂O₂Si 311.1462; Found 311.1460.

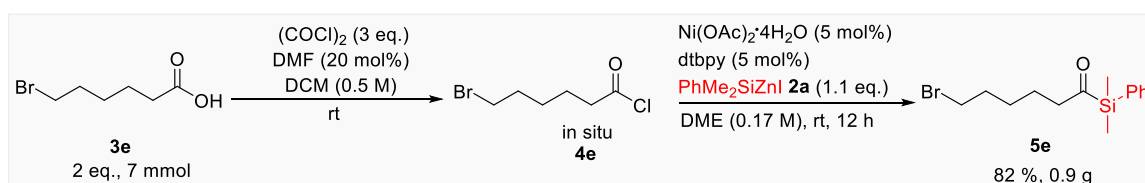
6. Large scale synthesis:

1-(dimethyl(phenyl)silyl)-3-(4-methoxyphenyl)propan-1-one (5a)



Under an inert atmosphere, 3-(4-methoxyphenyl)propanoic acid (**3a**, 8.4 mmol) was added into two neck round bottom flask containing dry dichloromethane (17 mL) and cooled in an ice bath. Then oxalyl chloride (12.6 mmol) and DMF (0.84 mmol) were added dropwise. After 2 h the solvent and other volatiles were removed under reduced pressure. The formed 3-(4-methoxyphenyl)propanoyl chloride was transferred into another round bottom Schlenk flask containing the stirred (5-10 min) mixture of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (5 mol %, 0.21 mmol, 53.9 mg), dtbpy (5 mol%, 0.21 mmol, 58.9 mg) and 1,2-dimethoxy ethane (10 mL). To this $\text{PhMe}_2\text{SiZnI} \cdot \text{TMEDA}$ (**2a**, 1.1 eq., 4.62 mmol, 6.32 mL) was added dropwise and the remaining 1,2-dimethoxy ethane (8 mL) was added to make up the overall concentration to 0.17 M. The reaction was then stirred at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate, quenched with saturated ammonium chloride (10 mL) and extracted with ethyl acetate three times. The organic layers were combined, dried over Na_2SO_4 , concentrated under reduced pressure and purified by column chromatography (2 % EtOAc/pet ether) to obtain pure product **5a** (1.01 g, 80%).

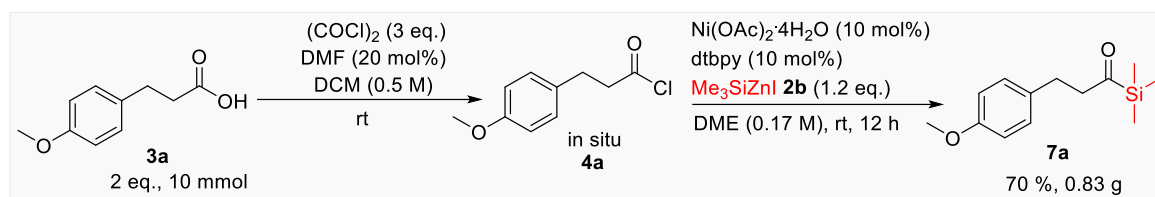
6-bromo-1-(dimethyl(phenyl)silyl)hexan-1-one (5e)



Into a two-neck round bottom flask, 6-bromohexanoic acid (**3e**, 7 mmol) and dry dichloromethane (14 mL) was added under nitrogen atmosphere. The flask was cooled in an ice bath, then oxalyl chloride (10.5 mmol) and DMF (0.7 mmol) were added dropwise. After 2 h, the solvent and other volatiles were removed under reduced pressure. The formed 6-bromohexanoyl chloride was transferred into another round bottom Schlenk flask containing the stirred (5-10 min) mixture of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (5 mol %, 0.175 mmol, 44.9 mg), dtbpy (5 mol%, 0.175 mmol, 48.4 mg) and 1,2-dimethoxyethane (10 mL). Following dropwise addition

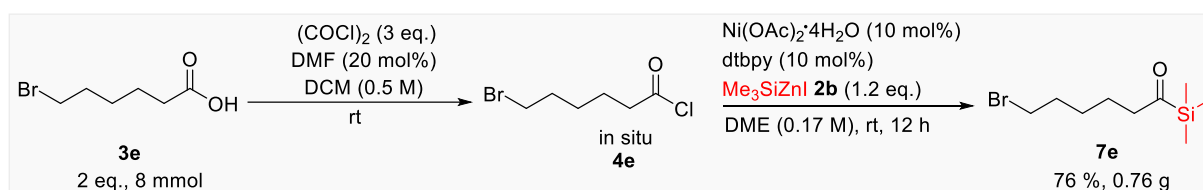
of $\text{PhMe}_2\text{SiZnI}\cdot\text{TMEDA}$ (**2a**, 1.1 eq., 4.62 mmol, 5.53 mL), the remaining 1,2-dimethoxy ethane (5 mL) was added and continued to stir at room temperature for 12 h. The reaction mixture was then diluted with ethyl acetate, quenched with saturated ammonium chloride (10 mL) and extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4 , concentrated under reduced pressure and then purified by column chromatography (3 % EtOAc/pet ether) to obtain pure product **5e** (0.9 g, 82 %).

3-(4-methoxyphenyl)-1-(trimethylsilyl)propan-1-one (**7a**)



3-(4-methoxyphenyl)propanoic acid (**3a**, 10 mmol) was taken into a flame dried two neck round bottom flask under nitrogen atmosphere, dry dichloromethane (20 mL) was added and cooled in an ice bath. Oxalyl chloride (15 mmol) and DMF (1 mmol) were added dropwise. After 2 h, solvent and other volatiles were removed under vacuum. The formed 3-(4-methoxyphenyl)propanoyl chloride was transferred to the round bottom Schlenk flask containing the stirred (5-10 min) mixture of $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (10 mol %, 0.5 mmol, 128 mg) and dtbpy (10 mol%, 0.5 mmol, 138 mg), 1,2-dimethoxy ethane (11 mL). Then $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ (**2b**, 1.2 eq., 6 mmol, 10.9 mL) was added dropwise and the remaining 1,2-dimethoxy ethane (8 mL) was added to make up the concentration to 0.17 M. Then it was allowed to stir at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate, quenched with saturated ammonium chloride (10 mL) and extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4 , concentrated under reduced pressure and then purified by column chromatography (1 - 1.5 % EtOAc/pet ether) to obtain pure product **7a** (0.83 g, 70%).

6-bromo-1-(trimethylsilyl)hexan-1-one (**7e**)



Under an inert atmosphere, 6-bromohexanoic acid (**3e**, 8 mmol) and dry dichloromethane (16 mL) was added into a flame dried two neck round bottom flask. Cooling in an ice bath, oxalyl

chloride (12 mmol) and DMF (0.8 mmol) were added dropwise. After 2 h, the solvent and other volatiles were removed under reduced pressure. The formed 6-bromohexanoyl chloride was transferred into another round bottom Schlenk flask containing the stirred (5-10 min) mixture of Ni(OAc)₂·4H₂O (10 mol %, 0.4 mmol, 103 mg), dtbpy (10 mol%, 0.4 mmol, 111 mg) and 1,2- dimethoxyethane (10 mL). Then to this solution, Me₃SiZnI·TMEDA (**2b**, 1.2 eq., 4.8 mmol, 8.73 mL) was added dropwise and the remaining 1,2-dimethoxyethane (5 mL) was added and allowed to stir at room temperature for 12 h. The reaction mixture was then diluted with ethyl acetate, quenched with saturated ammonium chloride (10 mL) and extracted with ethyl acetate three times. The combined organic layers were dried over Na₂SO₄, concentrated under reduced pressure and then purified by column chromatography (2.5 - 3 % EtOAc/pet ether) to obtain a pure product **7e** (0.76 g, 76 %).

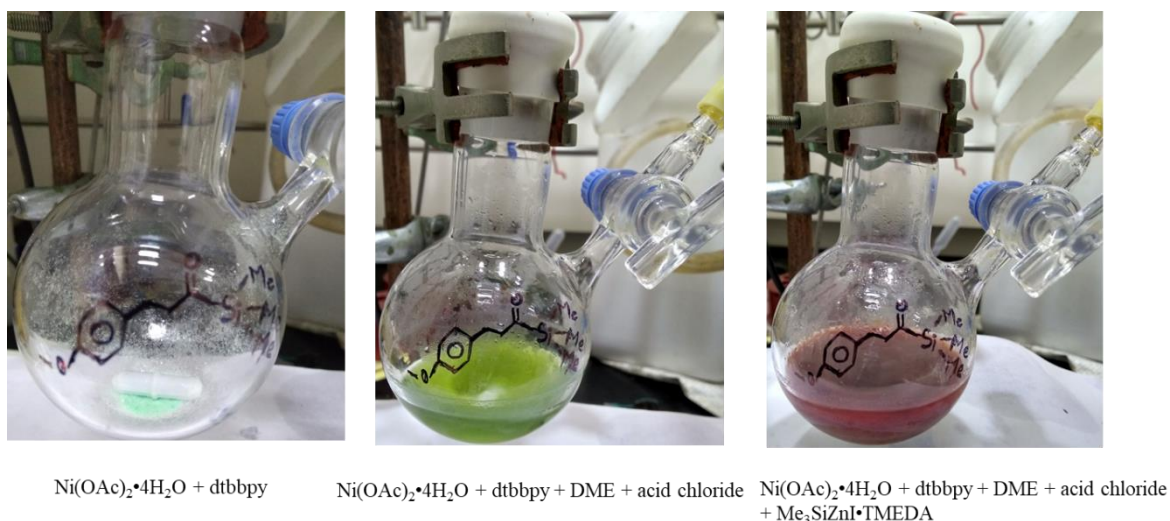
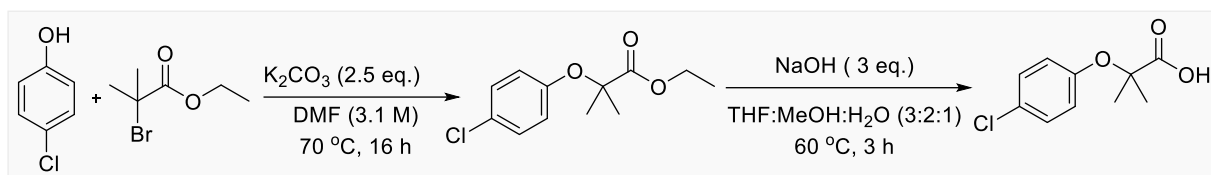


Figure 4: Large scale reaction

7. Synthesis of Starting material

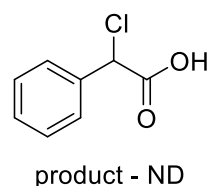
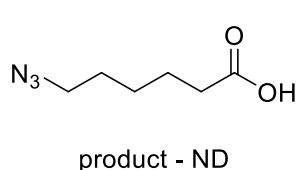
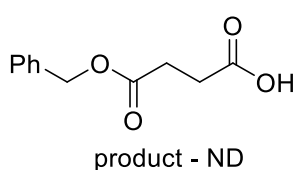
Carboxylic acids **3b**, **3c**, **3d**, **3e**, **3h**, **3i**, **3k**, **3l**, **3m**, **3n**, **3no**, **3o**, **3p**, **3q**, **3r**, **3s**, **3t**, **3u** and Starting material **8a**, **9a**, **10a**, **12a** are commercially available and used without purification. Carboxylic acid chloride **3bc**, **3f**, **3j** and **11a**, *o*-tolualdehyde, styrene are commercially available and used after distillation under inert conditions. Carboxylic acids **3a**²⁴, **3g**²⁵, **3hi**²⁶, chalcone **13a**²⁸, pyridinium salt **16a**⁷, redox ester **17a**²⁹ were synthesized according to the literature procedure and ¹H and ¹³C NMR data matches with the reported literature.

Synthesis of Clofibric acid (3ij)²⁷



Clofibric acid was synthesized according to the slightly modified literature procedure²⁷. To a solution of 4-chloro phenol (5 g, 38.9 mmol) in DMF (13 mL), anhydrous potassium carbonate (10.73 g, 97.25 mmol) and ethyl-2-bromo-isobutyrate (12.13 g, 77.8 mmol) were added. The resulting mixture was heated at 70 °C for 12 h. Upon completion of the reaction monitored by TLC, the solution was diluted with EtOAc (100 ml) and washed with 10 % NaOH, H₂O, brine (2 X 20 ml). The compound was extracted with EtOAc three times and the combined organic fractions were dried over Na₂SO₄ and concentrated under reduced pressure to obtain ethyl 2-(4-chlorophenoxy)-2-methylpropanoate which was taken to the next step without purification. To a solution of ethyl 2-(4-chlorophenoxy)-2-methylpropanoate in THF: MeOH: H₂O (3:2:1), was added NaOH (3.7 g, 117 mmol) and stirred for 16 h at 60 °C. After the completion of the reaction, the solvent was removed by using a rotary evaporator and the residue was diluted with ethyl acetate, water and cooled in an ice bath followed by acidification with 1N HCl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The pure product was obtained by using column chromatography (25- 30 % EtOAc/pet ether) in 74 % yield (6.15 g). **¹H NMR (500 MHz, CDCl₃) δ:** 7.25 – 7.21 (m, 2H, 2 X ArCH), 6.90 – 6.86 (m, 2H, 2 X ArCH), 1.60 (s, 6H, C(CH₃)₂). **¹³C NMR (126 MHz, CDCl₃) δ:** 178.2 (CO₂H), 153.0 (ArC), 129.4 (2 X ArCH), 128.5 (ArC), 121.1 (2 X ArCH), 85.5 (C(CH₃)₂), 24.96 (C(CH₃)₂). **EI-MS *m/z*:** [M]⁺ for C₁₀H₁₁ClO₃Si 214.0

Incompatible carboxylic acid coupling partners:



ND = not detected

8. Crystallization of Silyl Zinc reagent

8.1 (dimethyl(phenyl)silyl)zinc(II) iodide (2a)

A flame dried Schlenk tube was evacuated and refilled with nitrogen, to this (dimethyl(phenyl)silyl)zinc(II) iodide (0.71 M in toluene, 0.5 mL) was added followed by addition of 3 mL of toluene : pentene (1:1) mixture and cooled to -40 °C. After two days colourless crystals were obtained.

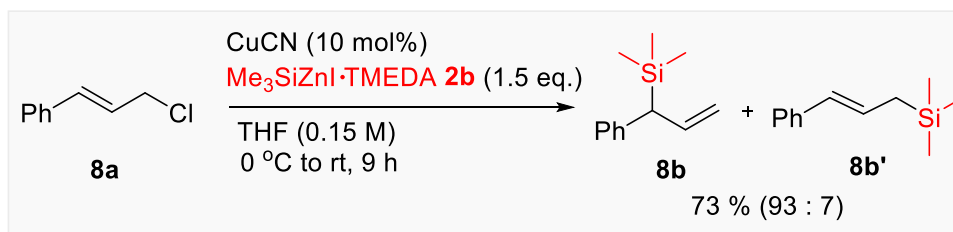
8.2 (trimethylsilyl)zinc(II) iodide (2b)

In a flame dried Schlenk tube (trimethylsilyl)zinc(II) iodide (0.66 M in toluene, 0.5 mL) was added under the nitrogen atmosphere. Approximately half the volume of toluene was evaporated under vacuum and the Schlenk tube was cooled to -40 °C. After one and half days colourless crystals were obtained.

9. Application of (trimethylsilyl)zinc(II) iodide (2b) in the solid form

9.1. Allylation reaction

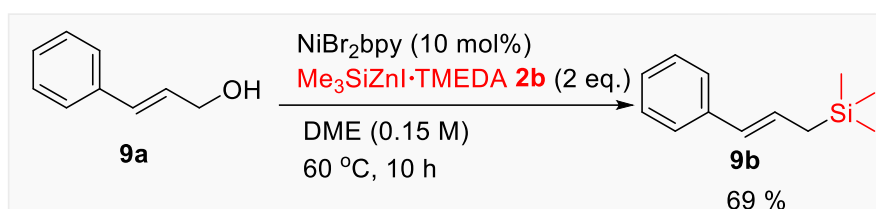
9.1.1. Synthesis of trimethyl(1-phenylallyl)silane (8b)³⁰



In a nitrogen filled Schlenk tube, copper(I) nitrile (10 mol%, 0.127 mmol, 11.6 mg) was taken from the glovebox, dry THF (5 mL) was added and the tube was cooled in an ice bath. The cinnamyl chloride (8a, 1 eq., 1.27 mmol, 200 mg) was added followed by (trimethylsilyl)zinc(II) iodide (2b, 1.5 eq., 1.91 mmol, 758 mg) weighed in a vial from the glovebox was added into the Schlenk tube, then remaining amount of dry THF (3.5 mL) was added and stirred at room temperature for 9 h. The reaction mixture was diluted with dichloromethane, passed through celite and purified by silica gel column chromatography (pet ether) giving a colourless oil 8b with 73 % (93:7/b : l) yield (174.8 mg). ¹H NMR (500 MHz, CDCl₃) δ: 7.26 (d, *J* = 10.0 Hz, 2H, 2 X ArCH), 7.12 (d, *J* = 7.1 Hz, 1H, 1 X ArCH), 7.08 (d, *J* = 7.7 Hz, 2H, 2 X ArCH), 6.27 – 6.13 (m, 1H, -CH=CH₂), 5.00 – 4.95 (m, 2H, CH=CH₂), 2.97 (d, *J* = 9.8 Hz, 1H, PhCH-), -0.02 (s, 9H, -Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃)

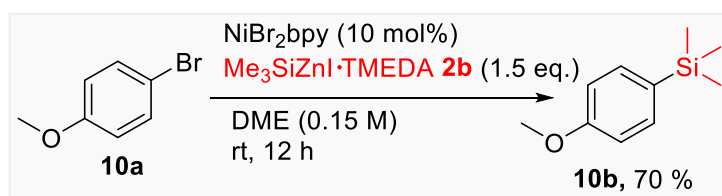
δ : 142.5 (1 X ArC-), 138.2 (-CH=CH₂), 128.4 (2 X ArCH), 127.3 (2 X ArCH), 124.7 (1 X ArCH), 112.7 (CH=CH₂), 44.8 (PhCH-), -2.9 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν : 3040, 2972, 1634, 1607, 1502, 1254, 1089, 903, 835, 745, 700, 640. **EI-MS (m/z)**: [M]⁺ for C₁₂H₁₈Si 190.10. Literature.^{30b}

9.1.2. Synthesis of cinnamyltrimethylsilane (**9b**)^{3b}



Cinnamyl alcohol (**9a**, 1 eq., 1.03 mmol, 141 mg) was added under the inert atmosphere to the Schlenk tube containing the NiBr₂bpy (10 mol%, 0.103 mmol, 39.4 mg), the dry 1,2-dimethoxy ethane (5 mL) was added and stirred for 5 min at room temperature. To this (trimethylsilyl)zinc(II) iodide (**2b**, 2 eq., 2.06 mmol, 819 mg), remaining amount of dry 1,2-dimethoxy ethane (1.9 mL) were added and stirred for 10 h at 60 °C. The crude was diluted with dichloromethane and passed through celite. The crude was purified by silica gel column chromatography (pet ether) to get a pure compound **9b** in 69 % yield (134.6 mg). **¹H NMR (500 MHz, CDCl₃)** δ : 7.33 – 7.27 (m, 4H, 4 X ArCH), 7.17 (t, *J* = 7.2 Hz, 1H, 1 X ArCH), 6.28 – 6.24 (m, 2H, -CH=CH), 1.70 – 1.67 (m, 2H, CH₂Si(CH₃)₃), 0.07 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃)** δ : 138.7 (1 X ArC-), 128.6 (2 X ArCH), 128.4 (PhCH=CH), 128.0 (1 X ArCH), 126.3 (PhCH=CH), 125.7 (2 X ArCH), 24.1 (CH₂Si(CH₃)₃), -1.7 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹)** ν : 3037, 2969, 1650, 1502, 1254, 1153, 966. **EI-MS (m/z)**: [M]⁺ for C₁₂H₁₈Si 190.09. Literature.³¹

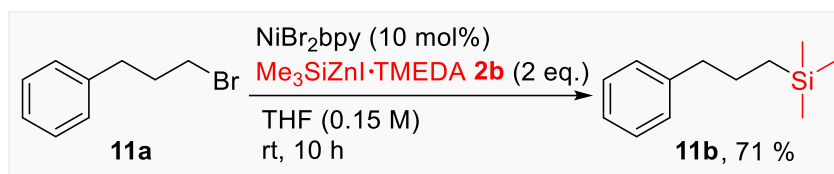
9.2. Arylation: Synthesis of (4-methoxyphenyl)trimethylsilane (**10b**)³²



A NiBr₂bpy (10 mol%, 0.101 mmol, 38.5 mg) was added into the Schlenk tube inside the glovebox. The Schlenk tube was evacuated and back filled with nitrogen three times, dry 1,2-dimethoxy ethane (4 mL) and 4-bromoanisole (**10a**, 1 eq., 1.01 mmol, 194 mg) were added. The (trimethylsilyl)zinc(II) iodide (**2b**, 1.5 eq., 1.52 mmol, 600 mg) weighed in a vial inside

the glovebox was added into the Schlenk tube, then remaining amount of dry 1,2-dimethoxy ethane (2.7 mL) was added and stirred at room temperature for 12 h. The crude was diluted with ethyl acetate, passed through the celite and purified by silica gel column chromatography (pet ether), obtained a colourless oil **10b** in 70 % yield (127 mg). ¹H NMR (500 MHz, CDCl₃) δ: δ 7.47 (d, *J* = 8.6 Hz, 2H, 2 X ArCH), 6.93 (d, *J* = 8.5 Hz, 2H, 2 X ArCH), 3.83 (s, 3H, Ar-OCH₃), 0.26 (s, 9H, Ar-Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 160.4 (ArC-OCH₃), 134.9 (2 X ArCH), 131.5 (ArC-Si(CH₃)₃), 113.6 (2 X ArCH), 55.2 ((Ar-OCH₃), -0.8 (Ar-Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2970, 1602, 1573, 1510, 1470, 1253, 1251, 1188, 1116, 1039, 840, 758, 715, 695. EI-MS (*m/z*): [M]⁺ for C₁₀H₁₆OSi 180.07. Literature.^{32c-e}

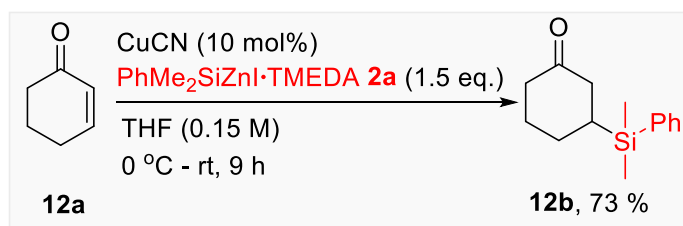
9.3. Alkylation: Synthesis of trimethyl(3-phenylpropyl)silane (**11b**)^{3a}



The Schlenk tube was evacuated and backfilled nitrogen, NiBr₂bpy (10 mol%, 0.0889 mmol, 33.9 mg) weighed inside the glovebox was added into the tube. In a nitrogen filled Schlenk tube dry THF (4 mL) and (3-bromopropyl)benzene (**11a**, 1 eq., 0.889 mmol, 180 mg) were added. Then the (trimethylsilyl)zinc(II) iodide (**2b**, 2 eq., 1.77 mmol, 705 mg) in a vial (weighed inside the glovebox), dry THF (1.9 mL) were added and stirred at room temperature for 10 h. The crude was diluted with dichloromethane, passed through celite then further purified by silica gel column chromatography (pet ether) leads to the pure trimethyl(3-phenylpropyl)silane (**11a**) as colourless oil in 71 % yield (121.1 mg). ¹H NMR (500 MHz, CDCl₃) δ: 7.31 (t, *J* = 7.6 Hz, 2H, 2 X ArCH), 7.23 – 7.19 (m, 3H, 3 X ArCH), 2.65 (t, *J* = 7.7 Hz, 2H, PhCH₂CH₂CH₂), 1.70 – 1.61 (m, 2H, PhCH₂CH₂CH₂), 0.61 – 0.55 (m, 2H, PhCH₂CH₂CH₂), 0.01 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 142.9 (1 X ArC), 128.6 (2 X ArCH), 128.4 (2 X ArCH), 125.8 (1 X ArCH), 40.1 (PhCH₂CH₂CH₂), 26.3 (PhCH₂CH₂CH₂), 16.8 (PhCH₂CH₂CH₂), -1.5 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 3041, 2697, 1504, 1253, 836, 745, 697. EI-MS (*m/z*): [M]⁺ for C₁₂H₂₀Si 192.13. Literature.³³

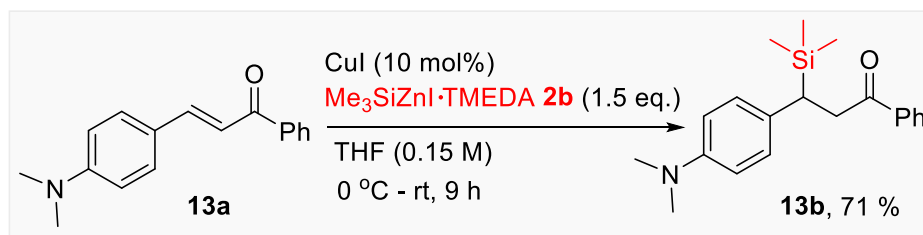
9.4. 1,4-addition^{6, 35-36}

9.4.1 Synthesis of 3-(dimethyl(phenyl)silyl)cyclohexan-1-one (**12b**)



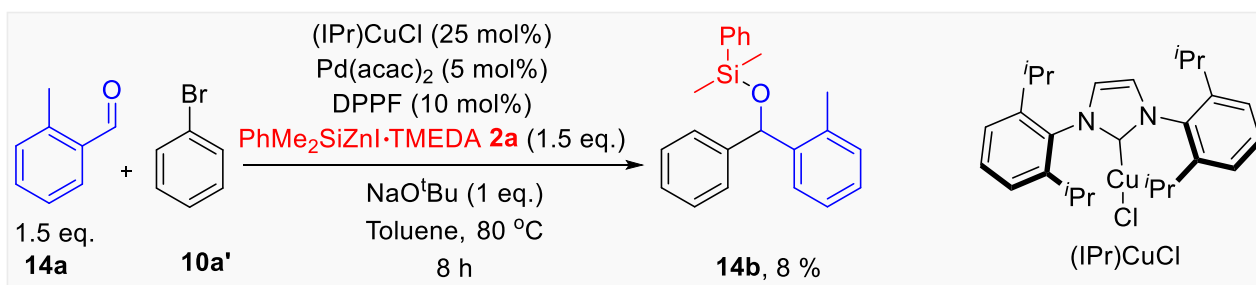
Copper(I) nitrile (10 mol%, 0.102 mmol, 9.32 mg) was taken into the nitrogen filled Schlenk tube, dry THF (5 mL) was added then cooled in an ice bath. (dimethyl(phenyl)silyl)zinc(II) iodide (**2a**, 1.5 eq., 1.53 mmol, 714 mg) was added and stirred at this temperature for 10-15 min, then cyclohex-2-en-1-one (**12a**, 1 eq., 1.02 mmol, 100 mg) and dry THF (1.8 mL) were added. The reaction slowly warmed to room temperature and stirred for 9 h. The crude was diluted with ethyl acetate, passed through celite and purified by silica gel column chromatography (5 % ethyl acetate/pet ether) giving a colourless oil **12b** in 73 % yield (173 mg). ¹H NMR (500 MHz, CDCl₃) δ: 7.48 (dd, *J* = 7.2, 2.2 Hz, 2H, 2 X ArCH), 7.40 – 7.34 (m, 3H, 3 X ArCH), 2.40 – 2.22 (m, 3H, 3 X Alkyl-CH), 2.18 – 2.06 (m, 2H, 2 X Alkyl-CH), 1.82 (d, *J* = 13.4 Hz, 1H, 1 X Alkyl-CH), 1.74 – 1.64 (m, 1H, 1 X Alkyl-CH), 1.42 (qd, *J* = 12.9, 3.5 Hz, 1H, 1 X Alkyl-CH), 1.29 (tt, *J* = 13.0, 3.2 Hz, 1H, 1 X Alkyl-CH), 0.31 (s, 6H, SiPh(CH₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ: 212.8 (-CO-), 136.7 (1 X SiArC), 134.0 (2 X ArCH), 129.4 (1 X ArCH), 128.0 (2 X ArCH), 42.5 (-CH₂COCH₂-), 42.0 (-CH₂COCH₂-), 29.9 (1 X AlkylCH₂), 27.8 (1 X AlkylCH₂), 26.2 ((1 X AlkylCH), -5.2 (PhSi(CH₃)₂), -5.3 (PhSi(CH₃)₂). FT-IR (neat, cm⁻¹) ν: 2968, 2944, 1716, 1432, 1318, 1257, 1234, 1196, 1118, 914, 814. EI-MS (*m/z*): [M]⁺ for C₁₄H₂₀OSi 232.11. Literature.^{6, 35-36}

9.4.2 Synthesis of 3-(4-(dimethylamino)phenyl)-1-phenyl-3-(trimethylsilyl)propan-1-one (**13b**)



Copper(I) iodide (10 mol%, 0.081 mmol, 15.8 mg) was taken into the Schlenk tube, inside the glovebox, dry THF (4 mL) was added under the nitrogen atmosphere then the tube was kept in an ice bath. (trimethylsilyl)zinc(II) iodide (**2b**, 1.5 eq., 1.22 mmol, 483 mg) was added and stirred for 15 min. To this (E)-3-(4-(dimethylamino)phenyl)-1-phenylprop-2-en-1-one (**13a**, 1 eq., 0.81 mmol, 210 mg) and dry THF (1.4 mL) were added then continue the stirring at room temperature for 9 h. The crude was diluted with ethyl acetate, passed through celite and purified by column chromatography (2 % ethyl acetate/pet ether) giving a pure compound **13b** as yellow oil 71 % (187 mg). **¹H NMR (500 MHz, CDCl₃) δ:** 7.91 (d, *J* = 7.7 Hz, 2H, 2 X ArCH), 7.52 (t, *J* = 7.2 Hz, 1H, 1 X ArCH), 7.43 (t, *J* = 7.6 Hz, 2H, 2 X ArCH), 6.95 (d, *J* = 8.5 Hz, 2H, 2 X ArCH), 6.64 (d, *J* = 8.6 Hz, 2H, 2 X ArCH), 3.46 (dd, *J* = 16.8, 9.5 Hz, 1H, 1 X PhCOCH₂), 3.26 (dd, *J* = 16.9, 5.0 Hz, 1H, CHSi(CH₃)₃), 2.88 (s, 6H, ArN(CH₃)₂), 2.77 (dd, *J* = 9.4, 5.0 Hz, 1H, 1 X PhCOCH₂), -0.01 (s, 9H, Si(CH₃)₃). **¹³C NMR (126 MHz, CDCl₃) δ:** 199.9 (PhCO), 148.3 (1 X ArC), 137.5 (1 X ArC), 132.8 (1 X ArCH), 131.4 (1 X ArC), 128.6 (2 X ArCH), 128.2 (2 X ArCH), 128.1 (2 X ArCH), 113.1 (2 X ArCH), 41.0 (ArN(CH₃)₂), 39.6 (PhCOCH₂), 30.1 (CHSi(CH₃)₃), -2.6 (Si(CH₃)₃). **FT-IR (neat, cm⁻¹) ν:** 2966, 2894, 1693, 1524, 1454, 1352, 1253, 1228, 981, 954, 839. **HRMS (ESI) *m/z*:** [M + H]⁺ Calcd for C₂₀H₂₇NOSi 326.1935; Found 326.1933.

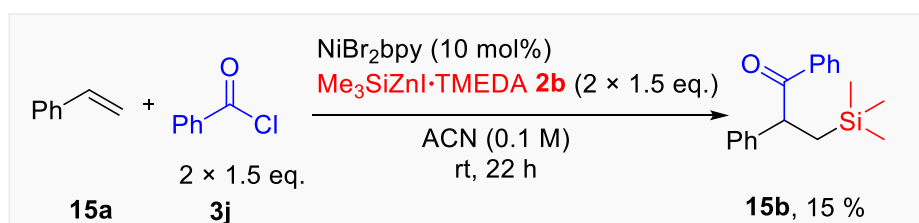
9.5. Synthesis of dimethyl(phenyl)(phenyl(*o*-tolyl)methoxy)silane (**14b**)



The title compound **14b** was prepared as a colourless oil by following the literature procedure³⁷ with slight modification. (IPr)CuCl (25 mol%, 0.12 mmol, 60 mg), NaO^tBu (0.12 mmol, 11.8 mg) were taken into the Schlenk tube from inside the glovebox, dry toluene (0.9 mL) was added under the nitrogen atmosphere and stirred at room temperature for 10 min. Next PhMe₂SiZnI·TMEDA (**2a**, 1.5 eq., 0.722 mmol, 337 mg), *o*-tolualdehyde (**14a**, 1.5 eq., 0.722 mmol, 91.3 mg) were added into the mixture (**mixture A**) and stirred for 1 h. Pd(acac)₂ (5 mol%, 0.0241 mmol, 7.5 mg), DPPF (10 mol%, 0.0481 mmol, 26.7 mg) were taken in another Schlenk tube from inside the glovebox, dry toluene (1.5 mL) was added under the nitrogen atmosphere and stirred at rt for 15 min. Next bromobenzene (**10a'**, 1 eq., 0.481 mmol, 77.1 mg)

was added, the mixture (**mixture B**) was stirred at rt for 20 min. Then the palladium solution (**mixture B**) was transferred to Schlenk tube (**mixture A**) containing the copper complex, mixture B tube washed with 0.2 mL of dry toluene and transferred to mixture A tube. Finally, NaO'Bu (11.8 mg \times 3, total: 0.361 mmol) was added portion wise (3 times) at intervals of 1 min. Then the reaction was heated to 80 °C and stirred for 8 h. The reaction mixture was diluted with ethyl acetate and filtered through celite, concentrated the filtrate. The crude was purified by flash column chromatography (1.5 % ethyl acetate/pet ether) gave **14b** in 8 % yield (12 mg, yield corresponds with slight impurity). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.48 (d, $J = 7.6$ Hz, 1H, 1 X ArCH), 7.45 – 7.42 (m, 2H, 2 X ArCH), 7.33 – 7.29 (m, 1H, 1 X ArCH), 7.28 – 7.23 (m, 3H, 3 X ArCH), 7.18 – 7.13 (m, 5H, 5 X ArCH), 7.10 – 7.06 (m, 1H, 1 X ArCH), 6.97 (d, $J = 7.4$ Hz, 1H, 1 X ArCH), 5.80 (s, 1H, ArCH(O)Ar), 2.00 (s, 3H, Ar-CH₃), 0.22 (s, 3H, PhSi(CH₃)), 0.19 (s, 3H, PhSi(CH₃)). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ : 143.7 (1 X ArC), 142.3 (1 X ArC), 137.8 (1 X ArC), 135.0 (1 X ArC), 133.8 (2 X ArCH), 130.5 (1 X ArCH), 129.7 (1 X ArCH), 128.2 (2 X ArCH), 127.9 (2 X ArCH), 127.4 (1 X ArCH), 127.3 (1 X ArCH), 127.1 (2 X ArCH), 127.0 (1 X ArCH), 126.0 (1 X ArCH), 74.6 (ArCH(O)Ar), 19.6 (Ar-CH₃), -1.1 (PhSi(CH₃)), -0.9 (PhSi(CH₃)). FT-IR (neat, cm^{-1}) ν : 3084, 3037, 2970, 1498, 1467, 1435, 1259, 1122, 1066, 878, 831, 787. EI-MS (m/z): $[\text{M}]^+$ for $\text{C}_{22}\text{H}_{24}\text{OSi}$ 332.13.

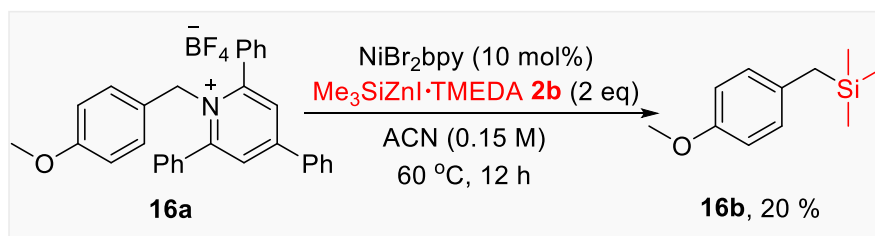
9.6. Synthesis of 1,2-diphenyl-3-(trimethylsilyl)propan-1-one (**15b**)



The 1,2-diphenyl-3-(trimethylsilyl)propan-1-one (**15b**) was obtained as a colourless oil by following the literature³⁸ procedure with slight modification. NiBr_2bpy (10 mol%, 0.103 mmol, 39.4 mg) was taken into the Schlenk tube inside the glovebox. Dry acetonitrile (8 mL), styrene (**15a**, 1 eq., 1.03 mmol, 0.121 mL) was added at room temperature followed by (trimethylsilyl)zinc(II) iodide (**2b**, 1.5 eq., 1.55 mmol, 615 mg), benzoyl chloride (**3j**, 1.5 eq., 1.55 mmol, 0.19 mL), dry acetonitrile (2.3 mL) were added and stirred at room temperature for 1 h before the second addition of (trimethylsilyl)zinc(II) iodide (**2b**, 1.5 eq., 1.55 mmol, 615 mg), benzoyl chloride (**3j**, 1.5 eq., 1.55 mmol, 0.19 mL). After this the reaction mixture was stirred for 22 h at room temperature. The reaction mixture was diluted with ethyl acetate and quenched with water. The organic layer was separated and the aqueous layer was washed with

ethyl acetate three times, combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude was treated with mixture of KOH (1 M) and THF for 24 h, due the same R_f of product and by product [phenyl(trimethylsilyl)methanone]. Then the crude purified by column chromatography (pet ether) gave **15b** in 15 % yield (43 mg, yield corresponds with slight impurity). ¹H NMR (500 MHz, CDCl₃) δ: 7.97 (d, *J* = 8.2 Hz, 2H, 2 X ArCH), 7.48 (t, *J* = 7.4 Hz, 1H, 1 X ArCH), 7.39 (t, *J* = 7.6 Hz, 2H, 2 X ArCH), 7.32 (d, *J* = 7.2 Hz, 2H, 2 X ArCH), 7.28 – 7.25 (m, 2H, 2 X ArCH), 7.17 (t, *J* = 7.3 Hz, 1H, 1 X ArCH), 4.68 (t, *J* = 7.6 Hz, 1H, PhCHCOPh), 1.54 – 1.49 (m, 1H, 1 X CH₂Si(CH₃)₃), 1.22 – 1.19 (m, 1H, 1 X CH₂Si(CH₃)₃), -0.11 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 200.6 (PhCOCHPh), 141.7 (1 X ArC), 136.9 (1 X ArC), 132.9 (1 X ArCH), 129.0 (2 X ArCH), 128.8 (2 X ArCH), 128.7 (2 X ArCH), 128.4 (2 X ArCH), 127.0 (1 X ArCH), 49.5 (PhCOCHPh), 22.3 (CHCH₂Si(CH₃)₃), -1.0 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 3050, 2968, 1729, 1691, 1256, 1229, 1183, 970, 862, 837, 757. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₈H₂₂OSi 283.1513; Found 283.1512.

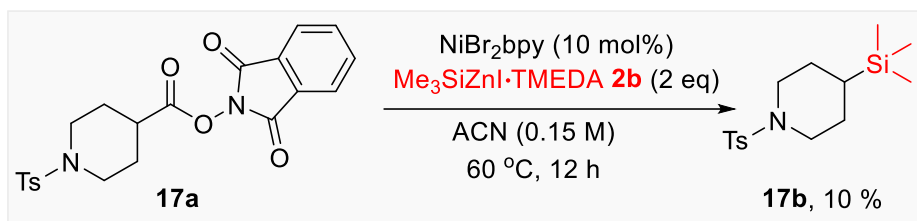
9.7. Synthesis of (4-methoxybenzyl)trimethylsilane (**16b**) via C-N bond cleavage



NiBr₂bpy (10 mol%, 0.119 mmol, 45 mg) weighed into the Schlenk tube inside the glovebox. To this 1-(4-methoxybenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (**16a**, 1 eq., 1.19 mmol, 625 mg), acetonitrile (6 mL) were added, stirred for 3-5 mins then (trimethylsilyl)zinc(II) iodide (**2b**, 2 eq., 2.38 mmol, 936 mg) was added, stirred at 60 °C for overnight. The reaction mixture was diluted with ethyl acetate then passed through celite. The crude was purified through silica gel column chromatography (1.5 % ethyl acetate/pet ether) giving a colourless oil **16b** in 20 % yield (46.3 mg). ¹H NMR (500 MHz, CDCl₃) δ: 6.91 (d, *J* = 8.3 Hz, 2H, 2 X ArCH), 6.78 (d, *J* = 8.5 Hz, 2H, 2 X ArCH), 3.78 (s, 3H, Ar-OCH₃), 2.01 (s, 2H, CH₂Si-), -0.02 (s, 9H, Si(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ: 156.6 (1 X ArC-OMe), 132.5 (1 X ArC-CH₂Si(CH₃)₃), 128.9 (2 X ArCH), 113.8 (2 X ArCH), 55.4 (Ar-OCH₃), 25.8 (CH₂Si(CH₃)₃), -1.8 (Si(CH₃)₃). FT-IR (neat, cm⁻¹) ν: 2970, 1602, 1510, 1470, 1283,

1251, 1188, 1116, 1039, 840. **HRMS (ESI) m/z :** $[M + H]^+$ Calcd for $C_{11}H_{18}OSi$ 195.1200; Found 195.1200. Literature.³⁹

9.8. Synthesis of 1-tosyl-4-(trimethylsilyl)piperidine (17b) via decarboxylation of redox active ester

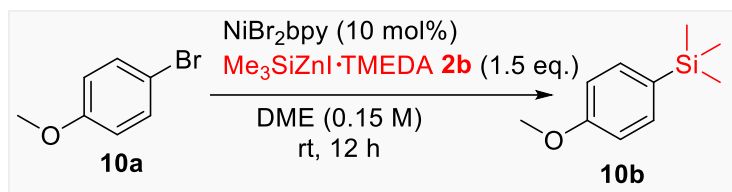


In a nitrogen filled Schlenk tube, $NiBr_2bpy$ (10 mol%, 0.0679 mmol, 26 mg) was added inside the glovebox. Then 1,3-dioxoisindolin-2-yl 1-tosylpiperidine-4-carboxylate (**17a**, 1 eq., 0.679 mmol, 300 mg) and dry acetonitrile (3.5 mL) were added. To this (trimethylsilyl)zinc(II) iodide (**2b**, 2 eq., 1.02 mmol, 540 mg) and dry acetonitrile (1 mL) were added and stirred at 60 °C for overnight. The reaction mixture was diluted with ethyl acetate and passed through the celite. The crude was purified by silica gel column chromatography (2 % ethyl acetate/pet ether) to obtain a white solid of **17b** in 10 % yield (21 mg). **Melting point** : 143.3 – 145 °C. **1H NMR (500 MHz, $CDCl_3$) δ :** 7.63 (d, $J = 8.0$ Hz, 2H, 2 X ArCH), 7.31 (d, $J = 7.9$ Hz, 2H, 2 X ArCH), 3.82 (d, $J = 11.7$ Hz, 2H, alkylCH₂), 2.42 (s, 3H, Ar-CH₃), 2.12 (td, $J = 11.7, 2.7$ Hz, 2H, alkylCH₂), 1.64 (d, $J = 11.3$ Hz, 2H, alkylCH₂), 1.45 (qd, $J = 13.0, 4.1$ Hz, 2H, alkylCH₂), 0.40 (tt, $J = 13.1, 3.4$ Hz, 1H, CHSi(CH₃)₃), -0.08 (s, 9H, Si(CH₃)₃). **^{13}C NMR (126 MHz, $CDCl_3$) δ :** 143.4 (1 X ArC), 133.4 (1 X ArC), 129.6 (2 X ArCH), 127.9 (2 X ArCH), 48.0 (CH₂NCH₂), 26.1 (CH₂ CH₂N CH₂CH₂), 23.3 (CHSi(CH₃)₃), 21.6 (Ar-CH₃), -3.7 (Si(CH₃)₃). **FT-IR (neat, cm^{-1}) ν :** 2936, 2668, 1339, 1255, 1213, 1160, 1094, 1052, 924. **HRMS (ESI) m/z :** $[M + H]^+$ Calcd for $C_{15}H_{25}NO_2SSi$ 312.1448; Found 312.1445.

10. Effect of storage temperature on the stability of $Me_3SiZnI \cdot TMEDA$ (**2b**)

The sample of solid $Me_3SiZnI \cdot TMEDA$ prepared from TMSI by the following procedure in section 3.2.1 was stored at -23 °C, 4 °C, room temperature at two different locations [one is inside the desiccator and another at outside the desiccator (chemical cabinet) at rt]. After two months, the stability/reactivity of these reagents was analyzed through the arylation reaction with 4-bromoanisole. $NiBr_2bpy$ (10 mol%, 0.0201 mmol, 7.7 mg), 4-bromoanisole (**10a**, 1 eq., 0.201 mmol, 38.8 mg) with (trimethylsilyl)zinc(II) iodide (**2b**, 1.5 eq., 0.302 mmol, 121 mg)

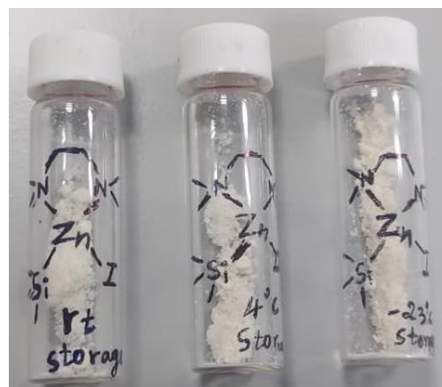
by following the procedure in section 9.2 gave (4-methoxyphenyl)trimethylsilane (**10b**) in 66 % (24 mg), 55 % (19.9 mg), 18 % (6.7 mg), trace yield w.r.t the $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ storage temperature 4 °C, -23 °C, inside the desiccator at rt, outside the desiccator at rt (chemical cabinet).



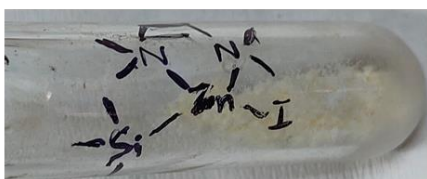
Storage temp. of 2b	Yield of 10b
4 °C	66 %
-23 °C	55 %
rt (desiccator)	18 %
rt	trace



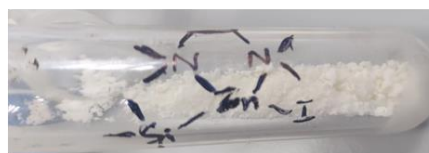
Before two months
 $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ stored at -23 °C, 4 °C, rt (desiccator)



After two months
 $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ stored at rt (desiccator), 4 °C, -23 °C



Before two months
 $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ stored at rt (outside the desiccator)



After two months
 $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ stored at rt (outside the desiccator)

Figure 5: $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ Stored at different temperature for two months

11. Reference

1. Cynthia J. Burrows, Shiow-Jyi Wey.; Nickel(II) Acetate, Encyclopedia of Reagents for Organic Synthesis, John Wiley & sons, Ltd.; 2001.
2. (a) M. V. George, D. J. Peterson and H. Gilman, *J. Am. Chem. Soc.* 1960, **82**, 403. (b) W. Xue, R. Shishido and M. Oestreich, *Angew. Chem. Int. Ed.* 2018, **57**, 12141. (c) V. Murugesan, V. Balakrishnan and R. Rasappan, *J. Catal.* 2019, **377**, 293.
3. (a) C. Chu, Y. Liang and G. Fu, *J. Am. Chem. Soc.* 2016, **138**, 6404. (b) B. Yang, and Z.-X. Wang, *Org. Lett.* 2019, **21**, 7965.
4. (a) A. Kunai, T. Sakurai, E. Toyoda, M. Ishikawa and Y. Yamamoto, *Organometallics* 1994, **13**, 3233. (b) A. P Cinderella, B. Vulovic and D. A. Watson, *J. Am. Chem. Soc.* 2017, **139**, 7741.
5. P. Knochel and A. Krasovskiy, *Synthesis* 2006, **5**, 0890.
6. M. Oestreich and B. Weiner, *Synlett* 2004, 2139.
7. F. T. Pulikottil, R. Pilli, R.V. Suku and R. Rasappan, *Org. Lett.* 2020, **22**, 2902.
8. K. Tatsumi, S. Tanabe, Y. Tsuji and T. Fujihara, *Org. Lett.* 2019, **21**, 10130.
9. M. D. Paredes and R. Alonso, *J. Org. Chem.* 2000, **65**, 2292.
10. C. T. Clark, B.C. Milgram and K.A. Scheidt, *Org. Lett.* 2004, **6**, 3977.
11. L.-J. Cheng and N. P. Mankad, *J. Am. Chem. Soc.* 2020, **142**, 80.
12. B. F. Bonini, M. Comes-Franchini, G. Mazzanti, U. Passamonti, A. Ricchi and P. Zani, *Synthesis* 1995, **1995**, 92.
13. S.-Y. Chang, W.-T. Jiaang, C.-D. Cherng, K.-H. Tang, C.-H. Huang and Y.-M. Tsai, *J. Org. Chem.* 1997, **62**, 9089.
14. H. Azuma, K. Okano and H. Tokuyama, *Chem. Lett.* 2011, **40**, 959.
15. V. Cirriez, C. Rasson and O. Riant, *Adv. Synth. Catal.* 2013, **355**, 3137.
16. M. Honda, T. Takatera, R. Ui, K.-K. Kunimoto and M. Segi, *Tetrahedron Lett.* 2017, **58**, 864.
17. D. I. Gasking and G. H. Whitham, *J. Chem. Soc., Perkin Trans.* 1985, **1**, 409.
18. K. Ishida, H. Yamazaki, C. Hagiwara, M. Abe and H. Kusama, *Chem. Eur. J.* 2020, **26**, 1249.
19. K. Yamamoto, A. Hayashi, S. Suzuki and J. Tsuji, *Organometallics* 1987, **6**, 974.

20. M. Leiendecker, C.-C. Hsiao, L. Guo, N. Alandini and M. Rueping, *Angew. Chem. Int. Ed.* 2014, **53**, 12912.
21. X.-F. Wu, H. Neumann and M. Beller, *Tetrahedron Lett.* 2012, **53**, 582.
22. (a) A. Capperucci, A. Degl'Innocenti, C. Faggi, A. Ricci, P. Dembech and G. Seconi, *J. Org. Chem.* 1988, **53**, 3612. (b) F. Geng and R. E. Maleczka Jr, *Tetrahedron Lett.* 1999, **40**, 3113.
23. R. F. Cunico and C.-P. Zhang, *Tetrahedron Lett.* 1995, **51**, 9823.
24. M. Kawasaki, M. Goto, S. Kawabata and T. Kometani, *Tetrahedron: Asymmetry.* 2001, **12**, 585.
25. R. Taj and J. L. Sorensen, *Tetrahedron Lett.* 2015, **56**, 7108.
26. Y. Hu, R. Xu, D. Huang and C. Xu, *Improved Method for Synthesizing N-Methoxy-N-Methyl-1-Tosylpiperidine-4-Carboxamide*, 2010.
27. a) K. A. Mookhtiar, D. Bhuniya, B. Dave, G. S. Kapkoti, S. Basu, A. Chugh, S. De and V. P. Palle, *Preparation of Phenoxythiazolylalkylacetamide Derivatives and Analogs as Glucokinase Activators*, 2008. b) S. Basu, D. A. Barawkar, S. Thorat, Y. D. Shejul, M. Patel, M. Naykodi, V. Jain, Y. Salve, V. Prasad, S. Chaudhary, I. Ghosh, G. Bhat, A. Quraishi, H. Patil, S. Ansari, S. Menon, V. Unadkat, R. Thakare, M. S. Seervi, A.V. Meru, S. De, R. K. Bhamidipati, S. R. Rouduri, V. P. Palle, A. Chug and K. A. Mookhtiar, *J. Med. Chem.* 2017, **60**, 681.
28. M. M. Almahdi, A. E. M. Saeed and N. H. Metwally, *Eur. J. Chem.* 2019, **10**, 30.
29. W. Hagui, M. Cordier, J. Boixel and J.-F. Soulé, *Chem. Commun.*, 2021, **57**, 1038.
30. a) D. Vyas and M. Oestreich, *Chem. Commun.* 2010, **46**, 568. b) J. G. Smith, S. E. Drozda, S. P. Petraglia, N. R. Quinn, E. M. Rice, B. S. Taylor and M. Viswanathan, *J. Org. Chem.* 1984, **49**, 4112.
31. R. Moser, T. Nishikata and B. H. Lipshutz, *Org. Lett.* 2010, **12**, 28.
32. a) A. Postigo and R. A. Rossi, *Org. Lett.* 2001, **3**, 1197. b) H. Guo, X. Chen, C. Zhao and W. He, *Chem. Commun.* 2015, **51**, 17410. c) K. Hitoshio, H. Yamagishi, J. Shimokawa and H. Yorimitsu, *Chem. Commun.* 2021, **57**, 6867. d) T. Nagata, T. Inoue,

- X. Lin, S. Ishimoto, S. Nakamichi, H. Oka, R. Kondo, T. Suzuki and Y. Obora, *RSC Adv.* 2019, **9**, 17425. e) E. Shirakawa, T. Kurahashi, H. Yoshida and T. Hiyama, *Chem. Commun.* 2000, 1895.
33. G. E. Dobereiner, J. Yuan, R. R. Schrock, A. S. Goldman and J. D. Hackenberg, *J. Am. Chem. Soc.* 2013, **135**, 12572.
34. J. M. O'Brien and A. H. Hoveyda, *J. Am. Chem. Soc.* 2011, **133**, 7712.
35. A. Vaughan and R. D. Singer, *Tetrahedron Lett.* 1995, **36**, 5683.
36. C. Walter, G. Auer and M. Oestreich, *Angew. Chem., Int. Ed.* 2006, **45**, 5675.
37. M. Takeda, K. Yabushita, S. Yasuda and H. Ohmiya, *Chem. Commun.* 2018, **54**, 6776.
38. D. Ni and M. K. Brown, *ACS Catal.* 2021, **11**, 1858.
39. S. D. Dreher, S.-E. Lim, D. L. Sandrock and G. A. Molander, *J. Org. Chem.* 2009, **74**, 3626.

12. Crystallography data of Silyl Zinc reagent

Table S9. Crystal data and structure refinement for PhMe₂SiZnI (**2a**).

Identification code	CCDC 2089058
Empirical formula	C ₁₄ H ₂₇ I N ₂ Si Zn
Formula weight	443.73
Temperature	140(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 15.0253(19) Å a = 90°. b = 15.7490(19) Å b = 90°. c = 16.4568(17) Å g = 90°.
Volume	3894.2(8) Å ³
Z	8
Density (calculated)	1.514 Mg/m ³
Absorption coefficient	2.900 mm ⁻¹
F(000)	1776
Crystal size	0.085 x 0.075 x 0.045 mm ³
Theta range for data collection	2.245 to 24.999°.
Index ranges	-17<=h<=17, -18<=k<=18, -19<=l<=19
Reflections collected	63027
Independent reflections	3425 [R(int) = 0.1161]
Completeness to theta = 24.999°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.997 and 0.989
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3425 / 0 / 178
Goodness-of-fit on F ²	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.0892
R indices (all data)	R1 = 0.0795, wR2 = 0.1078
Extinction coefficient	n/a
Largest diff. peak and hole	0.830 and -0.804 e.Å ⁻³

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) PhMe₂SiZnI (**2a**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	3581(6)	4965(4)	4846(5)	73(2)
C(2)	4218(7)	3768(6)	5495(5)	102(3)
C(3)	2705(7)	4092(7)	5746(5)	105(4)
C(4)	1823(7)	4116(7)	5444(6)	107(4)
C(5)	920(6)	3827(8)	4271(6)	122(4)
C(6)	1294(6)	2678(7)	5158(7)	117(4)
C(7)	1916(5)	3822(5)	2174(5)	71(2)
C(8)	3698(6)	2966(5)	2217(5)	87(3)
C(9)	3534(4)	4830(4)	2636(3)	42(1)
C(10)	4397(5)	4930(5)	2371(4)	64(2)
C(11)	4787(6)	5721(6)	2311(5)	82(3)
C(12)	4311(7)	6426(6)	2507(5)	81(3)
C(13)	3462(6)	6353(4)	2773(5)	67(2)
C(14)	3079(5)	5569(4)	2835(4)	50(2)
I(1)	3462(1)	1804(1)	4486(1)	59(1)
N(1)	3382(4)	4101(3)	5132(3)	54(1)
N(2)	1612(4)	3470(4)	4800(4)	61(2)
Si(1)	2980(1)	3757(1)	2770(1)	43(1)
Zn(1)	2846(1)	3346(1)	4158(1)	37(1)

Table S11. Bond lengths [\AA] and angles [$^\circ$] for PhMe₂SiZnI (**2a**).

C(1)-N(1)	1.471(8)
C(2)-N(1)	1.486(10)
C(3)-C(4)	1.416(13)
C(3)-N(1)	1.434(10)
C(4)-N(2)	1.503(12)
C(5)-N(2)	1.467(9)
C(6)-N(2)	1.459(10)
C(7)-Si(1)	1.878(7)
C(8)-Si(1)	1.883(7)

C(9)-C(10)	1.378(9)
C(9)-C(14)	1.390(8)
C(9)-Si(1)	1.896(6)
C(10)-C(11)	1.380(10)
C(11)-C(12)	1.359(11)
C(12)-C(13)	1.354(11)
C(13)-C(14)	1.366(9)
I(1)-Zn(1)	2.6552(8)
N(1)-Zn(1)	2.152(5)
N(2)-Zn(1)	2.144(5)
Si(1)-Zn(1)	2.3835(17)

C(4)-C(3)-N(1)	114.5(8)
C(3)-C(4)-N(2)	115.3(8)
C(10)-C(9)-C(14)	116.2(6)
C(10)-C(9)-Si(1)	123.5(5)
C(14)-C(9)-Si(1)	120.2(5)
C(9)-C(10)-C(11)	121.7(7)
C(12)-C(11)-C(10)	119.9(8)
C(13)-C(12)-C(11)	120.2(8)
C(12)-C(13)-C(14)	119.9(8)
C(13)-C(14)-C(9)	122.2(7)
C(3)-N(1)-C(1)	112.3(7)
C(3)-N(1)-C(2)	108.2(7)
C(1)-N(1)-C(2)	106.4(6)
C(3)-N(1)-Zn(1)	104.7(5)
C(1)-N(1)-Zn(1)	110.4(4)
C(2)-N(1)-Zn(1)	114.9(5)
C(6)-N(2)-C(5)	109.6(7)
C(6)-N(2)-C(4)	111.3(8)
C(5)-N(2)-C(4)	108.0(8)
C(6)-N(2)-Zn(1)	113.8(5)
C(5)-N(2)-Zn(1)	110.8(5)
C(4)-N(2)-Zn(1)	103.0(5)
C(7)-Si(1)-C(8)	105.7(4)
C(7)-Si(1)-C(9)	105.3(3)
C(8)-Si(1)-C(9)	106.4(3)
C(7)-Si(1)-Zn(1)	116.4(3)

C(8)-Si(1)-Zn(1)	109.4(3)
C(9)-Si(1)-Zn(1)	112.96(18)
N(2)-Zn(1)-N(1)	84.6(2)
N(2)-Zn(1)-Si(1)	121.36(16)
N(1)-Zn(1)-Si(1)	122.21(15)
N(2)-Zn(1)-I(1)	106.51(16)
N(1)-Zn(1)-I(1)	102.94(15)
Si(1)-Zn(1)-I(1)	114.46(5)

Table S12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for PhMe₂SiZnI (**2a**). The anisotropic

displacement factor exponent takes the form: $-2p^2 [h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	105(7)	45(4)	70(5)	-3(4)	-8(4)	-21(4)
C(2)	129(9)	75(6)	101(7)	-3(5)	-70(6)	-7(6)
C(3)	138(10)	121(8)	58(6)	-35(5)	21(6)	-41(7)
C(4)	109(8)	140(10)	73(6)	-20(6)	34(6)	44(7)
C(5)	49(5)	202(12)	115(8)	56(8)	10(5)	41(7)
C(6)	79(7)	111(8)	162(10)	49(7)	58(6)	4(6)
C(7)	86(6)	67(5)	60(5)	16(4)	-22(4)	-19(4)
C(8)	134(8)	57(5)	69(5)	-9(4)	41(5)	19(5)
C(9)	47(4)	52(4)	27(3)	4(3)	2(3)	2(3)
C(10)	54(5)	74(5)	66(5)	10(4)	8(4)	1(4)
C(11)	60(6)	104(7)	81(6)	19(5)	-4(4)	-29(5)
C(12)	97(7)	66(6)	79(6)	16(4)	-20(5)	-36(5)
C(13)	89(6)	45(4)	68(5)	0(4)	-1(5)	-8(4)
C(14)	56(4)	48(4)	46(4)	5(3)	5(3)	-2(3)
I(1)	67(1)	39(1)	70(1)	3(1)	-13(1)	7(1)
N(1)	77(4)	49(3)	36(3)	-2(2)	-3(3)	-14(3)
N(2)	47(3)	79(4)	56(4)	18(3)	14(3)	9(3)
Si(1)	60(1)	37(1)	33(1)	2(1)	3(1)	4(1)
Zn(1)	40(1)	38(1)	34(1)	2(1)	1(1)	1(1)

Table S13. Hydrogen coordinates ($\text{\AA} \times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for PhMe₂SiZnI (**2a**).

Atom	x	y	z	U(eq)
H(1A)	3036	5230	4641	110
H(1B)	4024	4938	4409	110
H(1C)	3818	5303	5297	110
H(2A)	4401	4135	5946	152
H(2B)	4687	3759	5081	152
H(2C)	4117	3191	5697	152
H(3A)	2778	3572	6078	126
H(3B)	2796	4586	6109	126
H(4A)	1711	4689	5218	129
H(4B)	1408	4033	5904	129
H(5A)	747	3404	3864	183
H(5B)	1152	4334	3998	183
H(5C)	400	3982	4599	183
H(6A)	742	2785	5458	176
H(6B)	1746	2454	5531	176
H(6C)	1182	2263	4726	176
H(7A)	2053	3854	1592	107
H(7B)	1584	4329	2338	107
H(7C)	1555	3315	2280	107
H(8A)	3412	2407	2229	130
H(8B)	4281	2932	2482	130
H(8C)	3775	3147	1651	130
H(10)	4733	4442	2226	77
H(11)	5386	5773	2134	98
H(12)	4575	6972	2456	97
H(13)	3134	6846	2917	81
H(14)	2481	5529	3020	60

Table S14. Torsion angles [°] for PhMe₂SiZnI (**2a**).

N(1)-C(3)-C(4)-N(2)	51.0(13)
C(14)-C(9)-C(10)-C(11)	0.2(10)
Si(1)-C(9)-C(10)-C(11)	-177.5(6)
C(9)-C(10)-C(11)-C(12)	-0.8(12)
C(10)-C(11)-C(12)-C(13)	1.1(13)
C(11)-C(12)-C(13)-C(14)	-0.9(12)
C(12)-C(13)-C(14)-C(9)	0.3(11)
C(10)-C(9)-C(14)-C(13)	0.0(10)
Si(1)-C(9)-C(14)-C(13)	177.8(5)
C(4)-C(3)-N(1)-C(1)	82.9(10)
C(4)-C(3)-N(1)-C(2)	-160.0(9)
C(4)-C(3)-N(1)-Zn(1)	-37.0(10)
C(3)-C(4)-N(2)-C(6)	89.0(10)
C(3)-C(4)-N(2)-C(5)	-150.7(9)
C(3)-C(4)-N(2)-Zn(1)	-33.4(10)
C(10)-C(9)-Si(1)-C(7)	-127.0(6)
C(14)-C(9)-Si(1)-C(7)	55.3(6)
C(10)-C(9)-Si(1)-C(8)	-15.1(6)
C(14)-C(9)-Si(1)-C(8)	167.3(5)
C(10)-C(9)-Si(1)-Zn(1)	104.9(5)
C(14)-C(9)-Si(1)-Zn(1)	-72.7(5)

Table S15. Hydrogen bonds for PhMe₂SiZnI (**2a**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2C)...I(1)	0.98	3.12	3.691(8)	118.8

Table S16. Crystal data and structure refinement for Me₃SiZnI (**2b**).

Identification code	CCDC 2089062	
Empirical formula	C ₉ H ₂₅ I N ₂ Si Zn	
Formula weight	381.67	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 19.6510(16) Å	a = 90°.
	b = 10.2987(8) Å	b = 90°.
	c = 8.2925(6) Å	g = 90°.
Volume	1678.2(2) Å ³	
Z	4	
Density (calculated)	1.511 Mg/m ³	
Absorption coefficient	3.351 mm ⁻¹	
F(000)	760	
Crystal size	0.095 x 0.080 x 0.040 mm ³	
Theta range for data collection	2.865 to 24.998°.	
Index ranges	-23<=h<=23, -12<=k<=10, -9<=l<=9	
Reflections collected	25023	
Independent reflections	2952 [R(int) = 0.0432]	
Completeness to theta = 24.998°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.878 and 0.741	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2952 / 76 / 183	
Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0881	
R indices (all data)	R1 = 0.0493, wR2 = 0.0938	
Absolute structure parameter	0.03(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.001 and -0.977 e.Å ⁻³	

Table S17. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Me_3SiZnI (**2b**). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
C(1)	2066(6)	4160(20)	5410(20)	172(10)
C(2)	2465(7)	3192(14)	3027(16)	104(5)
C(5)	4363(9)	5374(16)	3100(20)	139(8)
C(6)	4173(10)	6433(13)	5600(20)	129(6)
I(1)	3401(1)	4113(1)	8485(1)	107(1)
N(2)	2622(4)	4126(8)	4279(10)	56(2)
N(1)	3878(4)	5561(7)	4412(10)	56(2)
Zn(1)	3598(1)	3690(1)	5376(2)	48(1)
C(7)	3857(13)	284(17)	5250(40)	130(11)
C(9)	5127(9)	1910(50)	5020(40)	109(12)
C(8)	4220(9)	1570(19)	2170(20)	92(7)
C(3)	3247(8)	6237(16)	4030(30)	89(7)
C(4)	2743(9)	5314(14)	3330(30)	87(6)
Si(1)	4210(4)	1835(7)	4414(11)	55(2)
Si(1')	4246(12)	1810(20)	5170(30)	60(4)
C(7')	3810(30)	530(70)	3980(100)	127(18)
C(8')	4360(40)	1110(70)	7230(50)	150(30)
C(9')	5140(30)	1960(130)	4400(120)	100(20)
C(3')	3296(13)	5780(40)	3360(40)	62(12)
C(4')	2623(17)	5539(13)	4240(50)	51(9)

Table S18. Bond lengths [\AA] and angles [$^\circ$] for Me_3SiZnI (**2b**).

C(1)-N(2)	1.440(16)
C(1)-C(4')	2.04(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-N(2)	1.448(14)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800

C(2)-H(2C)	0.9800
C(5)-N(1)	1.462(16)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.455(17)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
I(1)-Zn(1)	2.6431(15)
N(2)-C(4')	1.456(13)
N(2)-C(4)	1.474(11)
N(2)-Zn(1)	2.169(8)
N(1)-C(3)	1.455(11)
N(1)-C(3')	1.457(13)
N(1)-Zn(1)	2.158(8)
Zn(1)-Si(1')	2.32(2)
Zn(1)-Si(1)	2.395(7)
C(7)-Si(1)	1.875(15)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(9)-Si(1)	1.873(18)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(8)-Si(1)	1.882(16)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(3)-C(4)	1.492(19)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
Si(1')-C(7')	1.86(2)
Si(1')-C(8')	1.87(2)
Si(1')-C(9')	1.87(2)

C(7')-H(7'1)	0.9800
C(7')-H(7'2)	0.9800
C(7')-H(7'3)	0.9800
C(8')-H(8'1)	0.9800
C(8')-H(8'2)	0.9800
C(8')-H(8'3)	0.9800
C(9')-H(9'1)	0.9800
C(9')-H(9'2)	0.9800
C(9')-H(9'3)	0.9800
C(3')-C(4')	1.53(3)
C(3')-H(3'1)	0.9900
C(3')-H(3'2)	0.9900
C(4')-H(4'1)	0.9900
C(4')-H(4'2)	0.9900
N(2)-C(1)-C(4')	45.7(9)
N(2)-C(1)-H(1A)	109.5
C(4')-C(1)-H(1A)	76.9
N(2)-C(1)-H(1B)	109.5
C(4')-C(1)-H(1B)	92.0
H(1A)-C(1)-H(1B)	109.5
N(2)-C(1)-H(1C)	109.5
C(4')-C(1)-H(1C)	152.9
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(2)-C(2)-H(2A)	109.5
N(2)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
N(2)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
N(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-H(6A)	109.5

N(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
N(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(1)-N(2)-C(2)	108.9(11)
C(1)-N(2)-C(4')	89.3(17)
C(2)-N(2)-C(4')	130.4(19)
C(1)-N(2)-C(4)	116.5(14)
C(2)-N(2)-C(4)	101.7(12)
C(1)-N(2)-Zn(1)	113.8(9)
C(2)-N(2)-Zn(1)	110.5(7)
C(4')-N(2)-Zn(1)	102.4(15)
C(4)-N(2)-Zn(1)	104.7(8)
C(6)-N(1)-C(3)	101.0(12)
C(6)-N(1)-C(3')	129(2)
C(6)-N(1)-C(5)	109.1(12)
C(3)-N(1)-C(5)	117.3(15)
C(3')-N(1)-C(5)	94.8(19)
C(6)-N(1)-Zn(1)	113.6(8)
C(3)-N(1)-Zn(1)	106.8(9)
C(3')-N(1)-Zn(1)	99.2(17)
C(5)-N(1)-Zn(1)	109.0(8)
N(1)-Zn(1)-N(2)	83.4(3)
N(1)-Zn(1)-Si(1')	125.3(7)
N(2)-Zn(1)-Si(1')	128.8(6)
N(1)-Zn(1)-Si(1)	117.4(3)
N(2)-Zn(1)-Si(1)	118.0(3)
N(1)-Zn(1)-I(1)	104.6(2)
N(2)-Zn(1)-I(1)	104.2(2)
Si(1')-Zn(1)-I(1)	106.8(6)
Si(1)-Zn(1)-I(1)	122.0(2)
Si(1)-C(7)-H(7A)	109.5
Si(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
Si(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5

Si(1)-C(9)-H(9A)	109.5
Si(1)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
Si(1)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
Si(1)-C(8)-H(8A)	109.5
Si(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
Si(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(1)-C(3)-C(4)	110.2(13)
N(1)-C(3)-H(3A)	109.6
C(4)-C(3)-H(3A)	109.6
N(1)-C(3)-H(3B)	109.6
C(4)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
N(2)-C(4)-C(3)	115.3(15)
N(2)-C(4)-H(4A)	108.4
C(3)-C(4)-H(4A)	108.4
N(2)-C(4)-H(4B)	108.4
C(3)-C(4)-H(4B)	108.4
H(4A)-C(4)-H(4B)	107.5
C(9)-Si(1)-C(7)	107.0(18)
C(9)-Si(1)-C(8)	105.2(13)
C(7)-Si(1)-C(8)	104.3(13)
C(9)-Si(1)-Zn(1)	111.1(13)
C(7)-Si(1)-Zn(1)	111.7(8)
C(8)-Si(1)-Zn(1)	116.8(7)
C(7')-Si(1')-C(8')	106(4)
C(7')-Si(1')-C(9')	108(4)
C(8')-Si(1')-C(9')	103(4)
C(7')-Si(1')-Zn(1)	112(3)
C(8')-Si(1')-Zn(1)	109(3)
C(9')-Si(1')-Zn(1)	118(4)
Si(1')-C(7')-H(7'1)	109.5
Si(1')-C(7')-H(7'2)	109.5

H(7'1)-C(7')-H(7'2)	109.5
Si(1')-C(7')-H(7'3)	109.5
H(7'1)-C(7')-H(7'3)	109.5
H(7'2)-C(7')-H(7'3)	109.5
Si(1')-C(8')-H(8'1)	109.5
Si(1')-C(8')-H(8'2)	109.5
H(8'1)-C(8')-H(8'2)	109.5
Si(1')-C(8')-H(8'3)	109.5
H(8'1)-C(8')-H(8'3)	109.5
H(8'2)-C(8')-H(8'3)	109.5
Si(1')-C(9')-H(9'1)	109.5
Si(1')-C(9')-H(9'2)	109.5
H(9'1)-C(9')-H(9'2)	109.5
Si(1')-C(9')-H(9'3)	109.5
H(9'1)-C(9')-H(9'3)	109.5
H(9'2)-C(9')-H(9'3)	109.5
N(1)-C(3')-C(4')	111(3)
N(1)-C(3')-H(3'1)	109.3
C(4')-C(3')-H(3'1)	109.3
N(1)-C(3')-H(3'2)	109.3
C(4')-C(3')-H(3'2)	109.3
H(3'1)-C(3')-H(3'2)	108.0
N(2)-C(4')-C(3')	100(2)
N(2)-C(4')-C(1)	45.0(10)
C(3')-C(4')-C(1)	144(2)
N(2)-C(4')-H(4'1)	111.8
C(3')-C(4')-H(4'1)	111.8
C(1)-C(4')-H(4'1)	80.7
N(2)-C(4')-H(4'2)	111.8
C(3')-C(4')-H(4'2)	111.8
C(1)-C(4')-H(4'2)	94.3
H(4'1)-C(4')-H(4'2)	109.5

Table S19. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Me_3SiZnI (**2b**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	39(6)	360(30)	119(12)	-30(20)	15(9)	35(11)
C(2)	113(11)	97(10)	103(13)	-15(8)	-53(9)	1(8)
C(5)	173(16)	99(11)	145(19)	14(11)	89(15)	-21(11)
C(6)	189(16)	59(7)	138(14)	1(9)	-60(14)	-34(9)
I(1)	130(1)	153(1)	38(1)	1(1)	1(1)	-11(1)
N(2)	47(4)	62(4)	60(4)	-5(4)	-6(3)	-1(3)
N(1)	65(5)	46(5)	58(5)	5(4)	-4(4)	-4(4)
Zn(1)	49(1)	49(1)	45(1)	1(1)	0(1)	4(1)
C(7)	113(16)	53(10)	220(30)	19(18)	70(20)	1(10)
C(9)	78(12)	110(16)	140(30)	-30(20)	2(13)	38(12)
C(8)	76(12)	97(14)	103(15)	-41(12)	5(10)	6(10)
C(3)	102(14)	50(11)	114(18)	1(11)	-43(13)	20(9)
C(4)	83(7)	87(8)	90(8)	4(6)	-13(6)	8(6)
Si(1)	51(3)	38(2)	76(4)	0(3)	1(4)	8(2)
Si(1')	61(8)	56(8)	64(10)	9(12)	-5(11)	6(5)
C(7')	100(30)	80(30)	190(40)	-50(30)	20(40)	0(30)
C(8')	160(30)	150(30)	150(30)	4(14)	5(14)	9(14)
C(9')	100(40)	90(30)	110(50)	-30(40)	40(30)	-30(30)
C(3')	90(20)	29(19)	70(20)	3(17)	0(20)	-6(17)
C(4')	51(11)	49(11)	53(11)	-1(7)	-3(7)	9(7)

Table S20. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Me_3SiZnI (**2b**).

Atom	x	y	z	U(eq)
H(1A)	2168	4795	6262	257
H(1B)	1649	4423	4849	257
H(1C)	2004	3303	5889	257
H(2A)	2841	3159	2252	156

H(2B)	2402	2332	3511	156
H(2C)	2047	3452	2472	156
H(5A)	4167	4788	2290	209
H(5B)	4464	6213	2594	209
H(5C)	4784	4995	3524	209
H(6A)	4611	6083	5968	193
H(6B)	4243	7290	5118	193
H(6C)	3864	6511	6525	193
H(7A)	3376	207	4960	196
H(7B)	4110	-454	4808	196
H(7C)	3902	288	6430	196
H(9A)	5331	2713	4604	163
H(9B)	5161	1903	6200	163
H(9C)	5370	1161	4578	163
H(8A)	3751	1520	1768	138
H(8B)	4455	2294	1644	138
H(8C)	4458	757	1925	138
H(3A)	3340	6944	3255	106
H(3B)	3058	6629	5027	106
H(4A)	2304	5774	3198	104
H(4B)	2902	5058	2243	104
H(7'1)	3729	837	2878	190
H(7'2)	4090	-257	3950	190
H(7'3)	3368	321	4485	190
H(8'1)	4594	1743	7920	226
H(8'2)	3918	896	7692	226
H(8'3)	4640	318	7156	226
H(9'1)	5376	2636	5016	149
H(9'2)	5372	1132	4530	149
H(9'3)	5126	2203	3259	149
H(3'1)	3327	5190	2415	75
H(3'2)	3307	6683	2952	75
H(4'1)	2627	5916	5337	61
H(4'2)	2230	5886	3629	61

Table S21. Torsion angles [°] for Me₃SiZnI (**2b**).

C(4')-C(1)-N(2)-C(2)	-132.9(19)
C(4')-C(1)-N(2)-Zn(1)	103.3(18)
C(6)-N(1)-C(3)-C(4)	-158.5(18)
C(5)-N(1)-C(3)-C(4)	83(2)
Zn(1)-N(1)-C(3)-C(4)	-39(2)
C(1)-N(2)-C(4)-C(3)	93(2)
C(2)-N(2)-C(4)-C(3)	-148.9(17)
Zn(1)-N(2)-C(4)-C(3)	-34(2)
N(1)-C(3)-C(4)-N(2)	52(3)
C(6)-N(1)-C(3')-C(4')	-81(3)
C(5)-N(1)-C(3')-C(4')	159(3)
Zn(1)-N(1)-C(3')-C(4')	49(3)
C(1)-N(2)-C(4')-C(3')	168(2)
C(2)-N(2)-C(4')-C(3')	-77(3)
Zn(1)-N(2)-C(4')-C(3')	54(2)
C(2)-N(2)-C(4')-C(1)	114.6(17)
Zn(1)-N(2)-C(4')-C(1)	-114.2(10)
N(1)-C(3')-C(4')-N(2)	-76(4)
N(1)-C(3')-C(4')-C(1)	-61(6)

Table S22. Hydrogen bonds for Me₃SiZnI (**2b**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1A ^b)...I(1)	0.98	3.12	3.658(17)	115.8
C(6)-H(6C)...I(1)	0.98	3.09	3.704(18)	121.8
C(1)-H(1A ^b)...I(1)	0.98	3.12	3.658(17)	115.8
C(6)-H(6C)...I(1)	0.98	3.09	3.704(18)	121.8

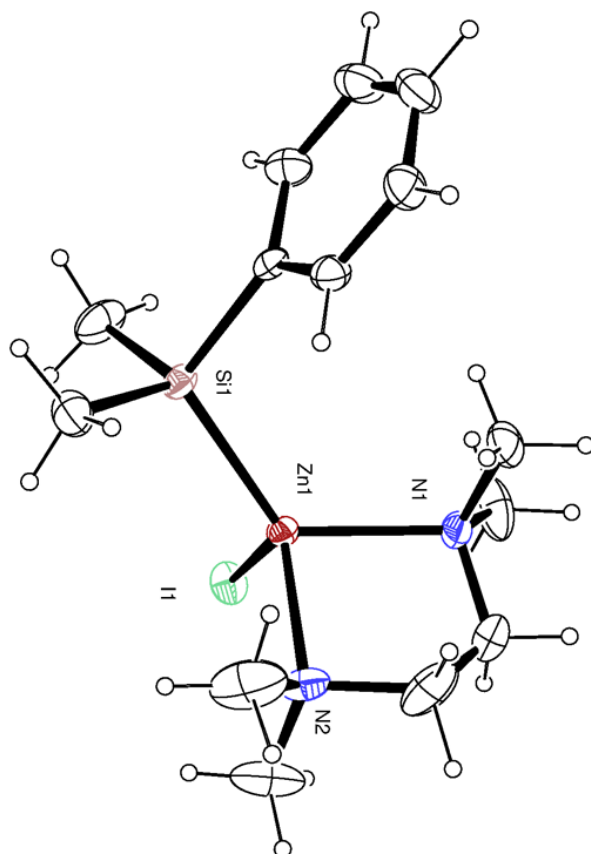


Figure 6a: ORTEP Diagram of $\text{PhMe}_2\text{SiZnI}\cdot\text{TMEDA}$ **2a**
CCSD deposition number 2089058

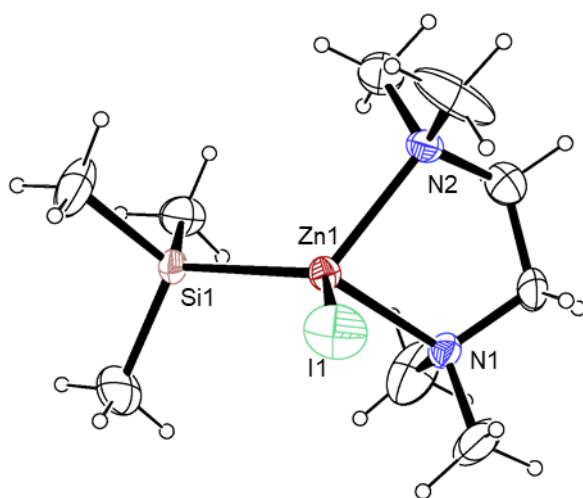
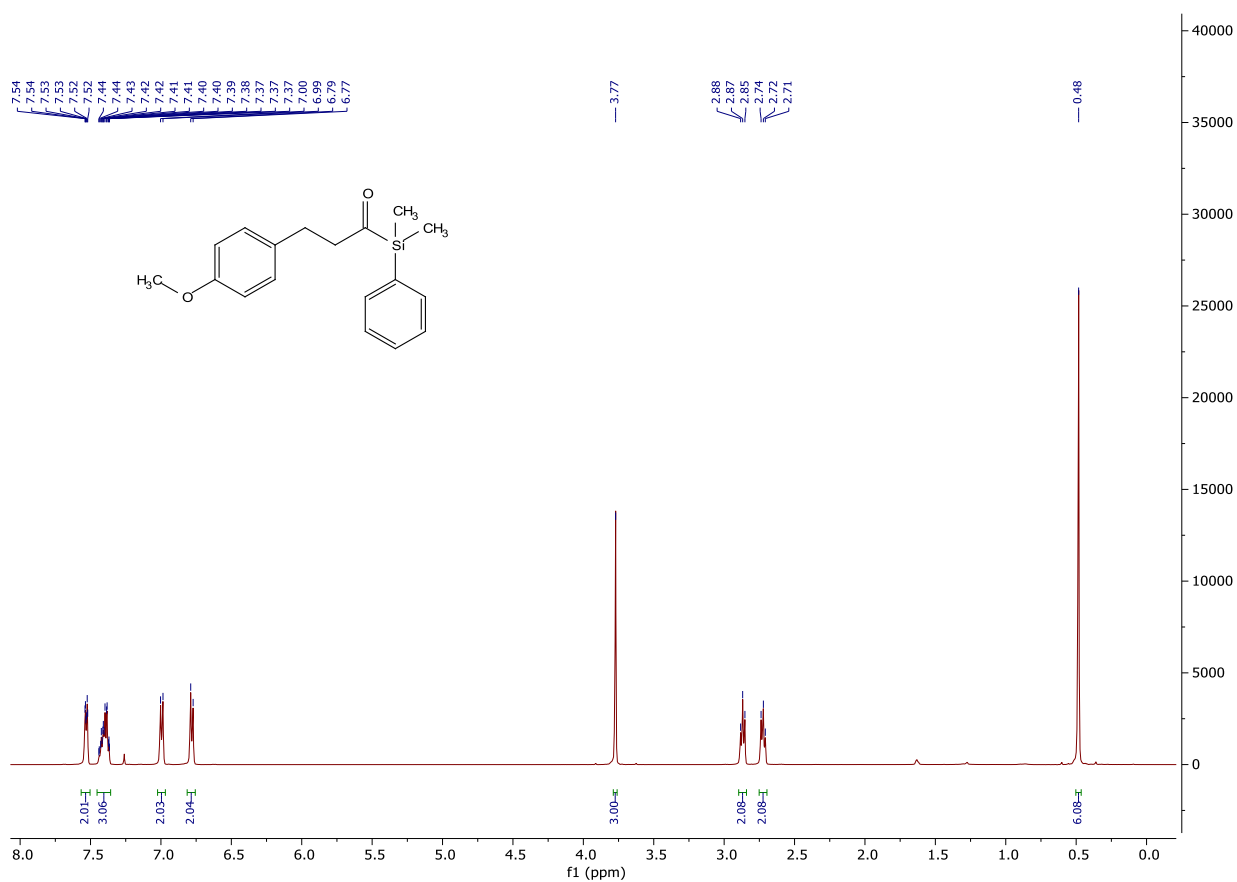


Figure 6b: ORTEP Diagram of $\text{Me}_3\text{SiZnI}\cdot\text{TMEDA}$ **2b**
CCSD deposition number 2089062

13. NMR Data

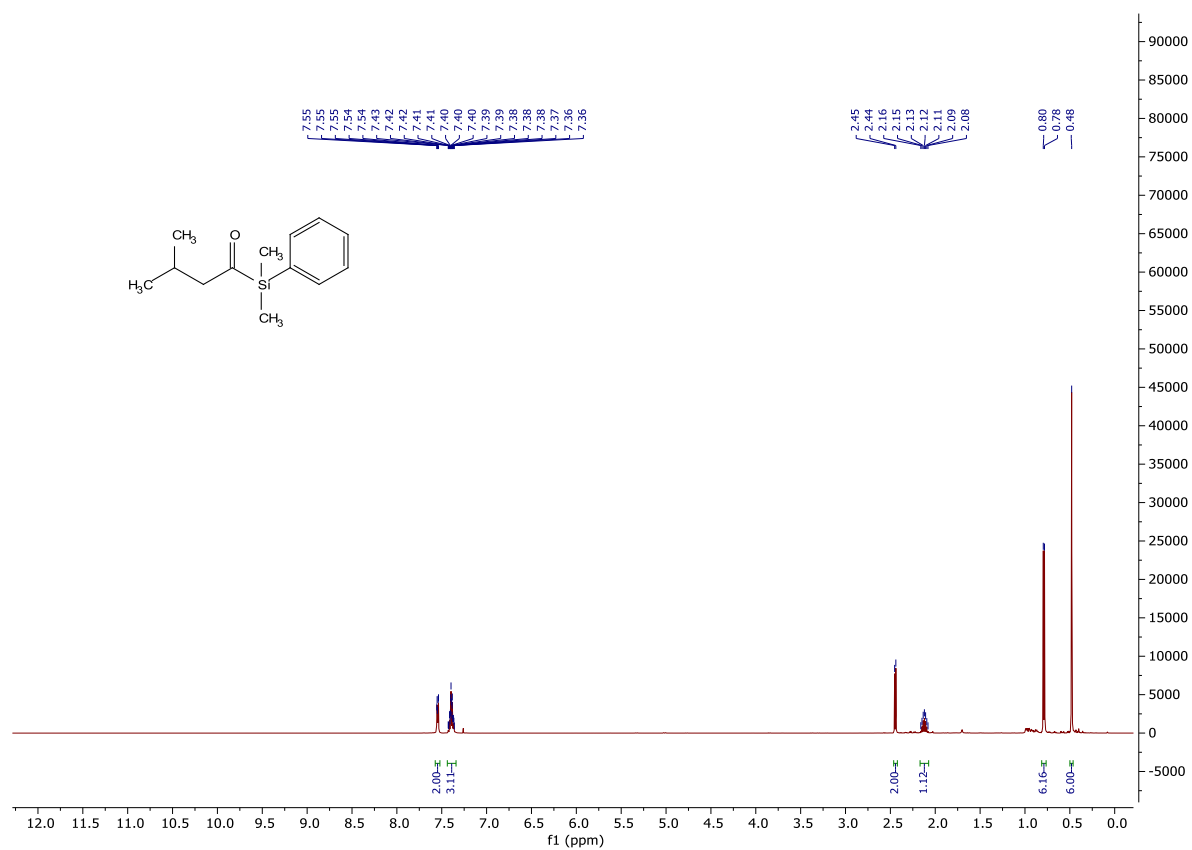
¹H NMR (500 MHz, CDCl₃) of 5a



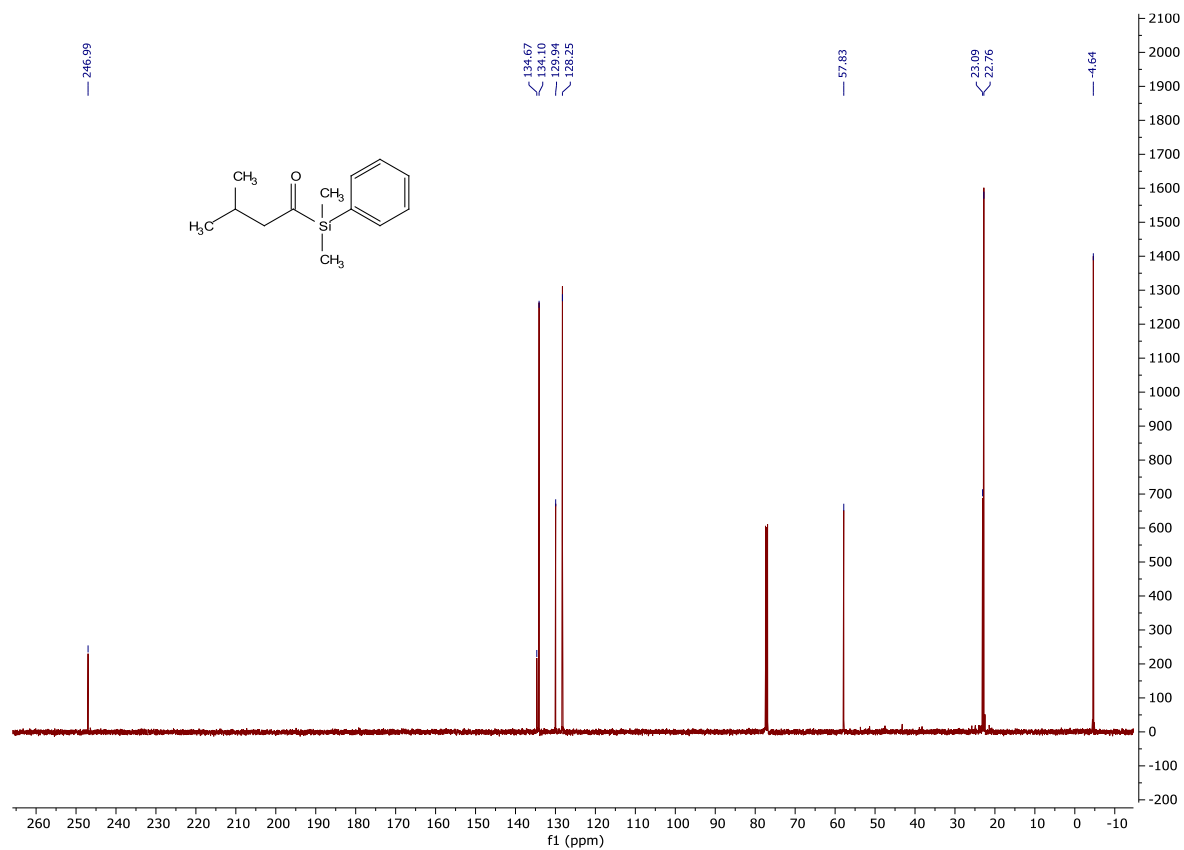
¹³C NMR (126 MHz, CDCl₃) of 5a



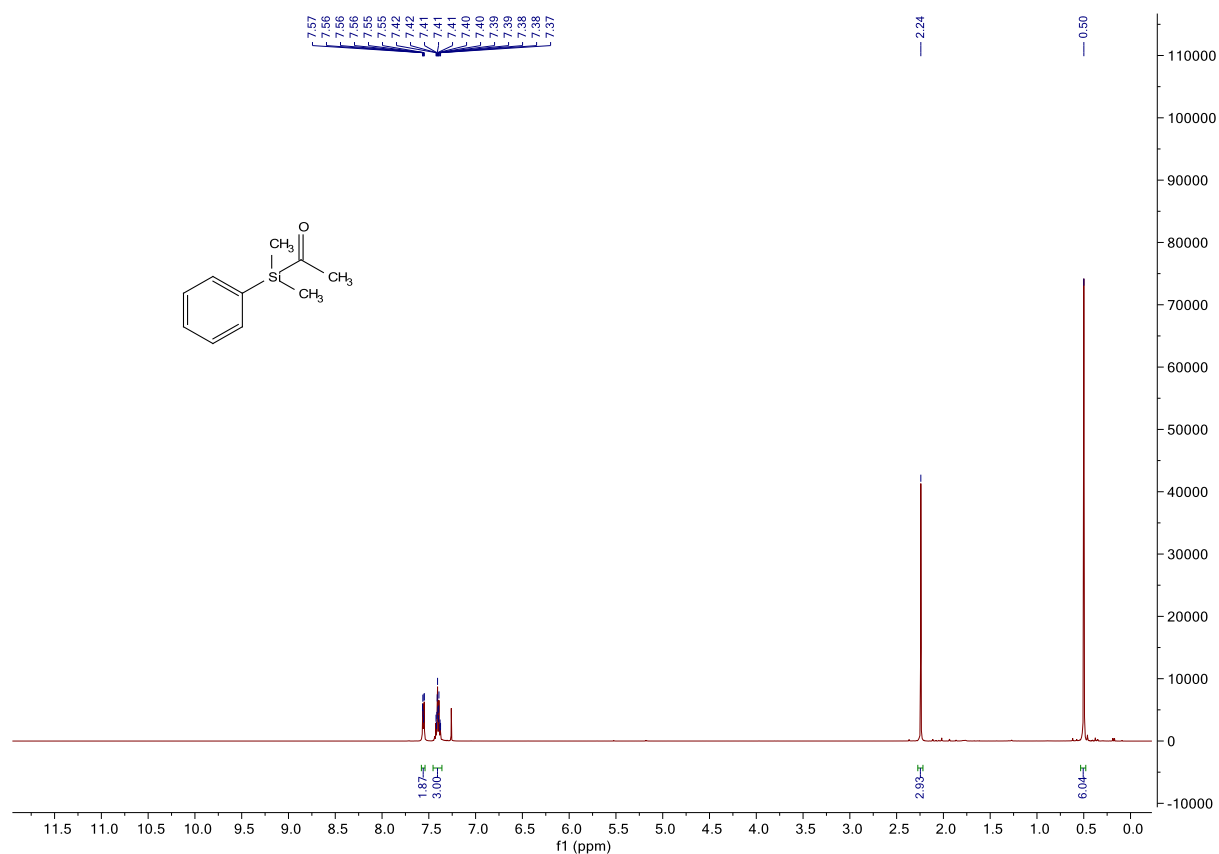
^1H NMR (500 MHz, CDCl_3) of **5b**



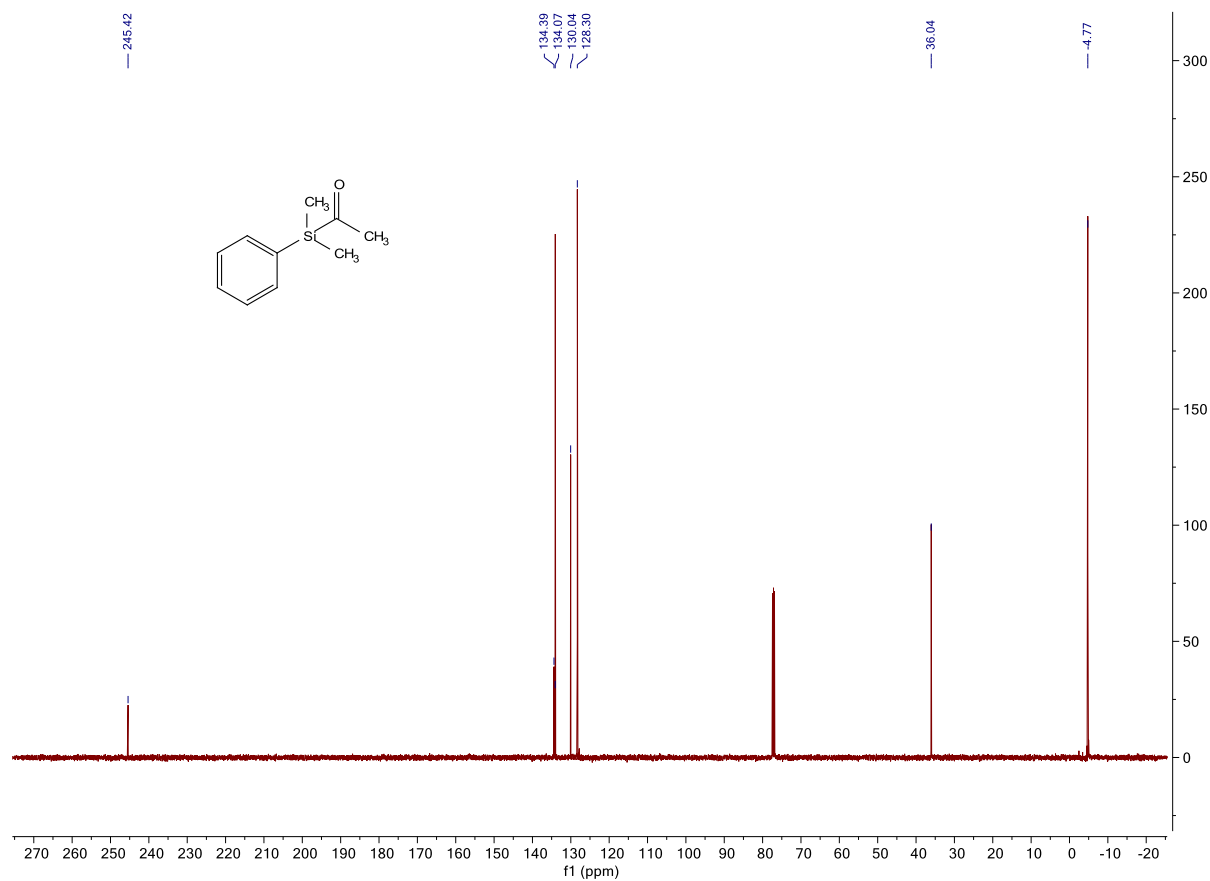
^{13}C NMR (126 MHz, CDCl_3) of **5b**



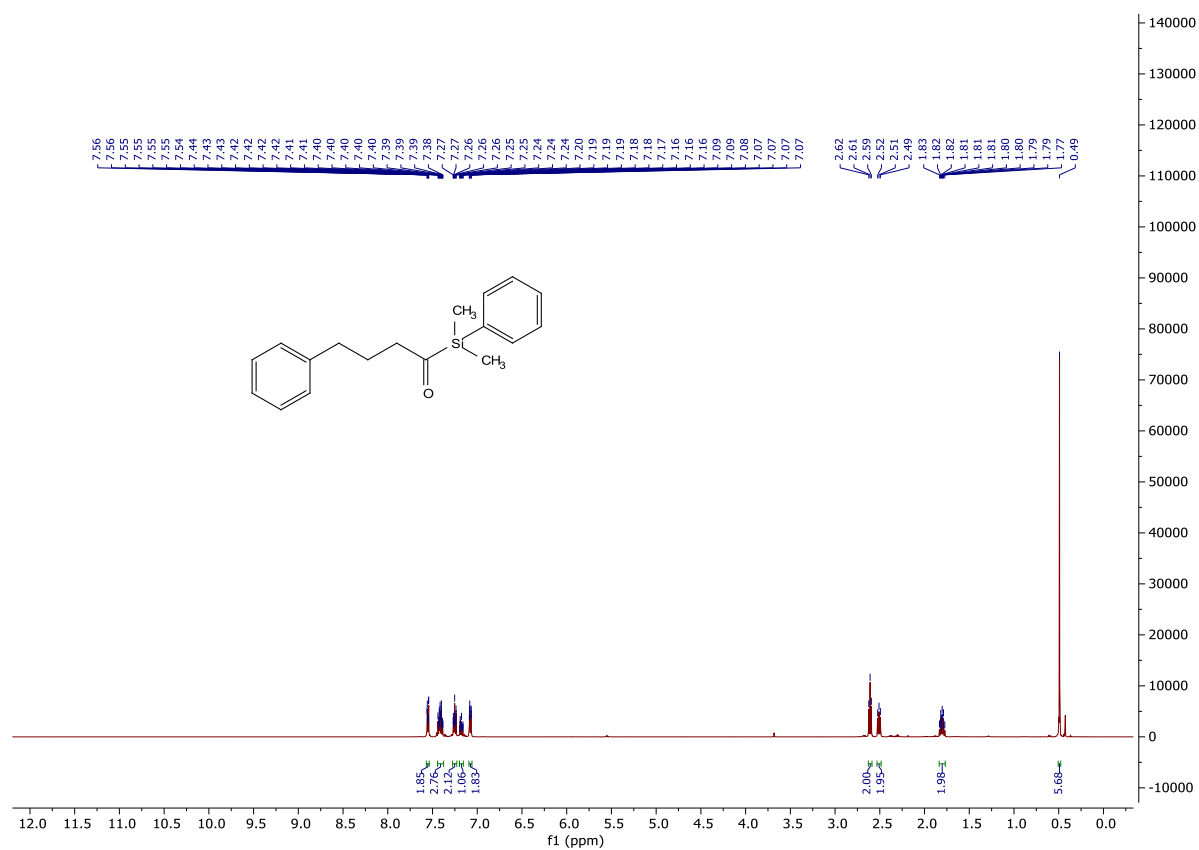
¹H NMR (500 MHz, CDCl₃) of 5bc



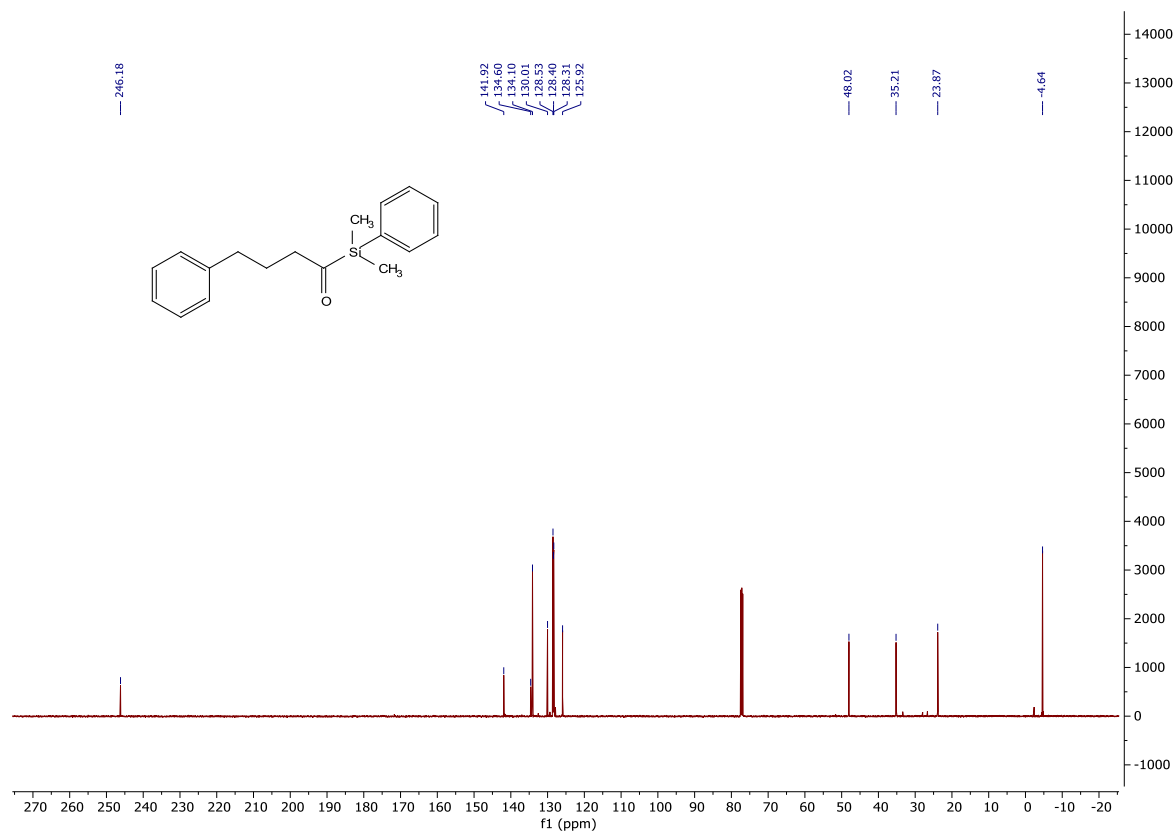
¹³C NMR (126 MHz, CDCl₃) of 5bc



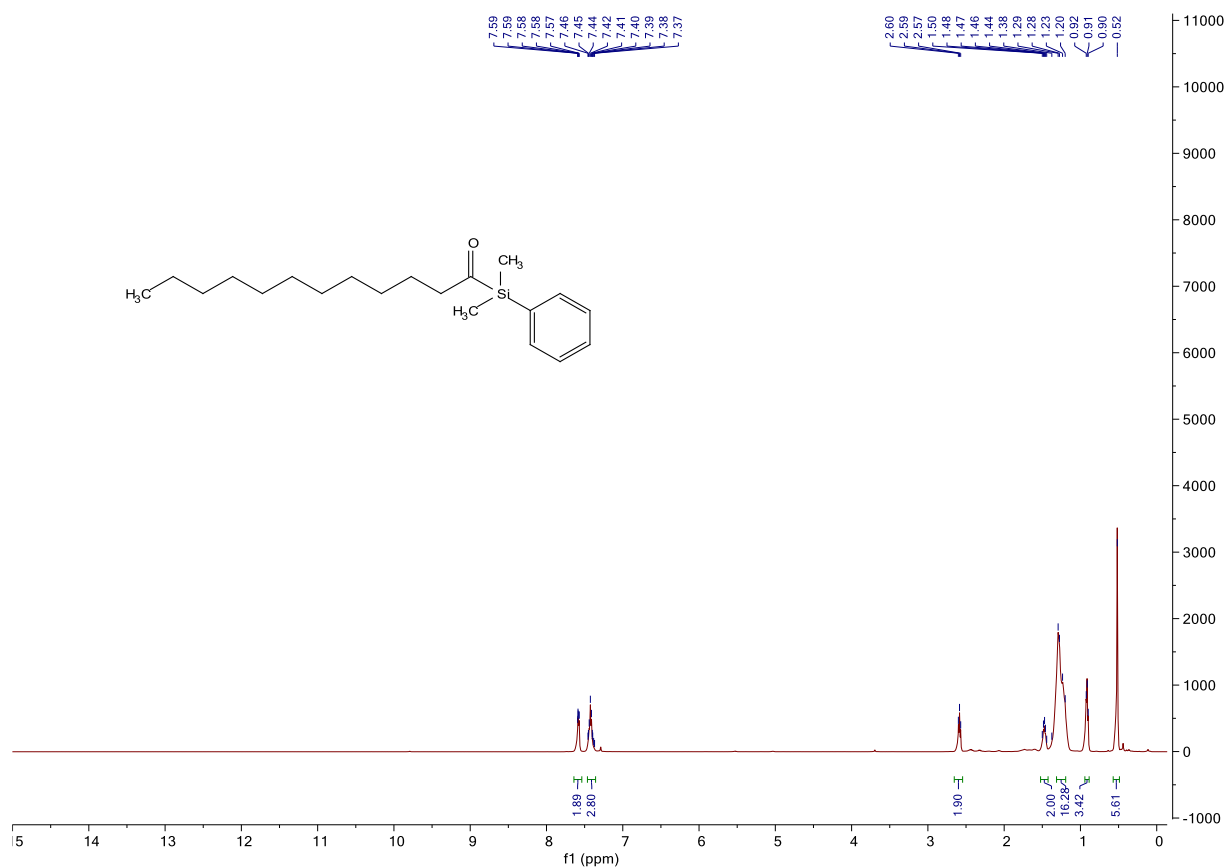
^1H NMR (500 MHz, CDCl_3) of **5c**



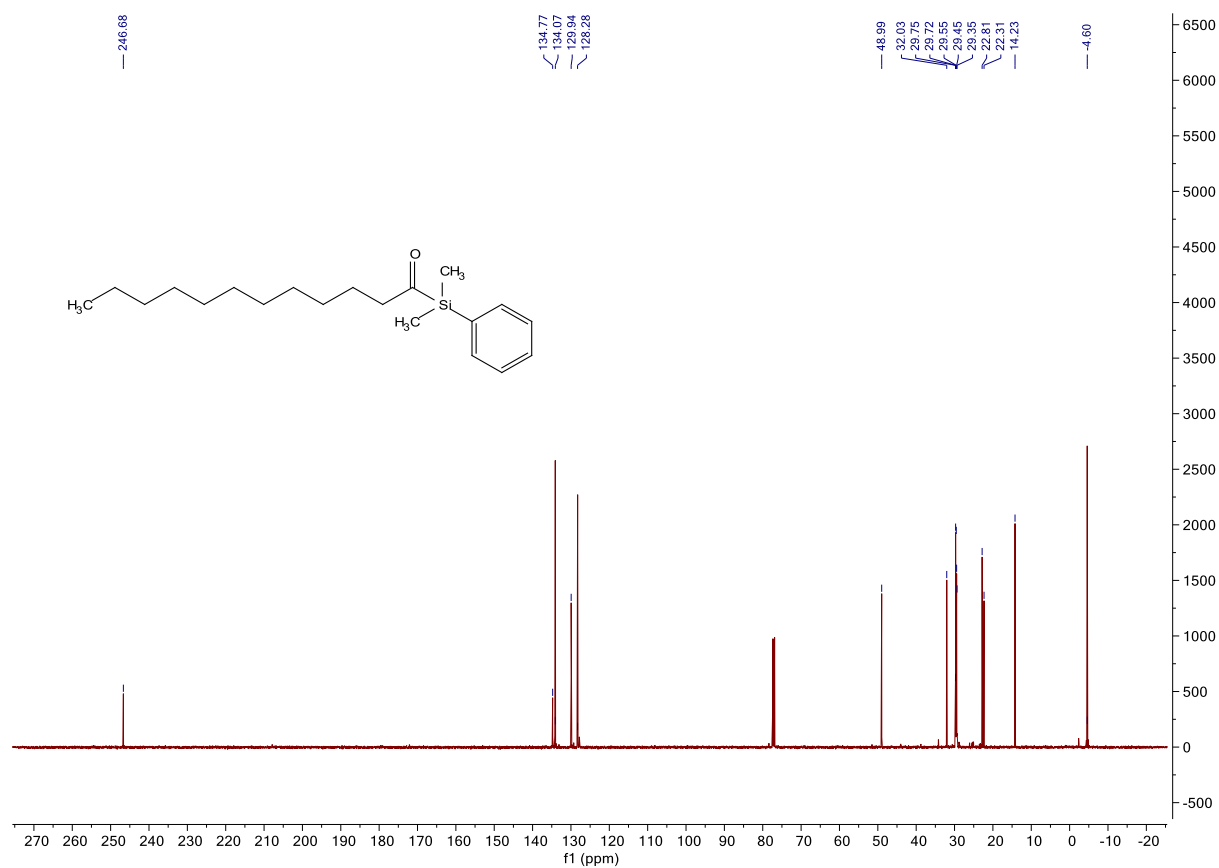
^{13}C NMR (126 MHz, CDCl_3) of **5c**



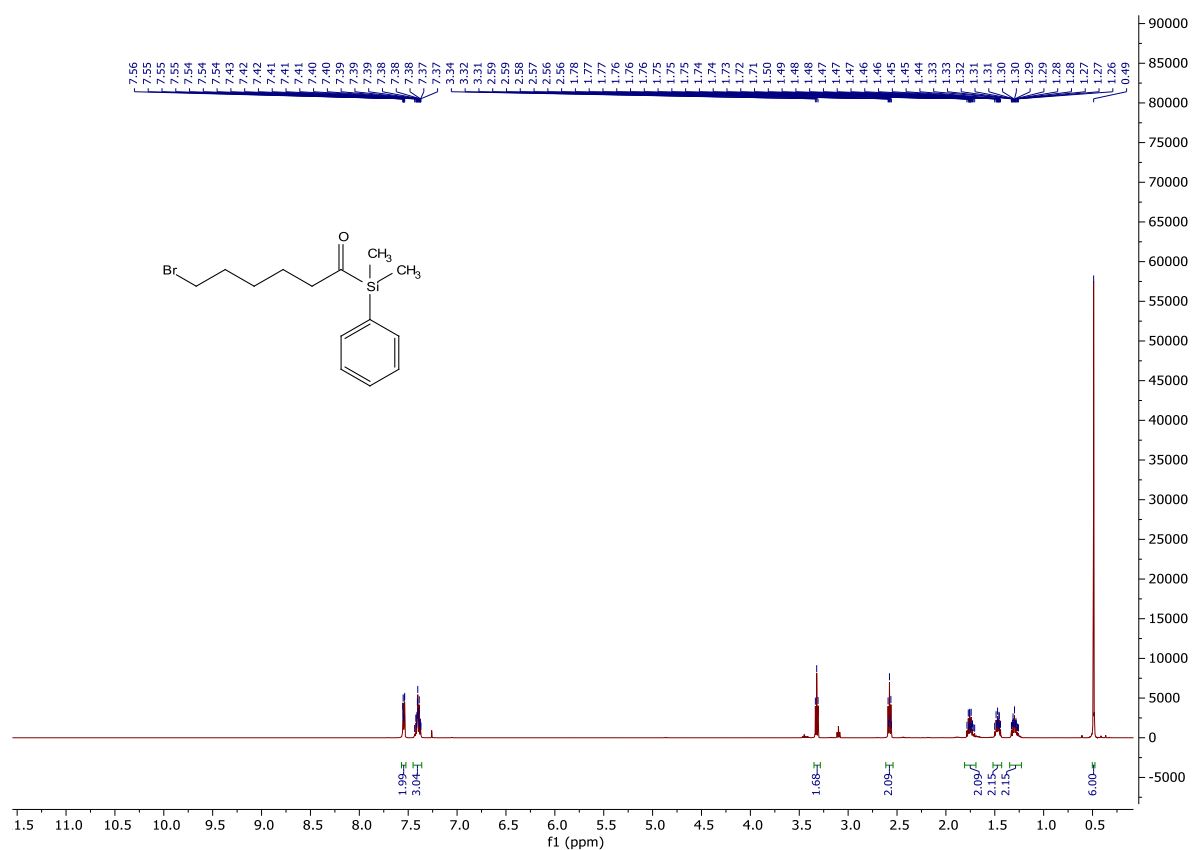
^1H NMR (500 MHz, CDCl_3) of **5d**



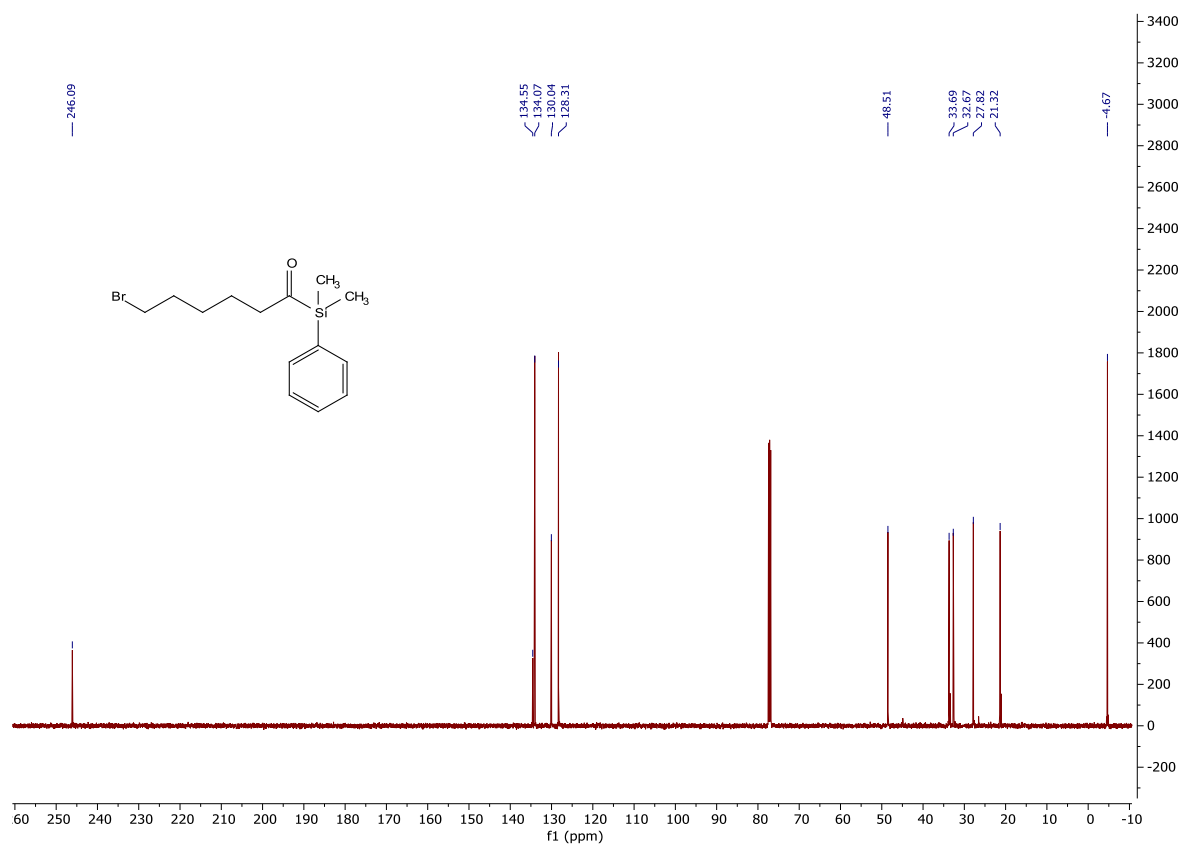
^{13}C NMR (126 MHz, CDCl_3) of **5d**



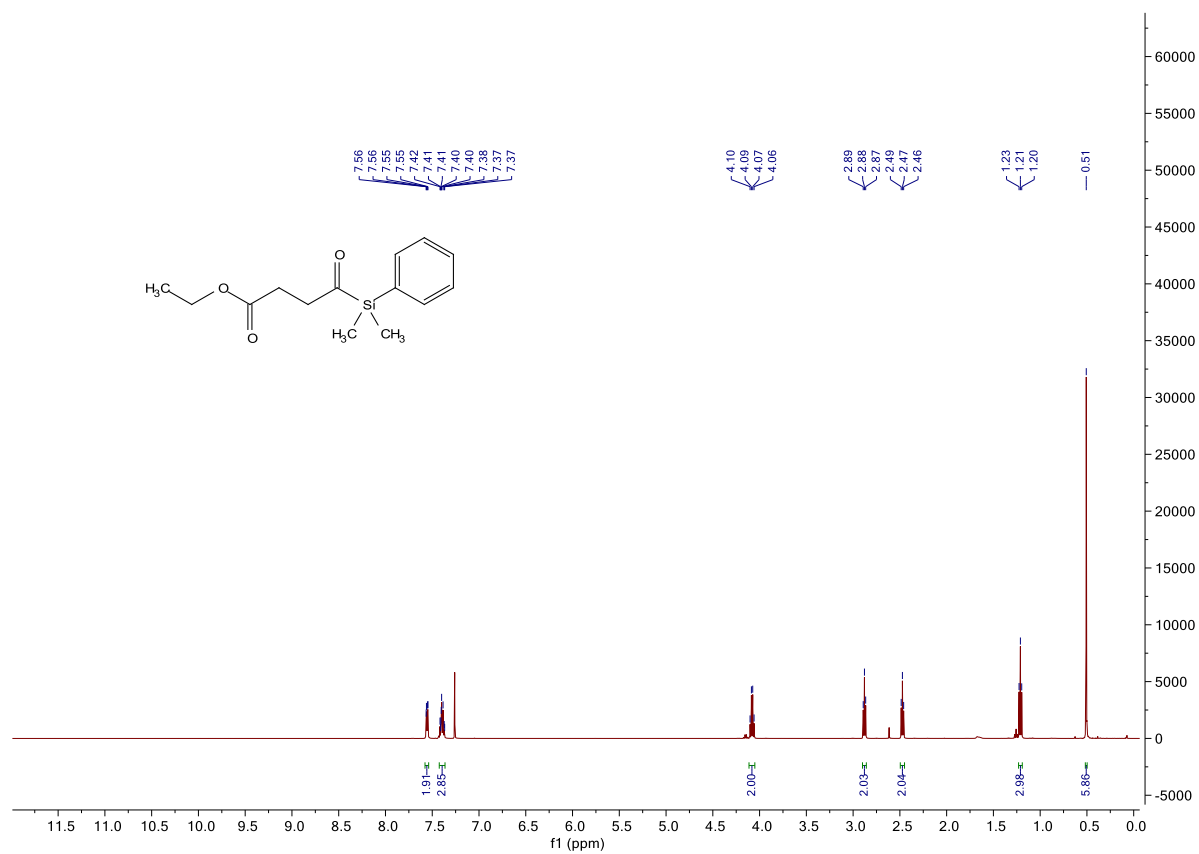
¹H NMR (500 MHz, CDCl₃) of 5e



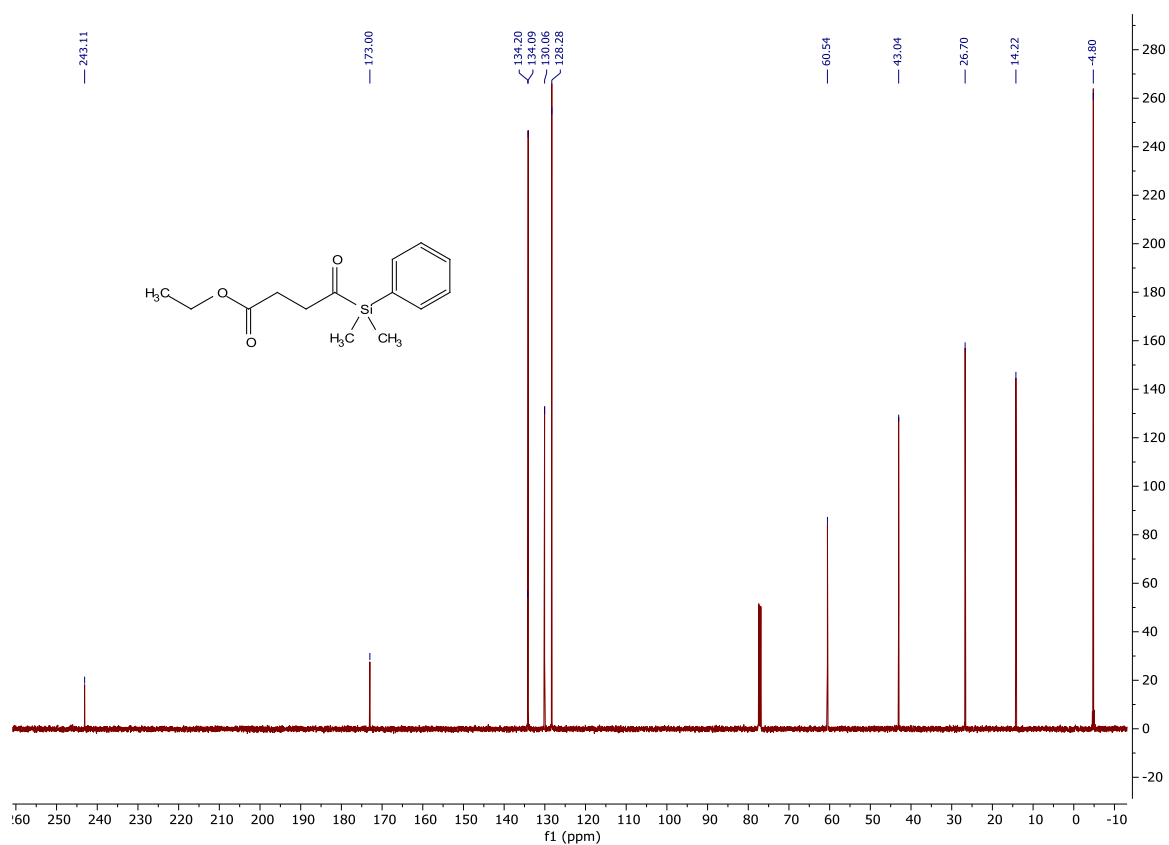
¹³C NMR (126 MHz, CDCl₃) of 5e



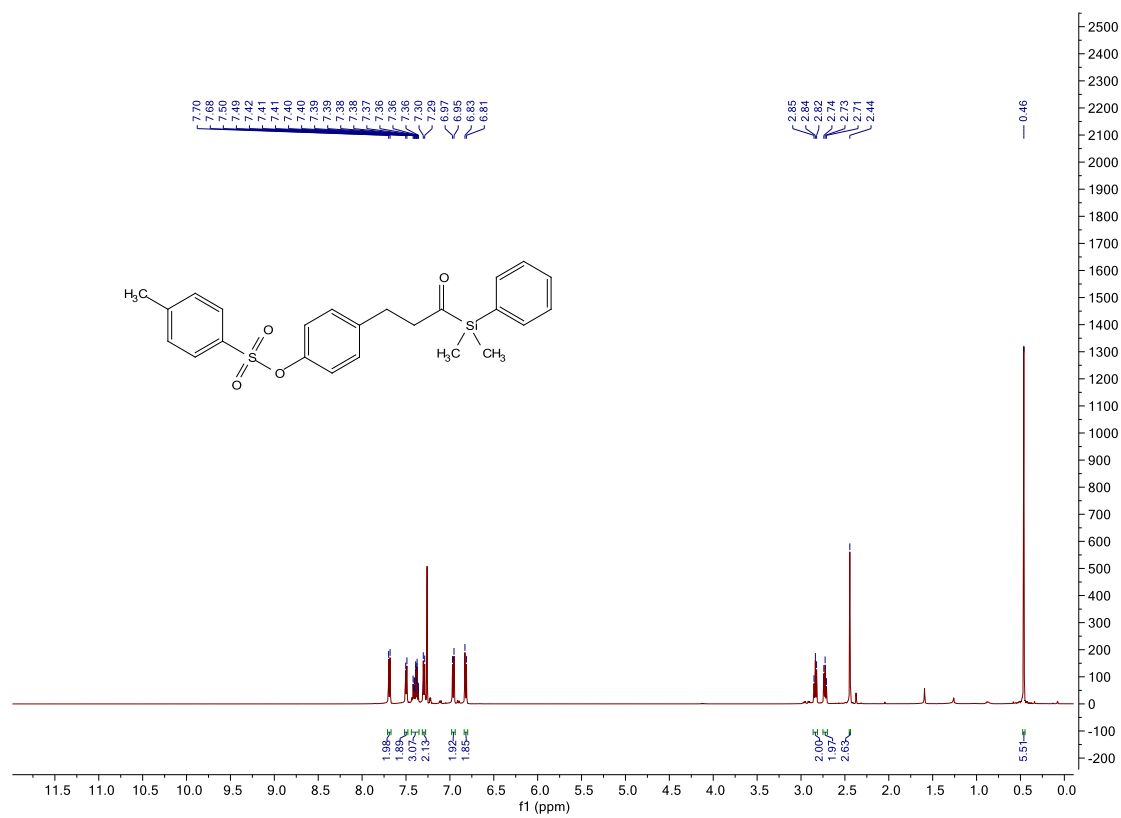
^1H NMR (500 MHz, CDCl_3) of **5f**



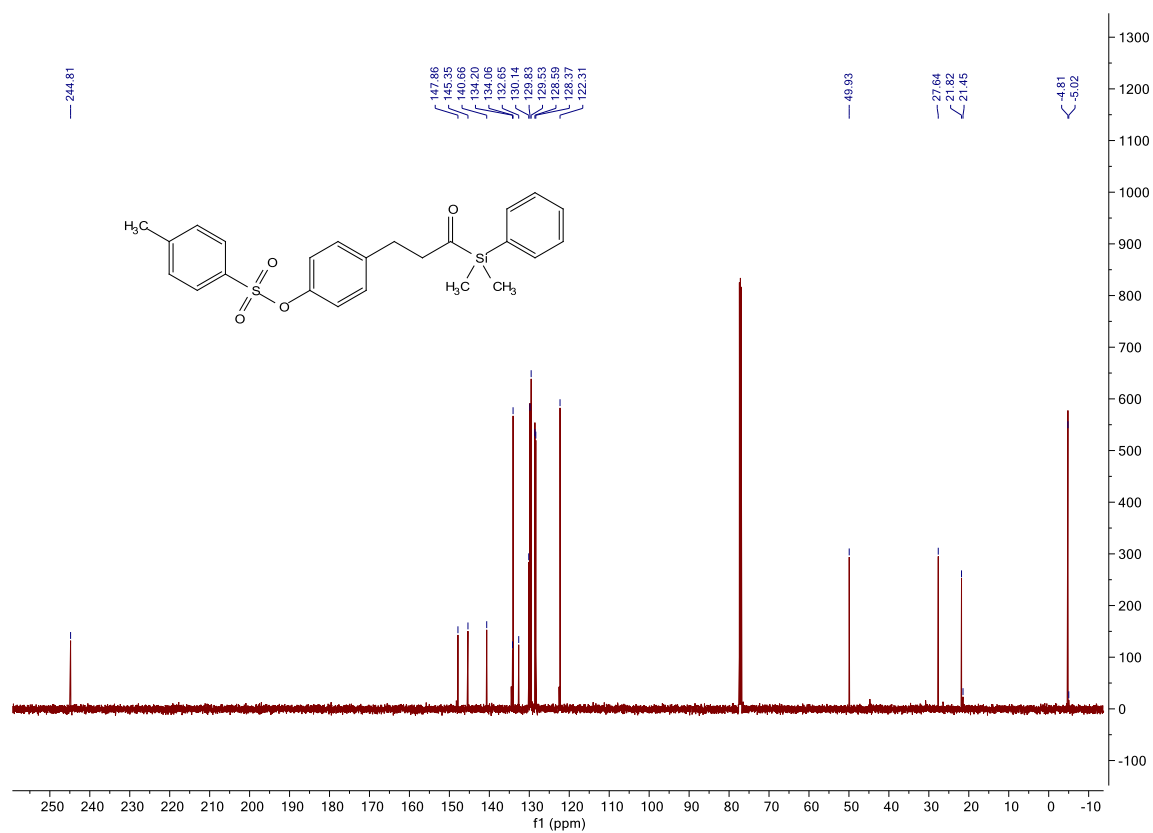
^{13}C NMR (126 MHz, CDCl_3) of **5f**



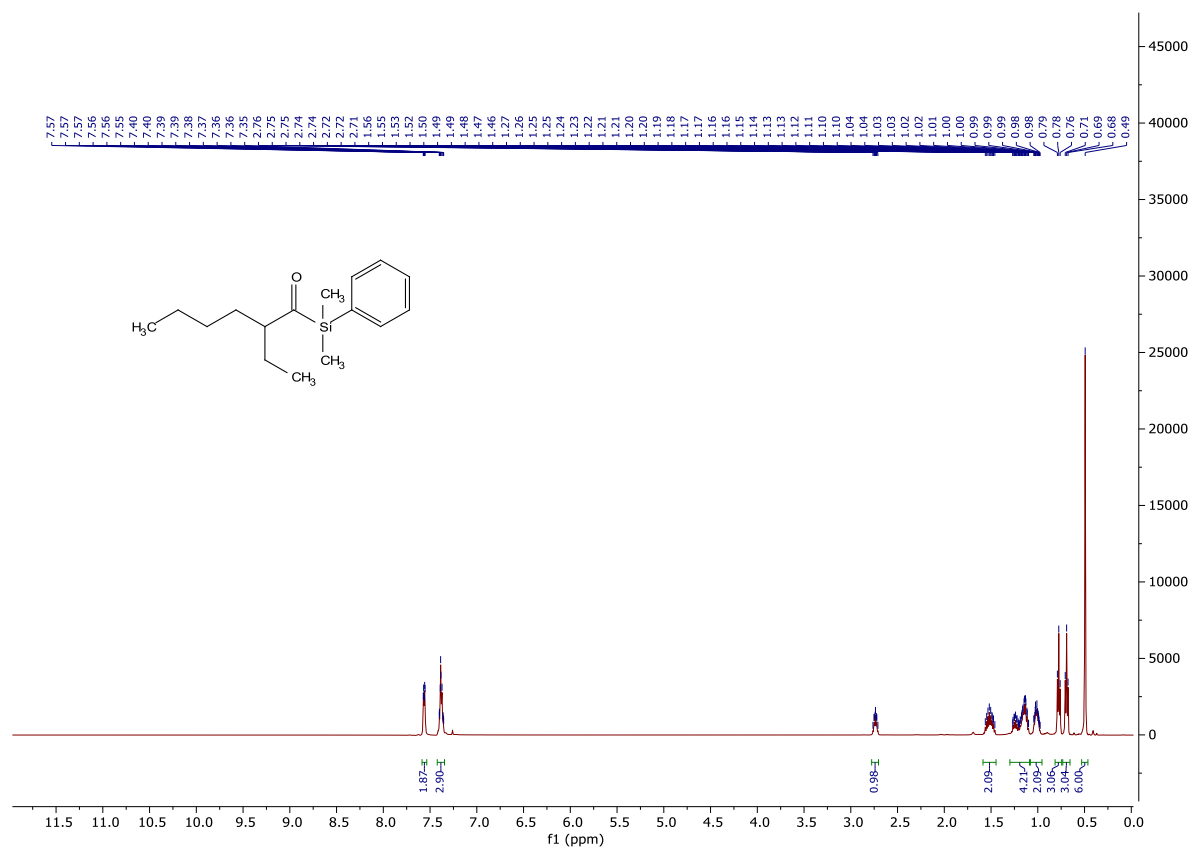
¹H NMR (500 MHz, CDCl₃) of 5g



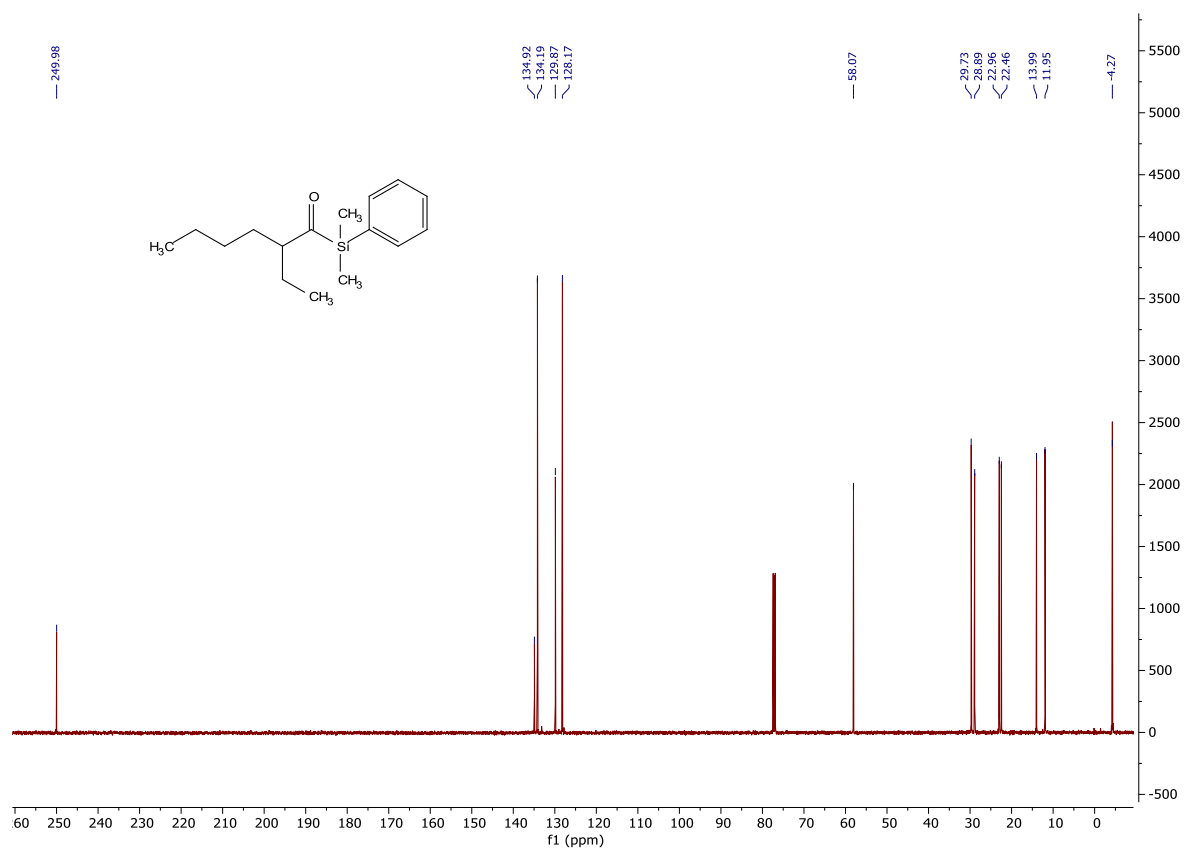
¹³C NMR (126 MHz, CDCl₃) of 5g



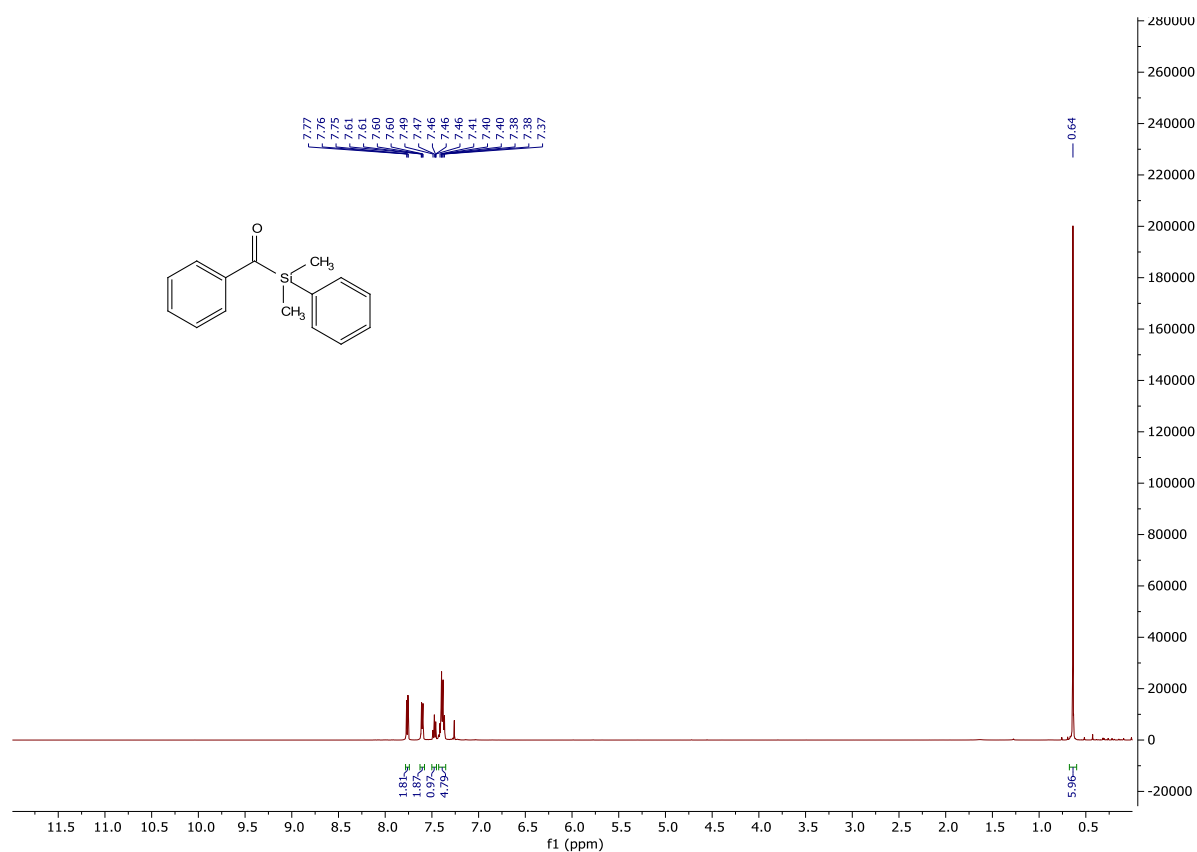
^1H NMR (500 MHz, CDCl_3) of **5i**



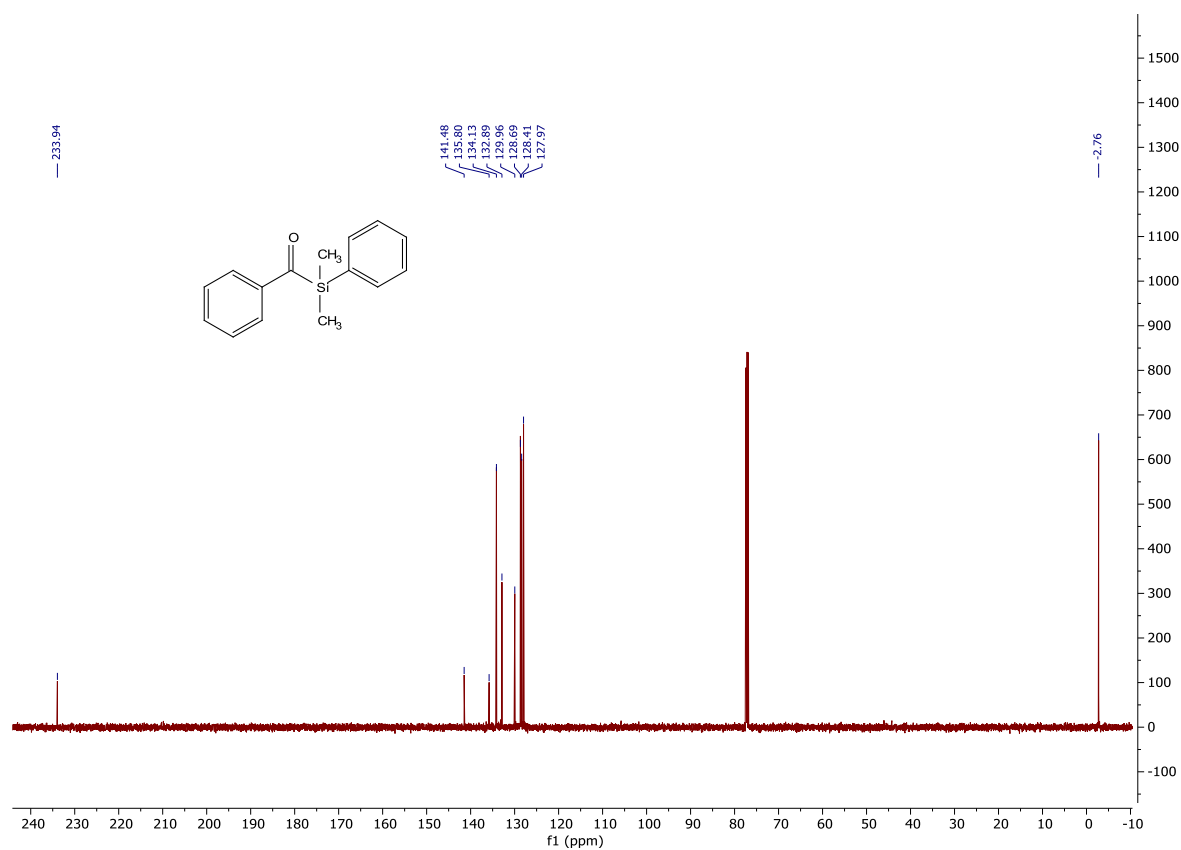
^{13}C NMR (126 MHz, CDCl_3) of **5i**



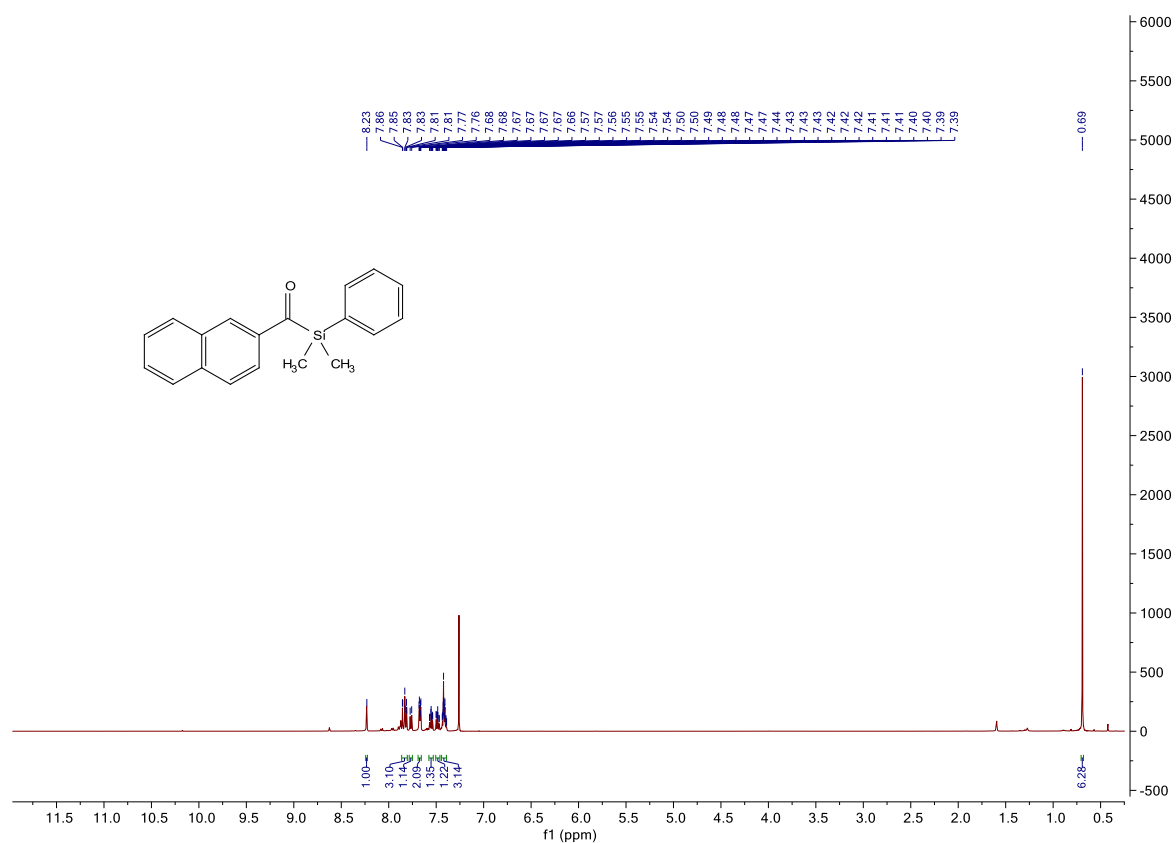
¹H NMR (500 MHz, CDCl₃) of 5j



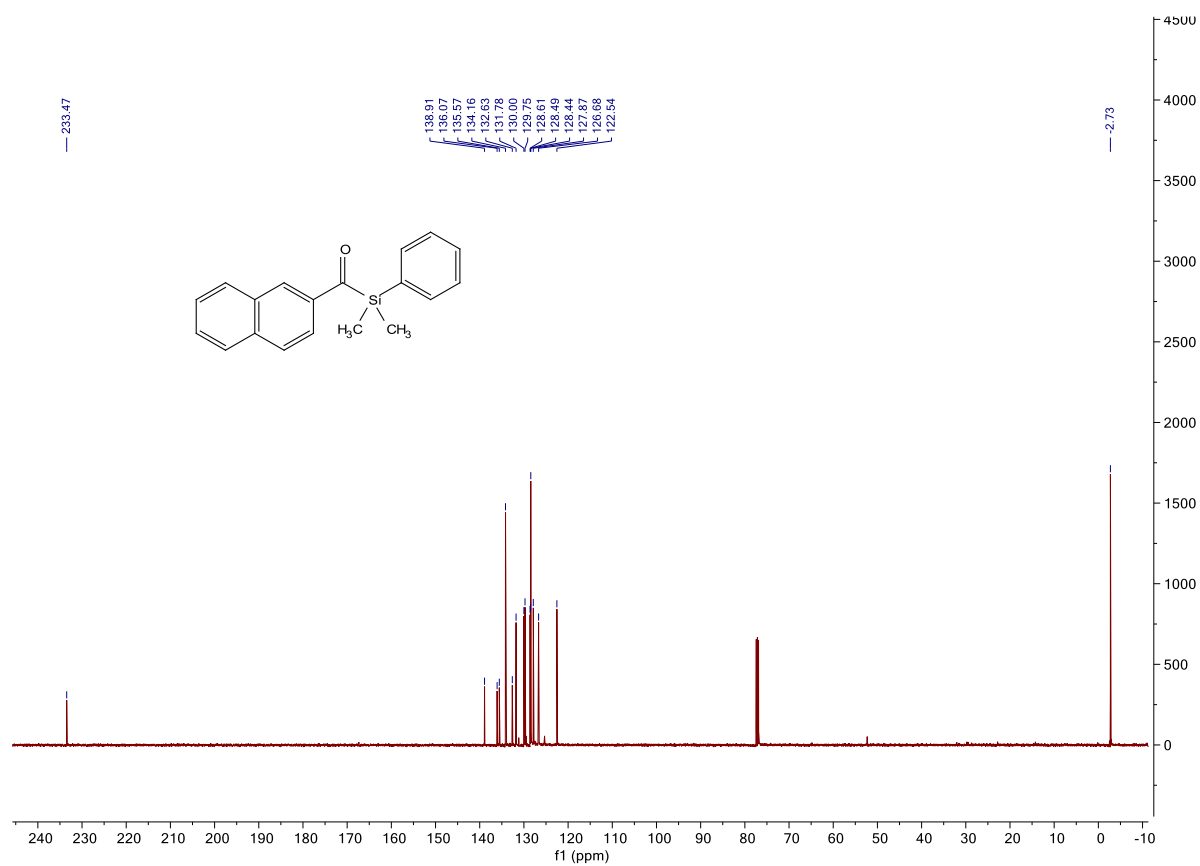
¹³C NMR (126 MHz, CDCl₃) of 5j



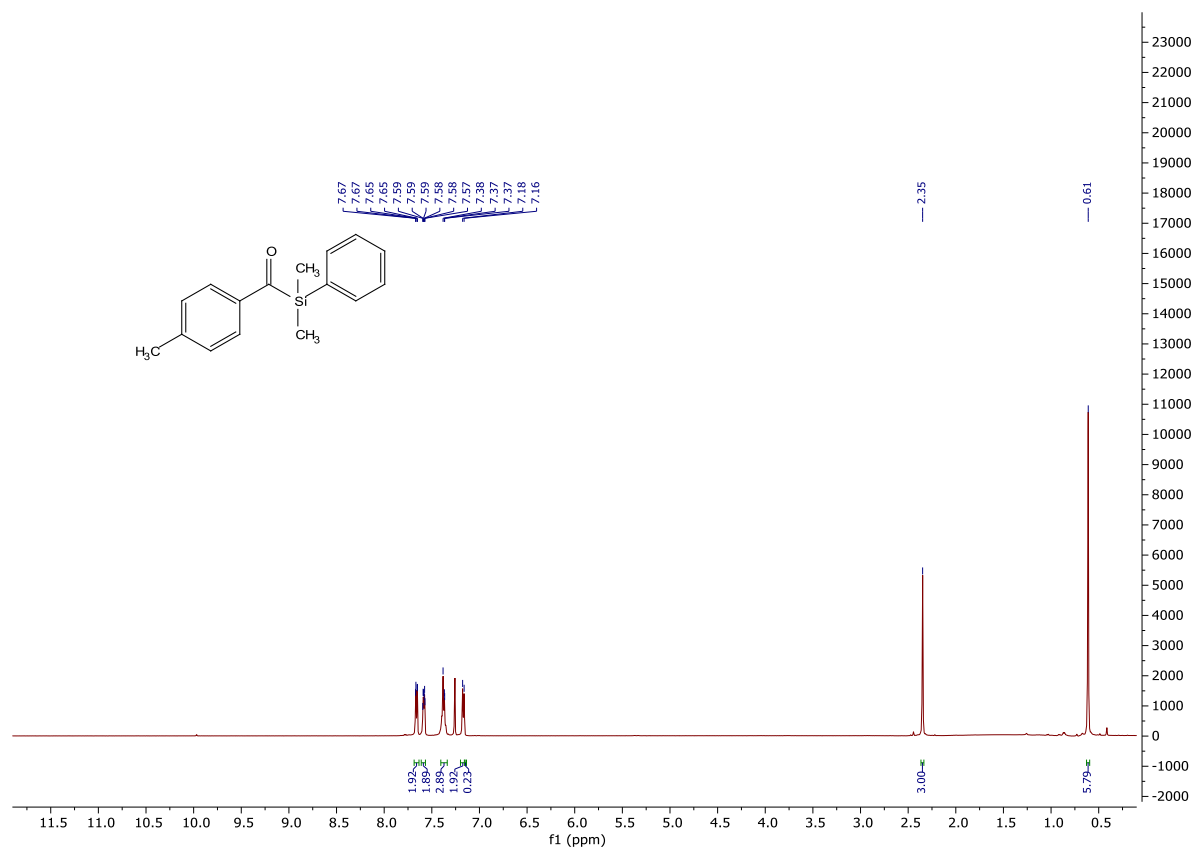
^1H NMR (500 MHz, CDCl_3) of 5k



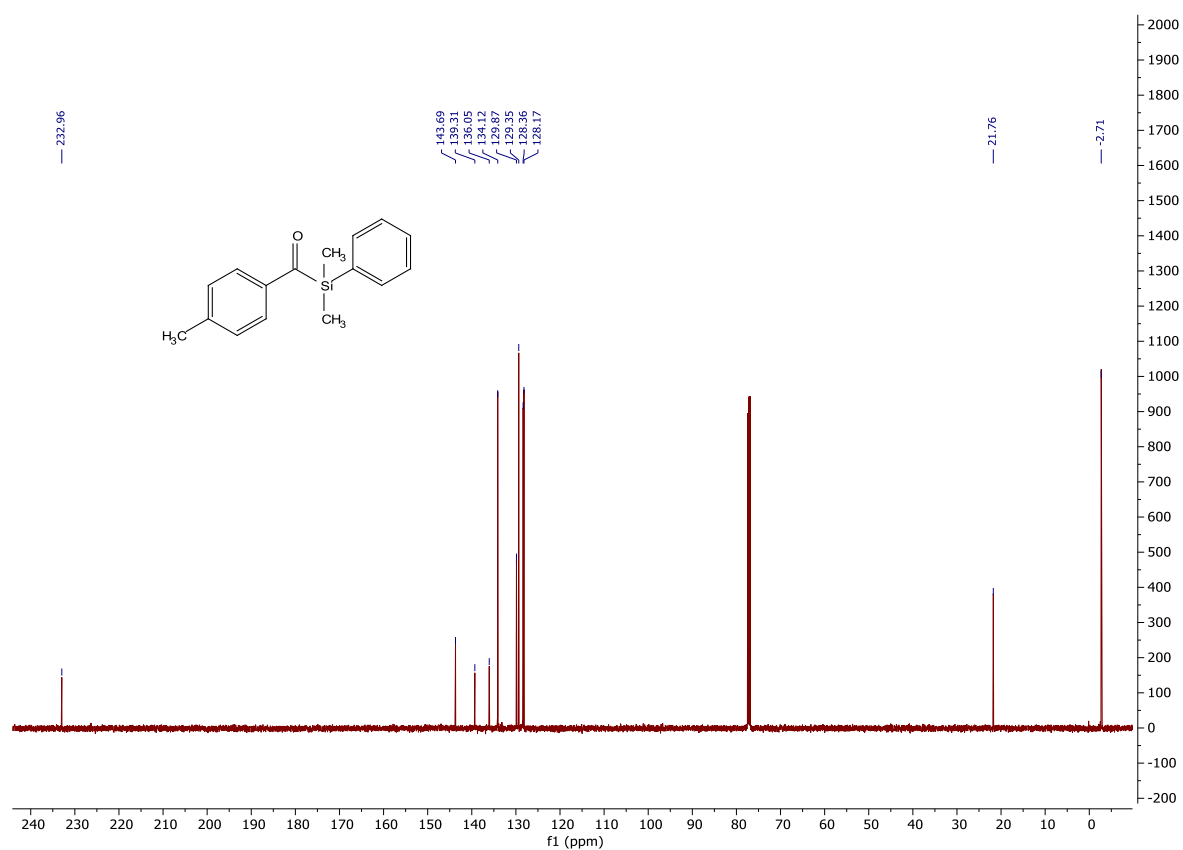
^{13}C NMR (126 MHz, CDCl_3) of 5k



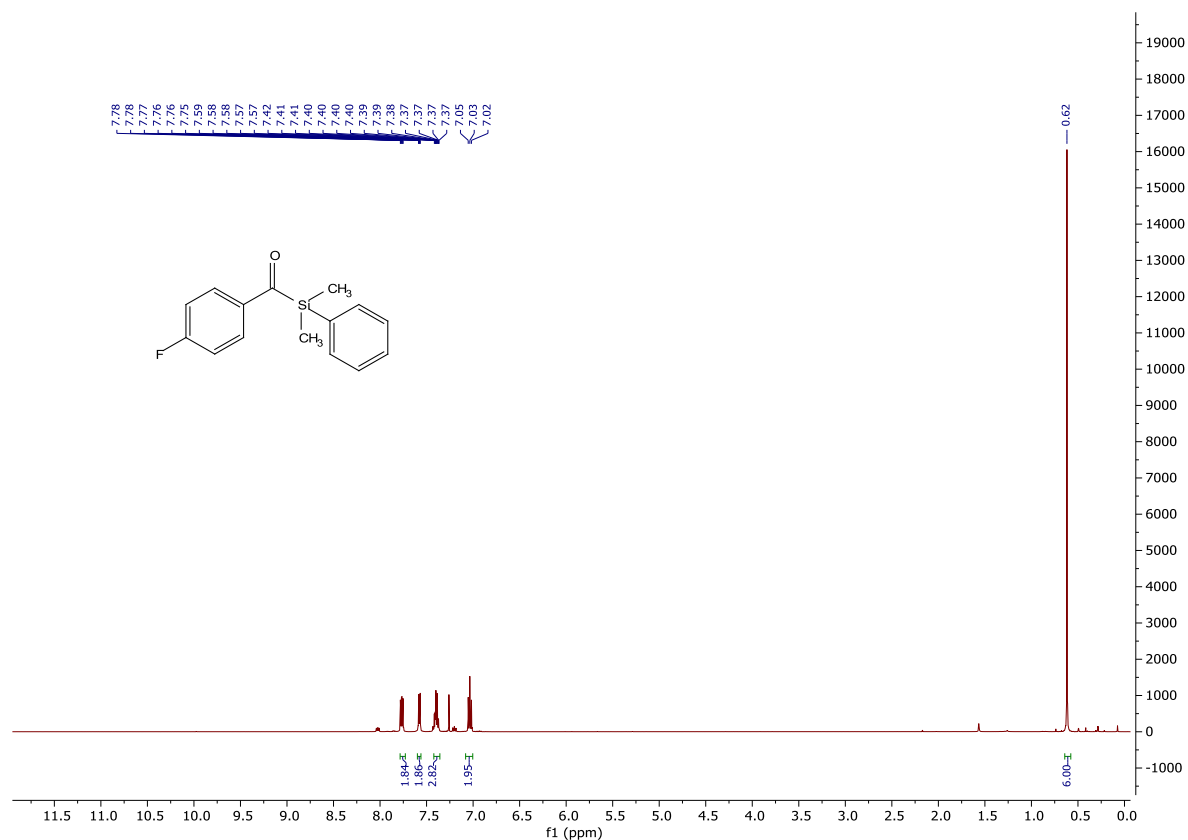
^1H NMR (500 MHz, CDCl_3) of **51**



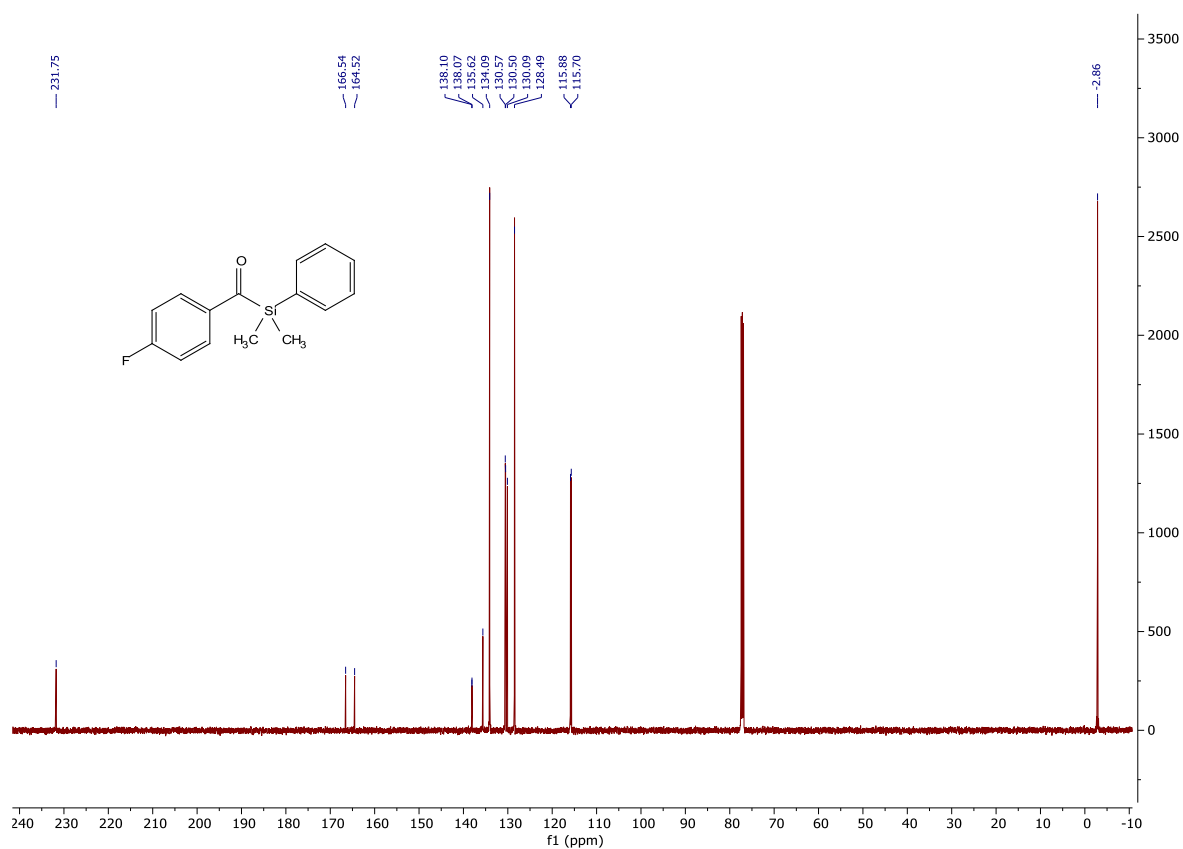
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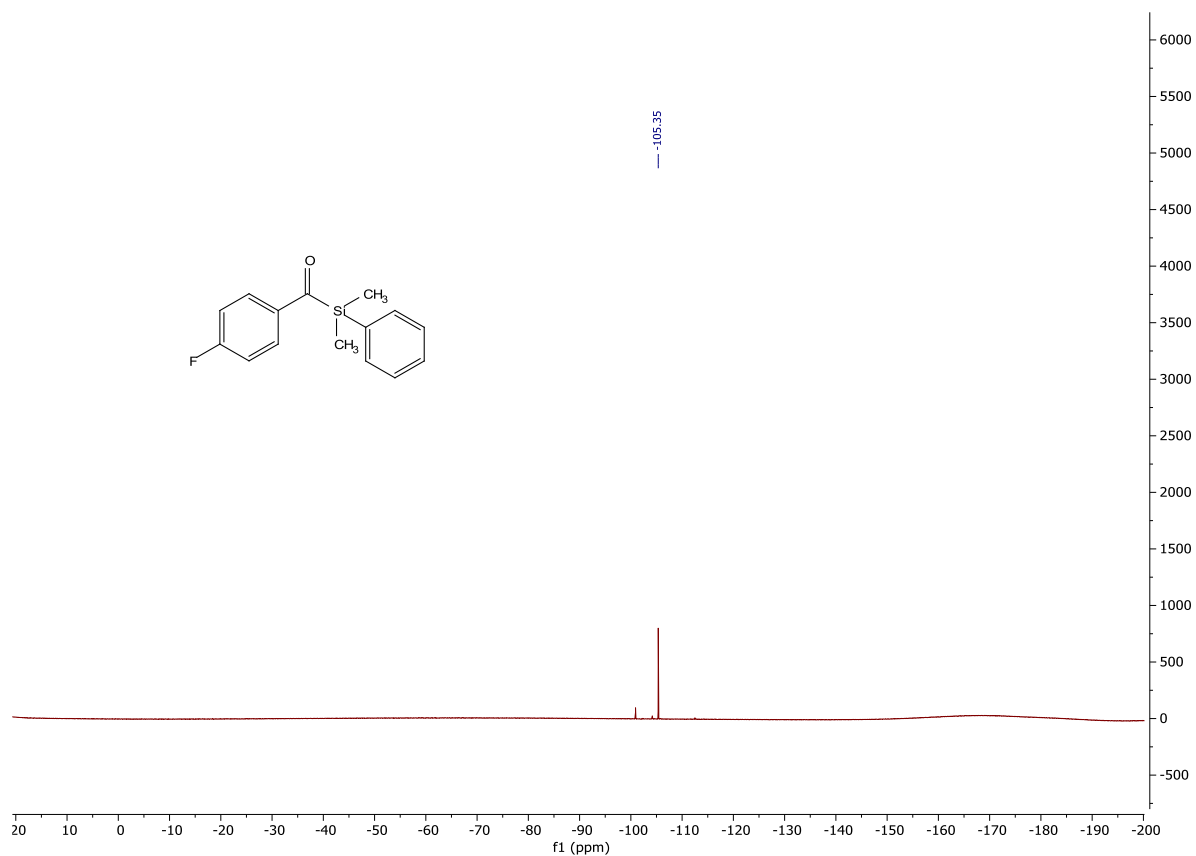
¹H NMR (500 MHz, CDCl₃) of 5m



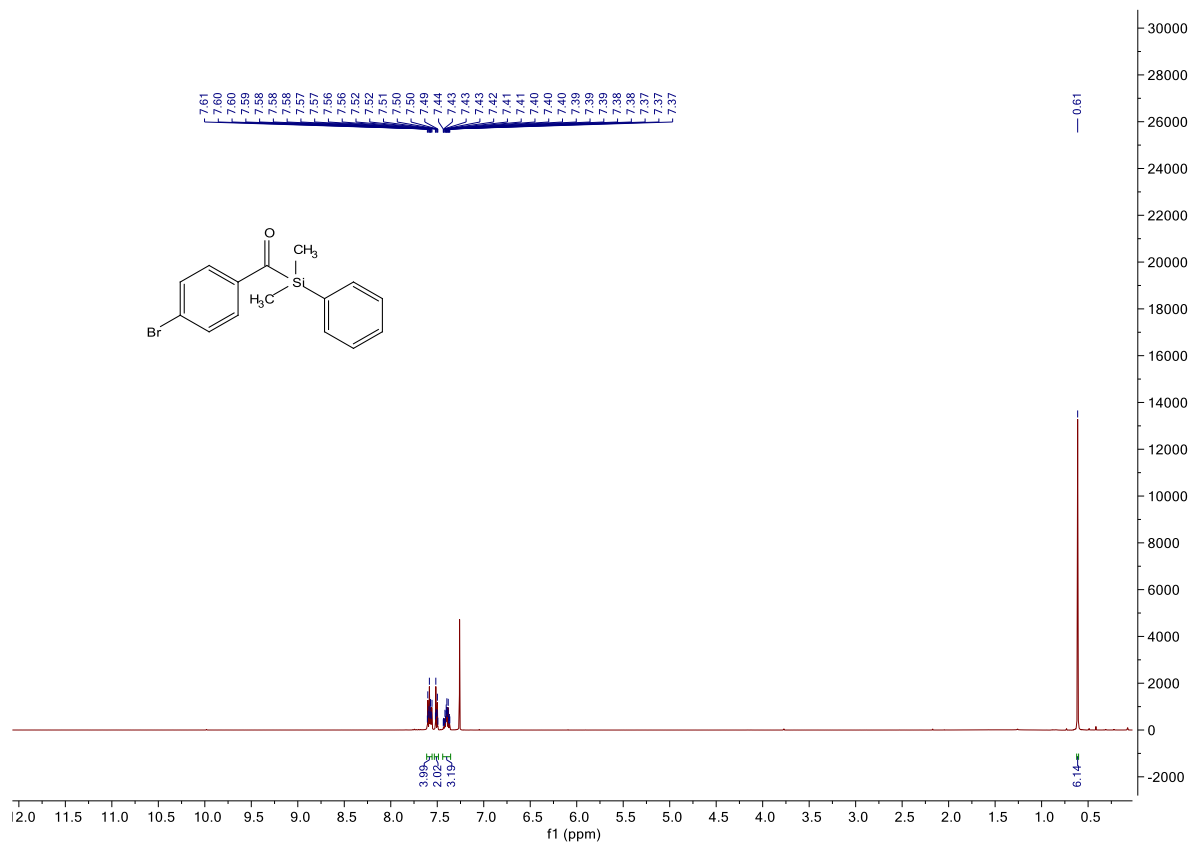
¹³C NMR (126 MHz, CDCl₃) of 5m



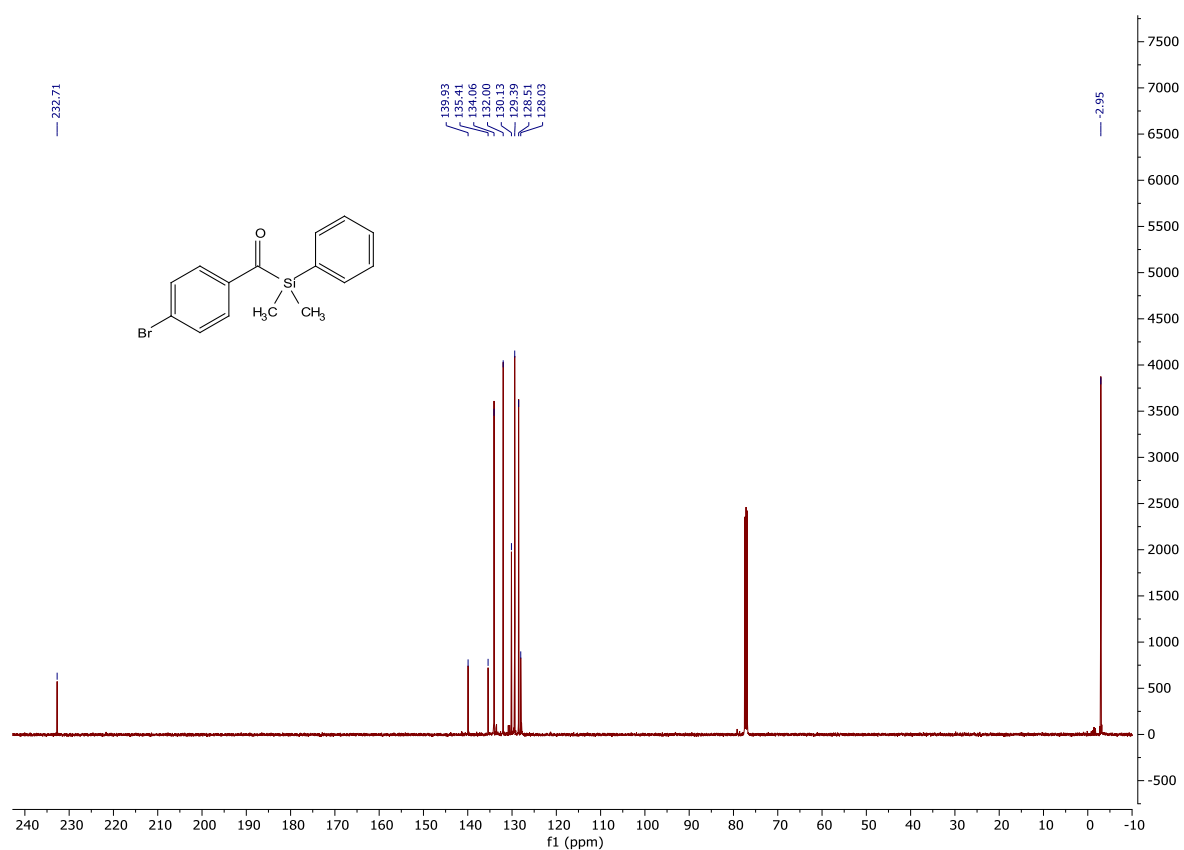
^{19}F NMR (471 MHz, CDCl_3) of **5m**



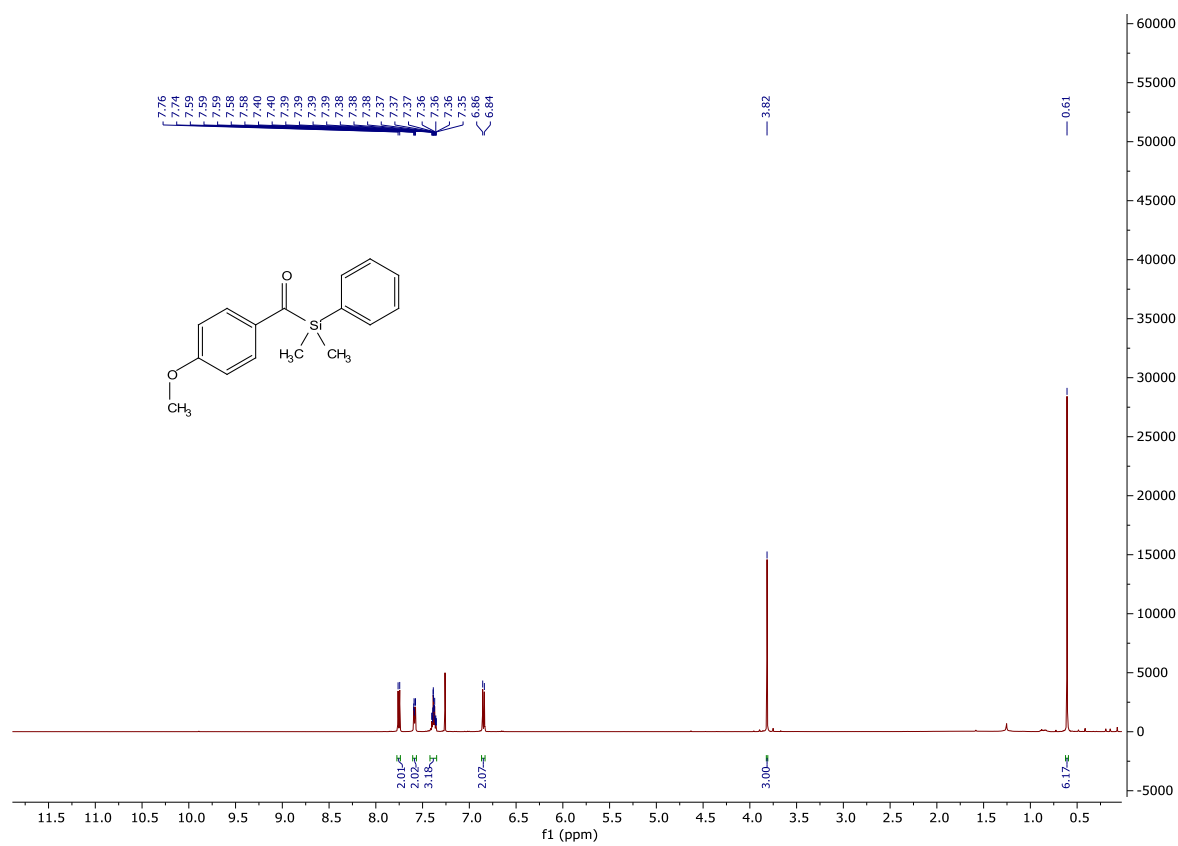
^1H NMR (500 MHz, CDCl_3) of **5mn**



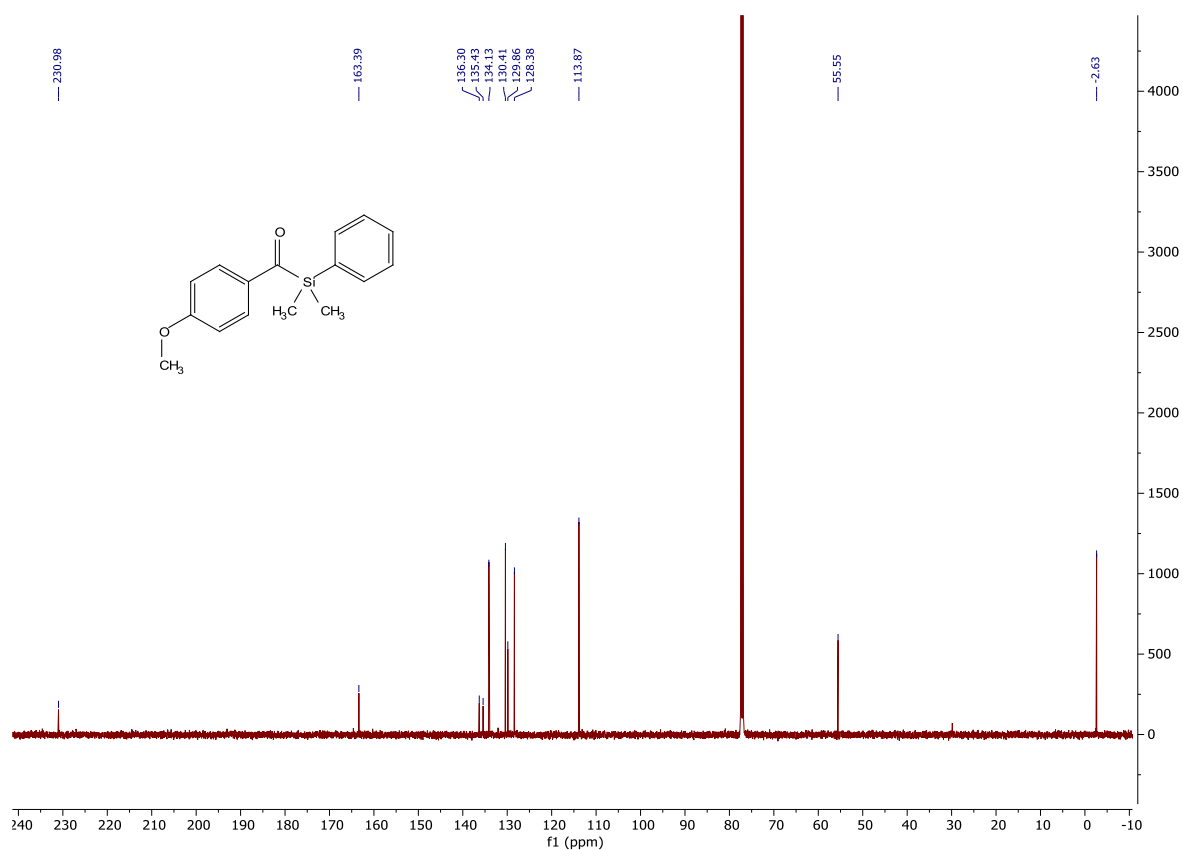
^{13}C NMR (126 MHz, CDCl_3) of **5m**



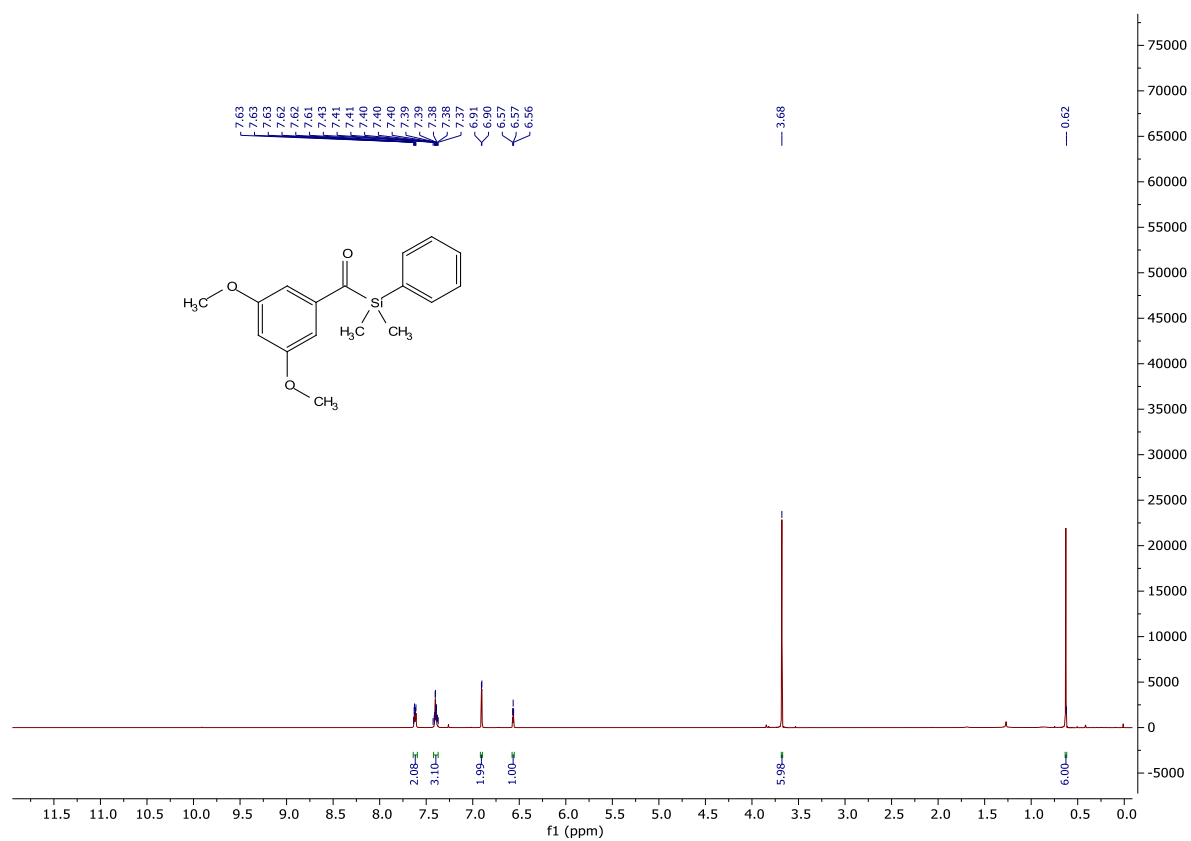
^1H NMR (500 MHz, CDCl_3) of **5n**



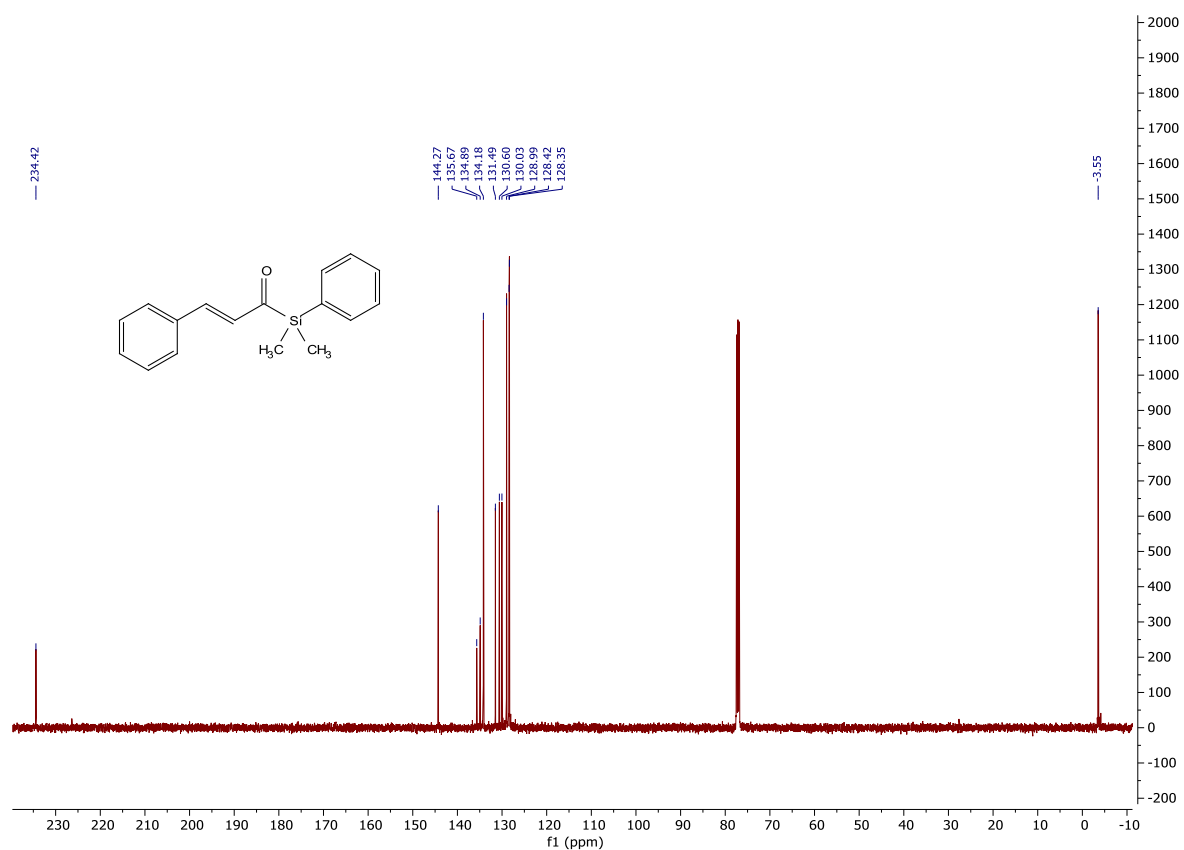
^{13}C NMR (126 MHz, CDCl_3) of **5n**



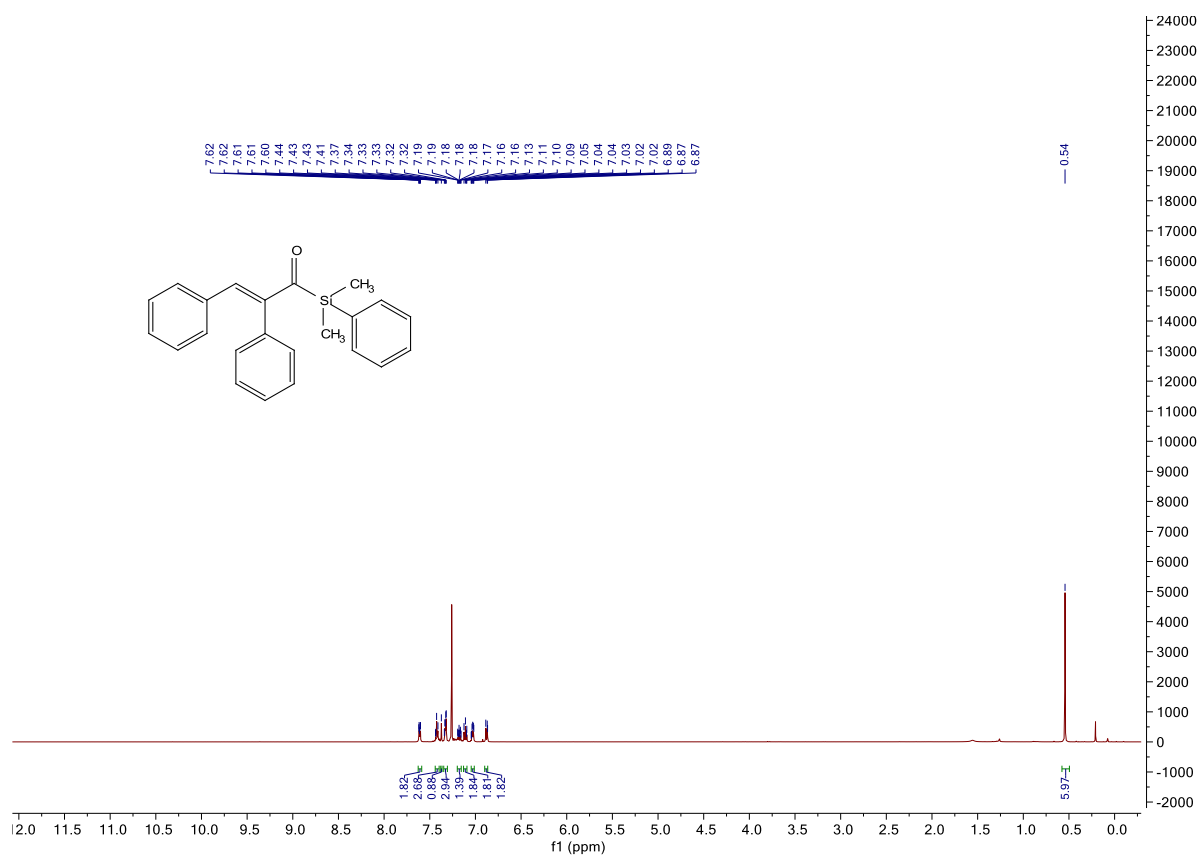
^1H NMR (500 MHz, CDCl_3) of **5n**



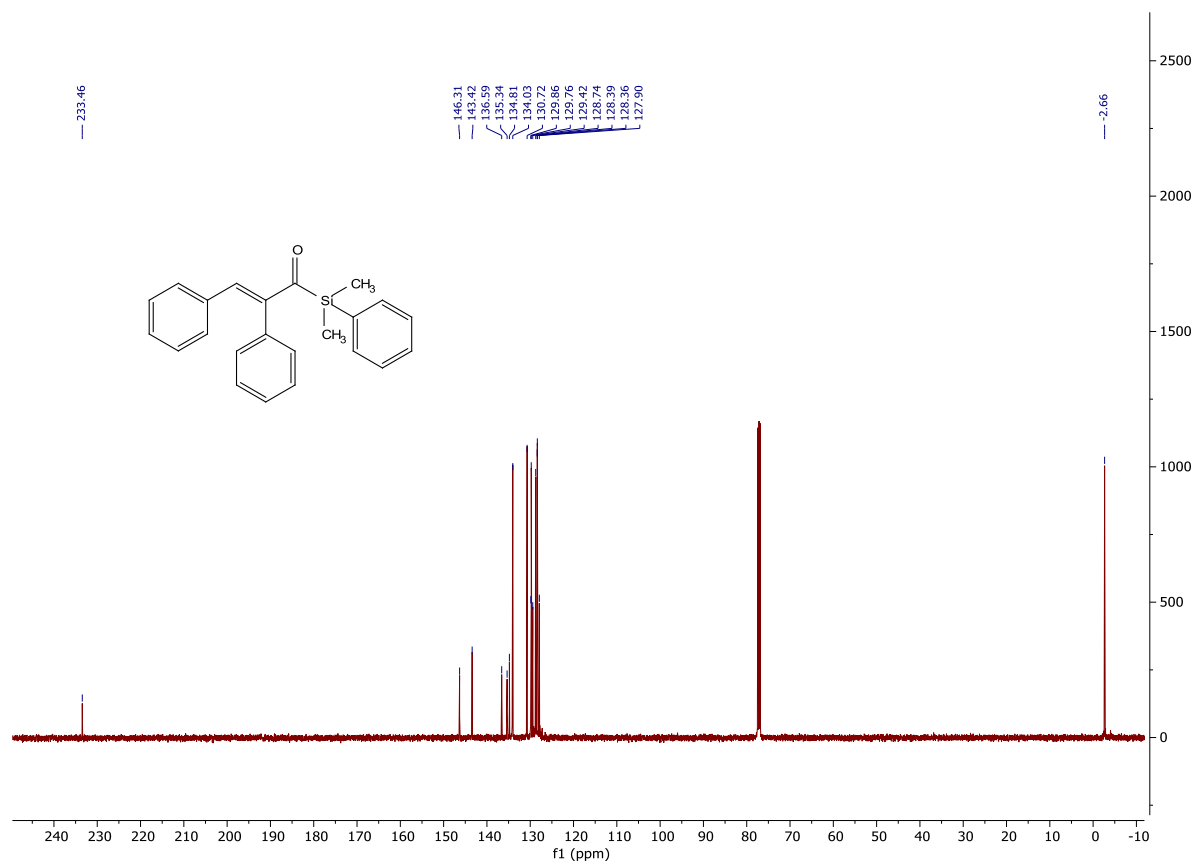
^{13}C NMR (126 MHz, CDCl_3) of **5o**



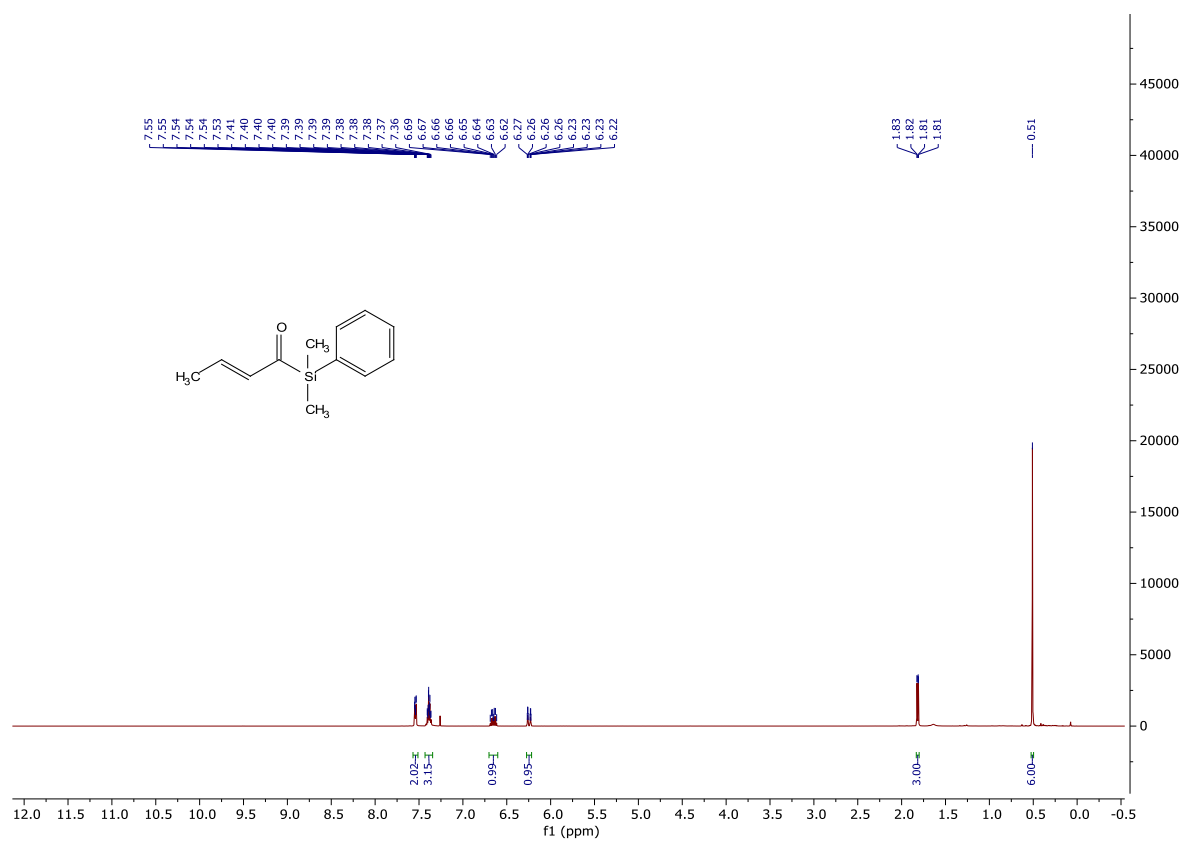
^1H NMR (500 MHz, CDCl_3) of **5p**



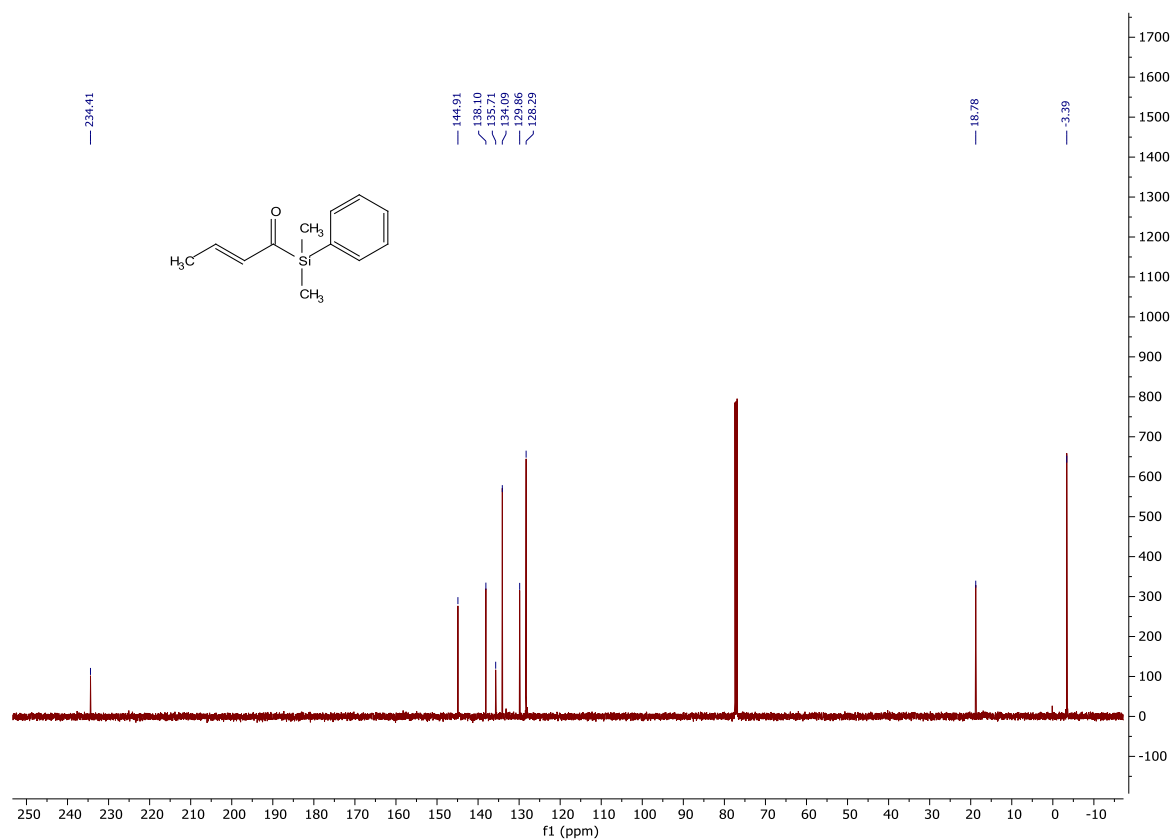
^{13}C NMR (126 MHz, CDCl_3) of **5p**



^1H NMR (500 MHz, CDCl_3) of **5q**



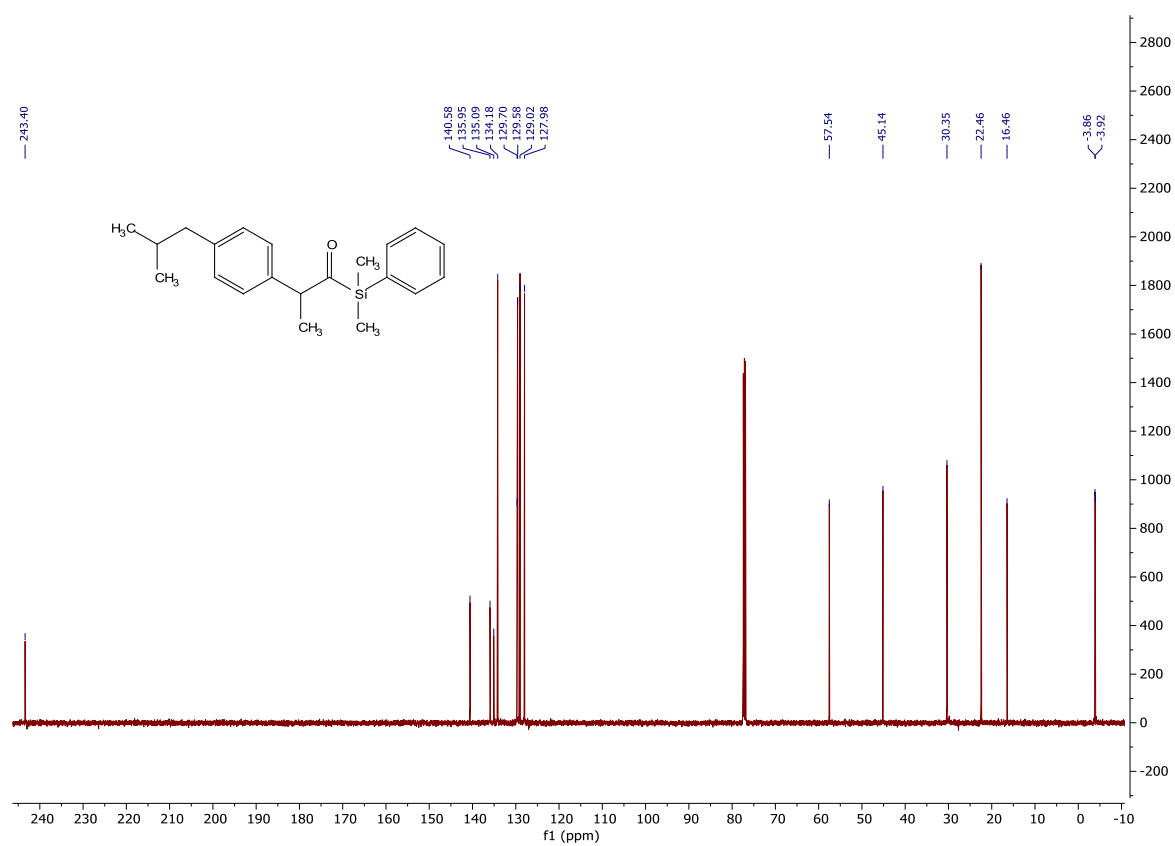
^{13}C NMR (126 MHz, CDCl_3) of **5q**



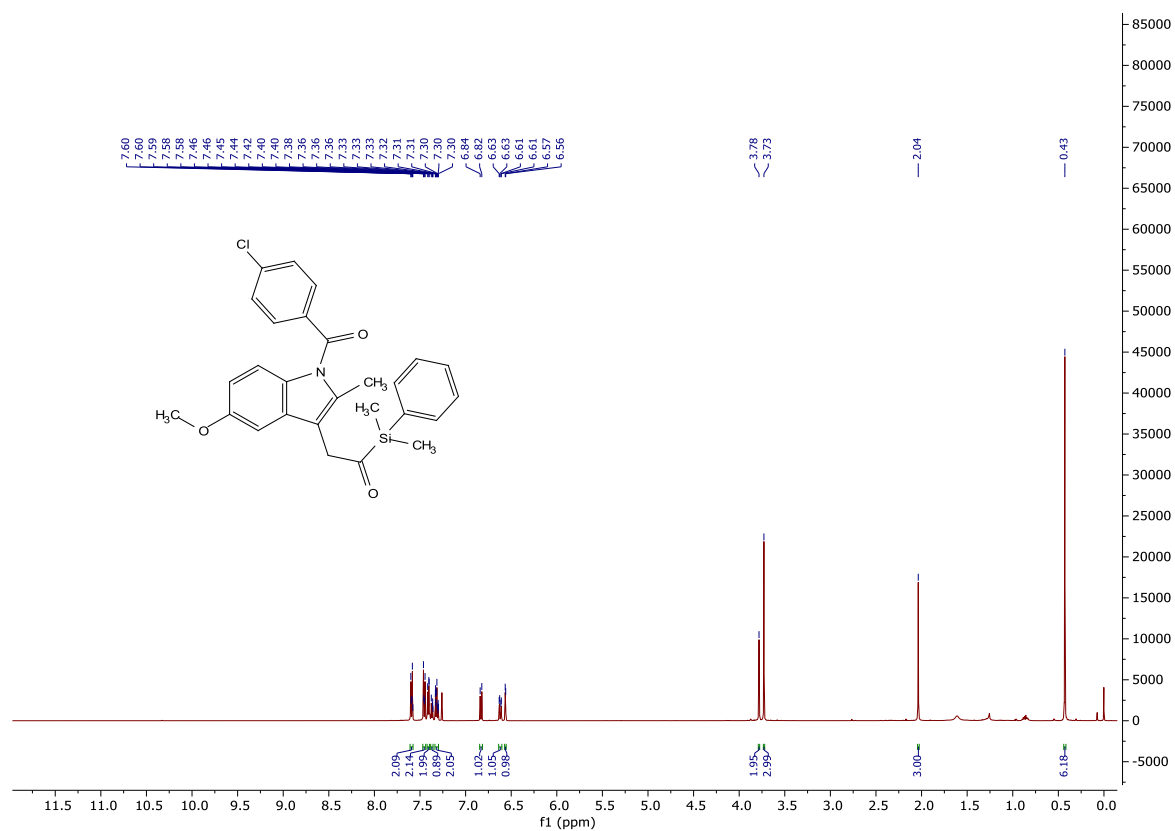
^1H NMR (500 MHz, CDCl_3) of **5r**



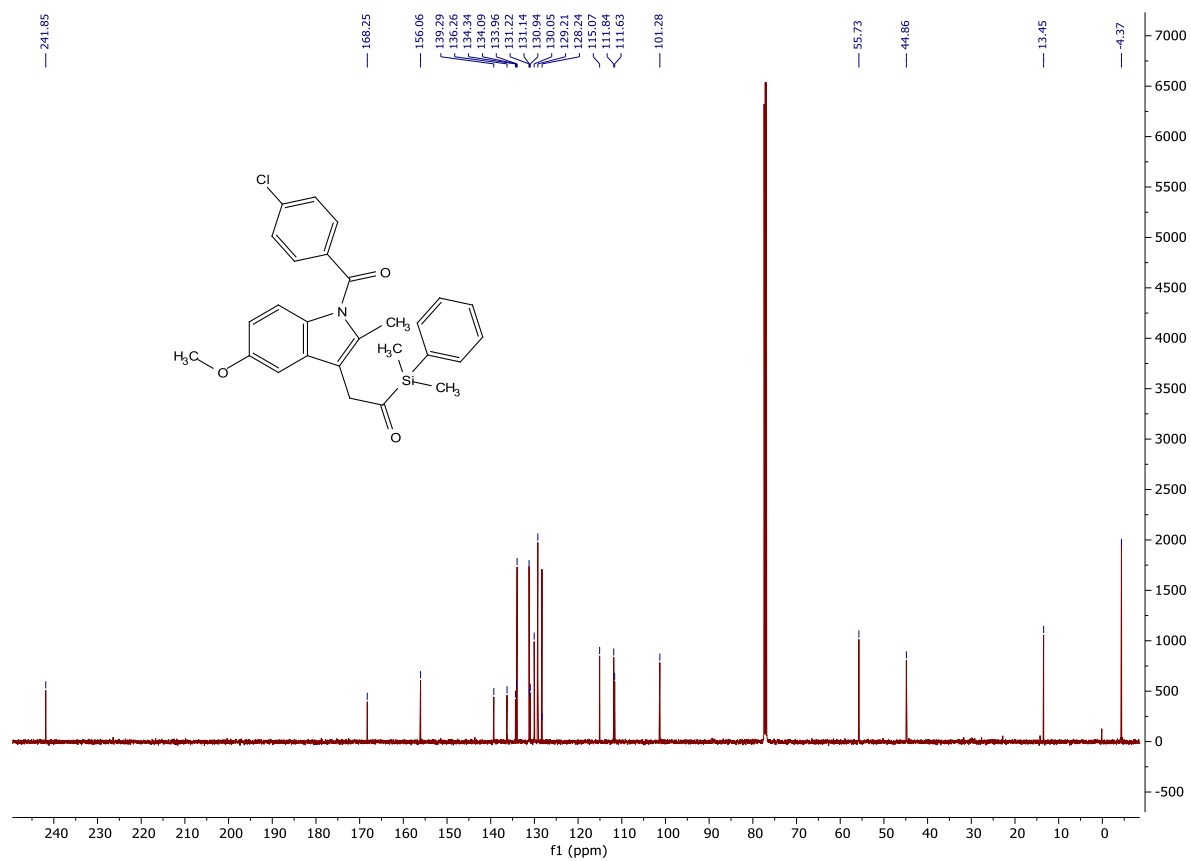
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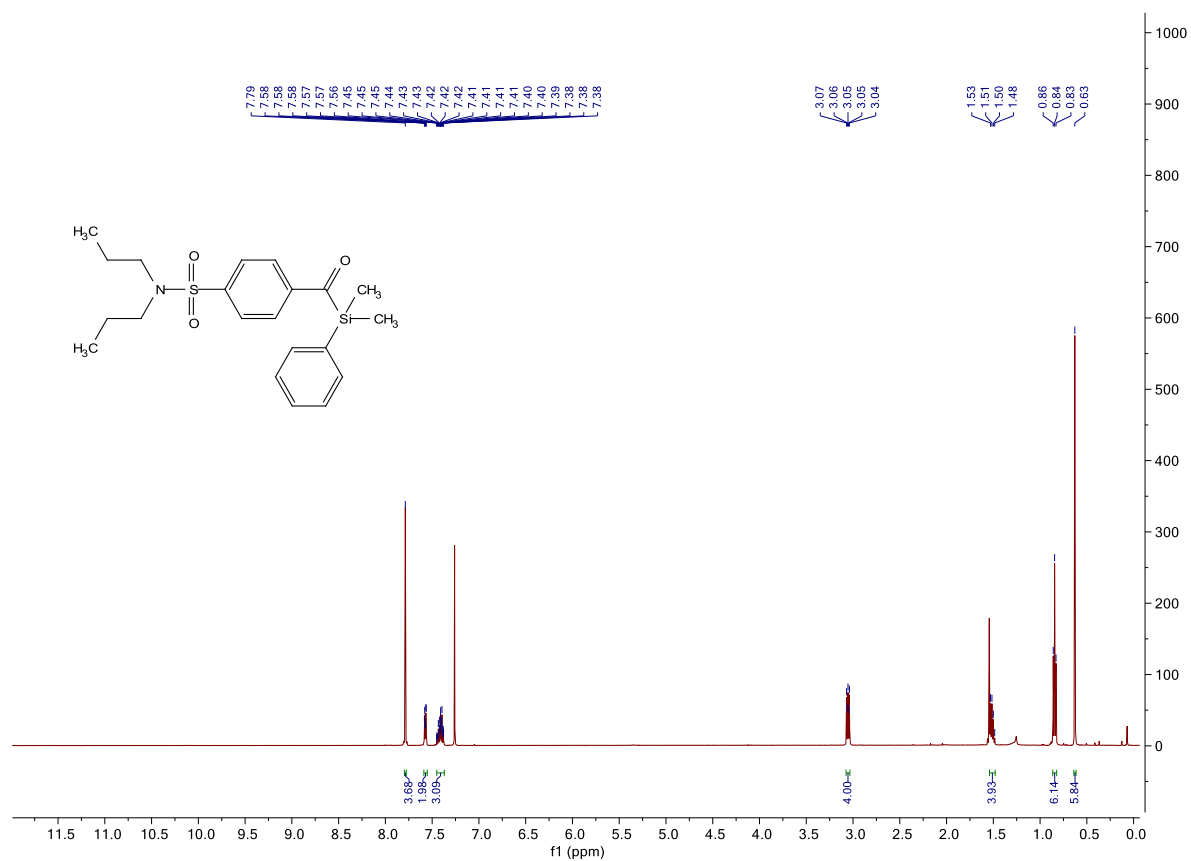
^1H NMR (500 MHz, CDCl_3) of **5s**



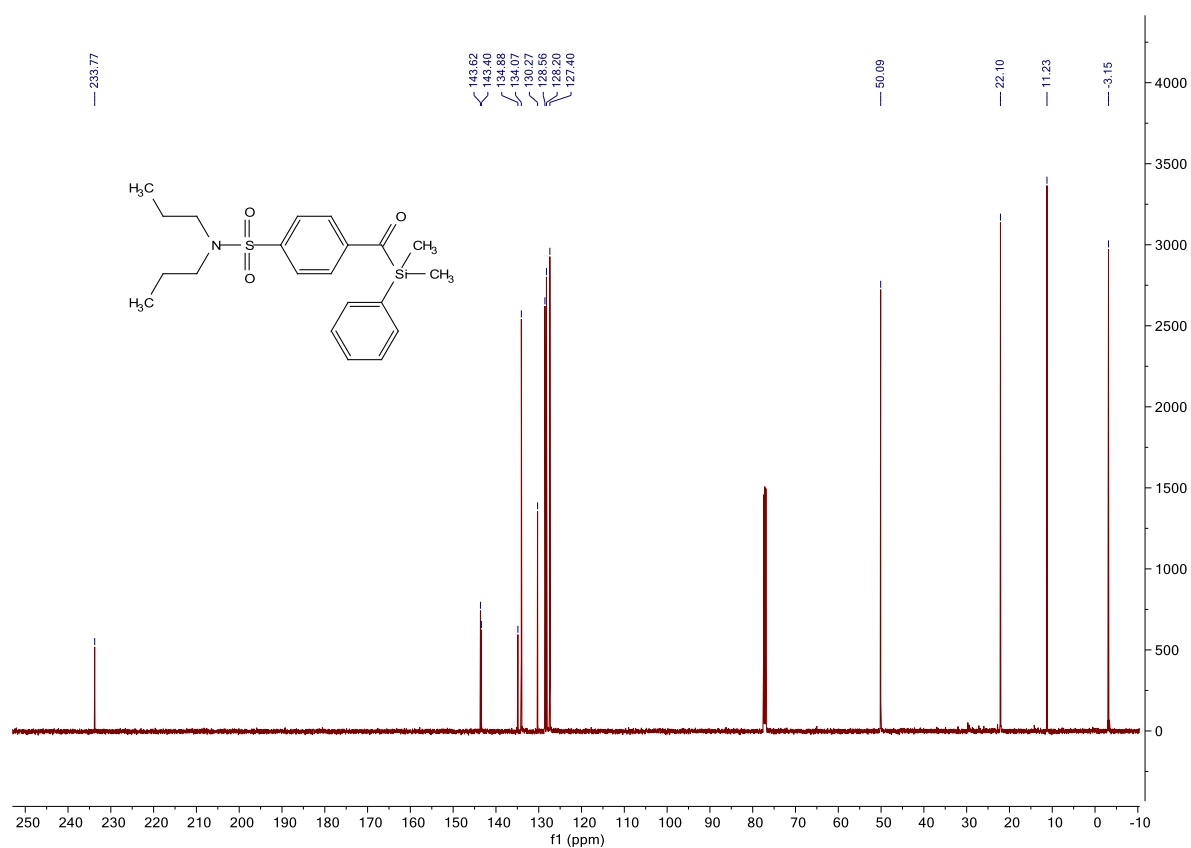
^{13}C NMR (126 MHz, CDCl_3) of **5s**



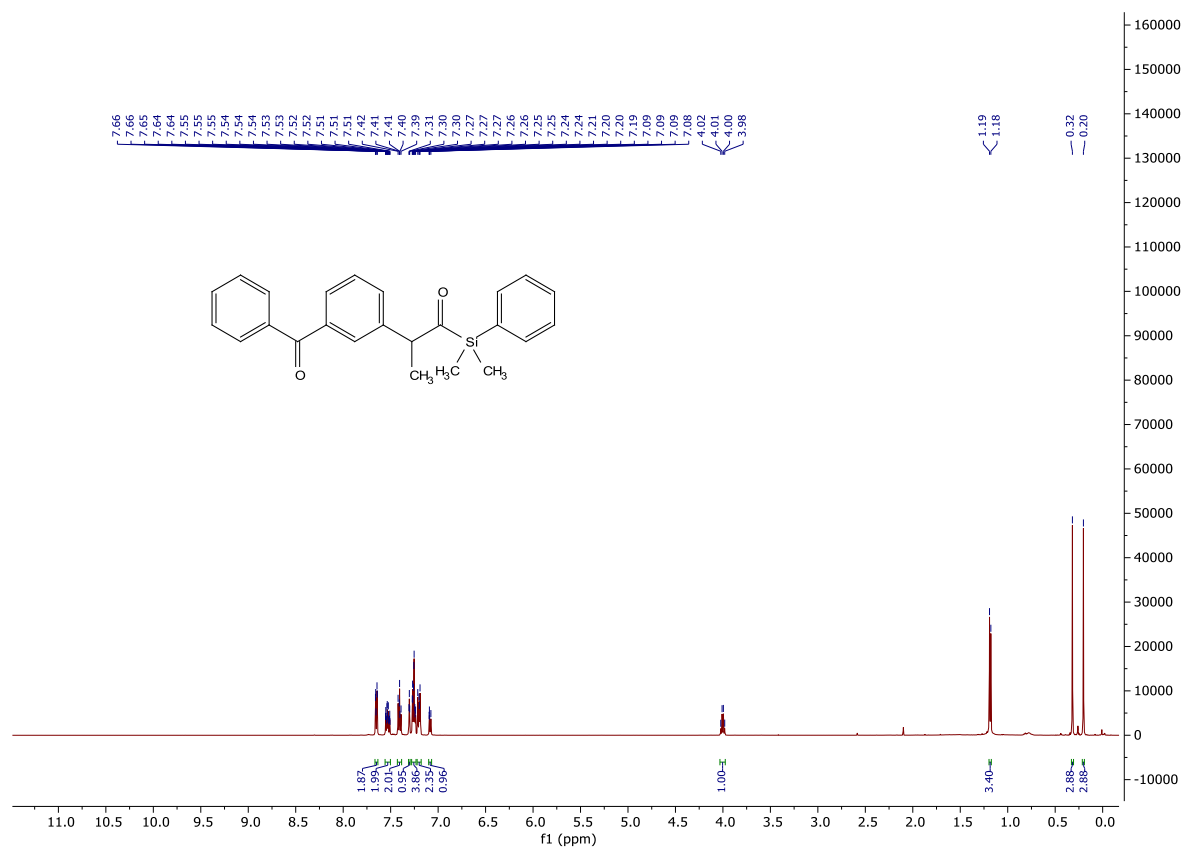
^1H NMR (500 MHz, CDCl_3) of **5t**



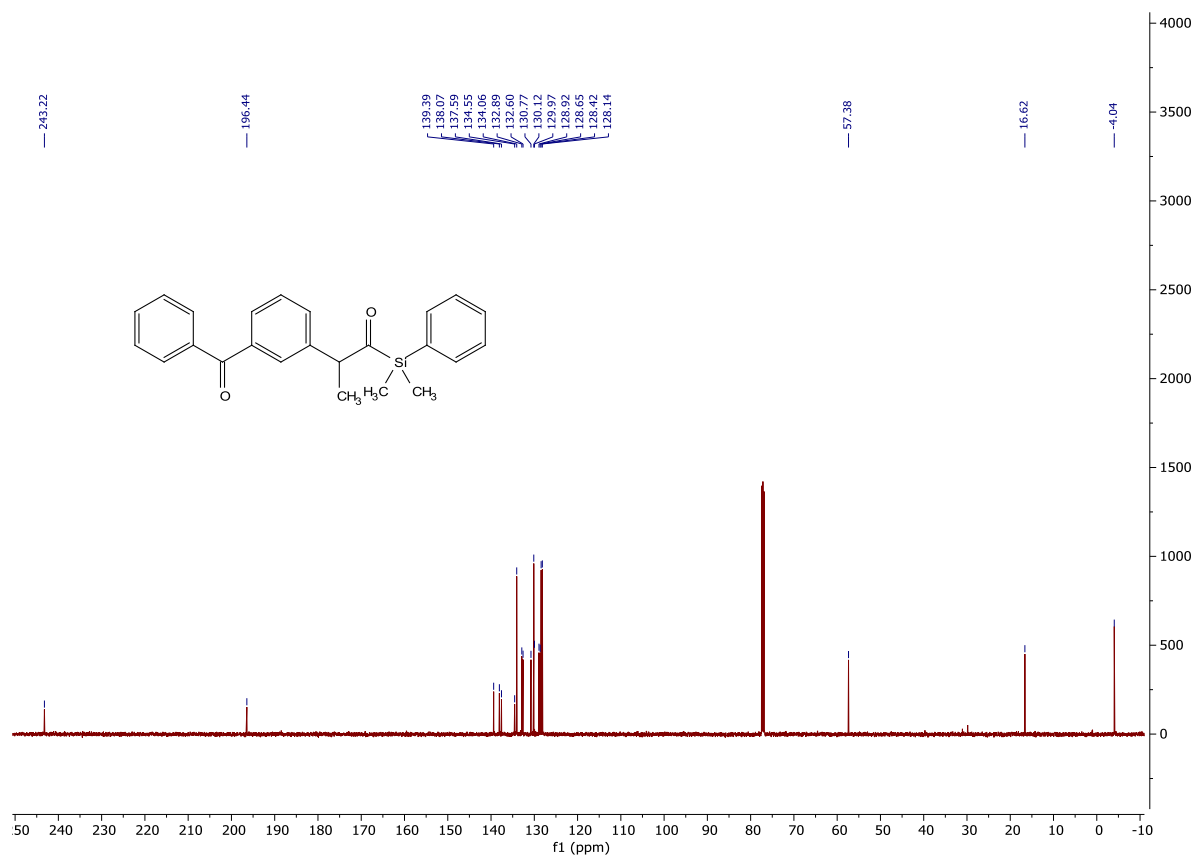
^{13}C NMR (126 MHz, CDCl_3) of **5t**



^1H NMR (500 MHz, CDCl_3) of **5u**



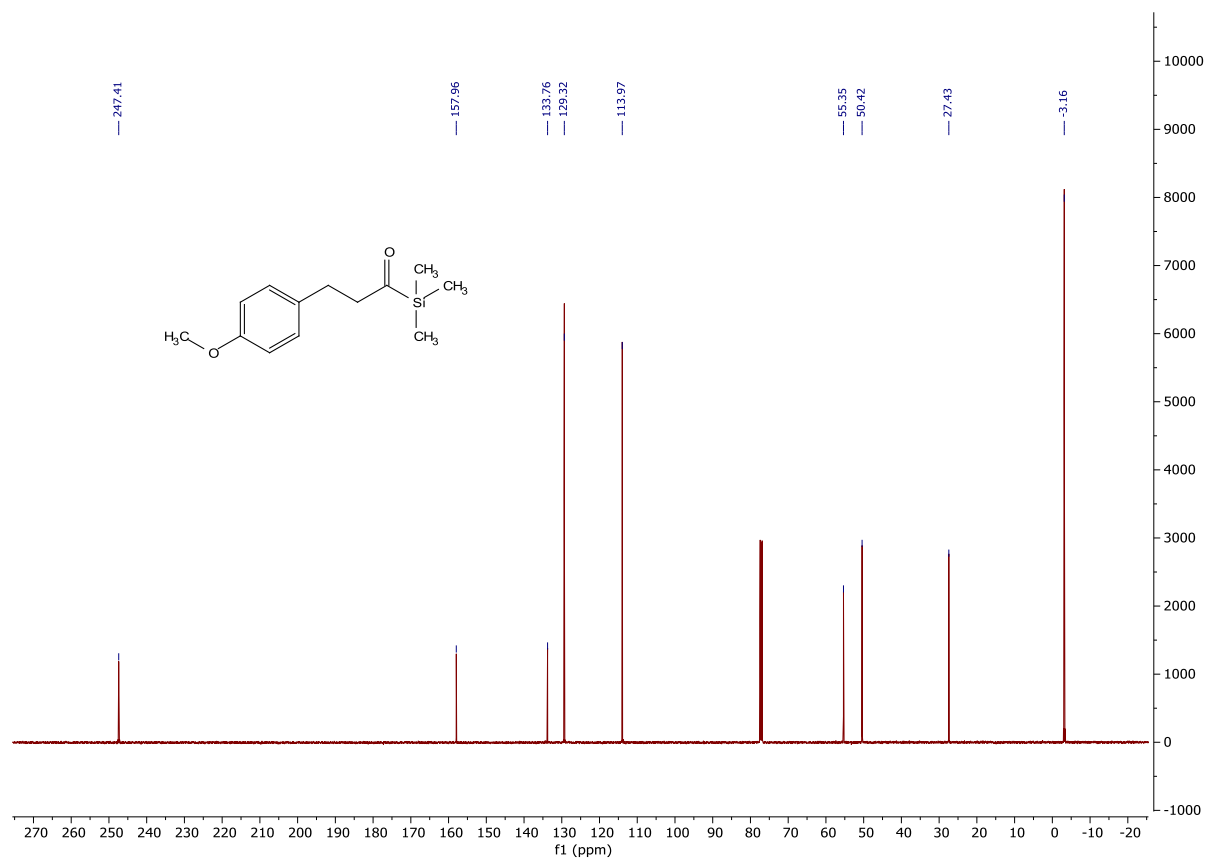
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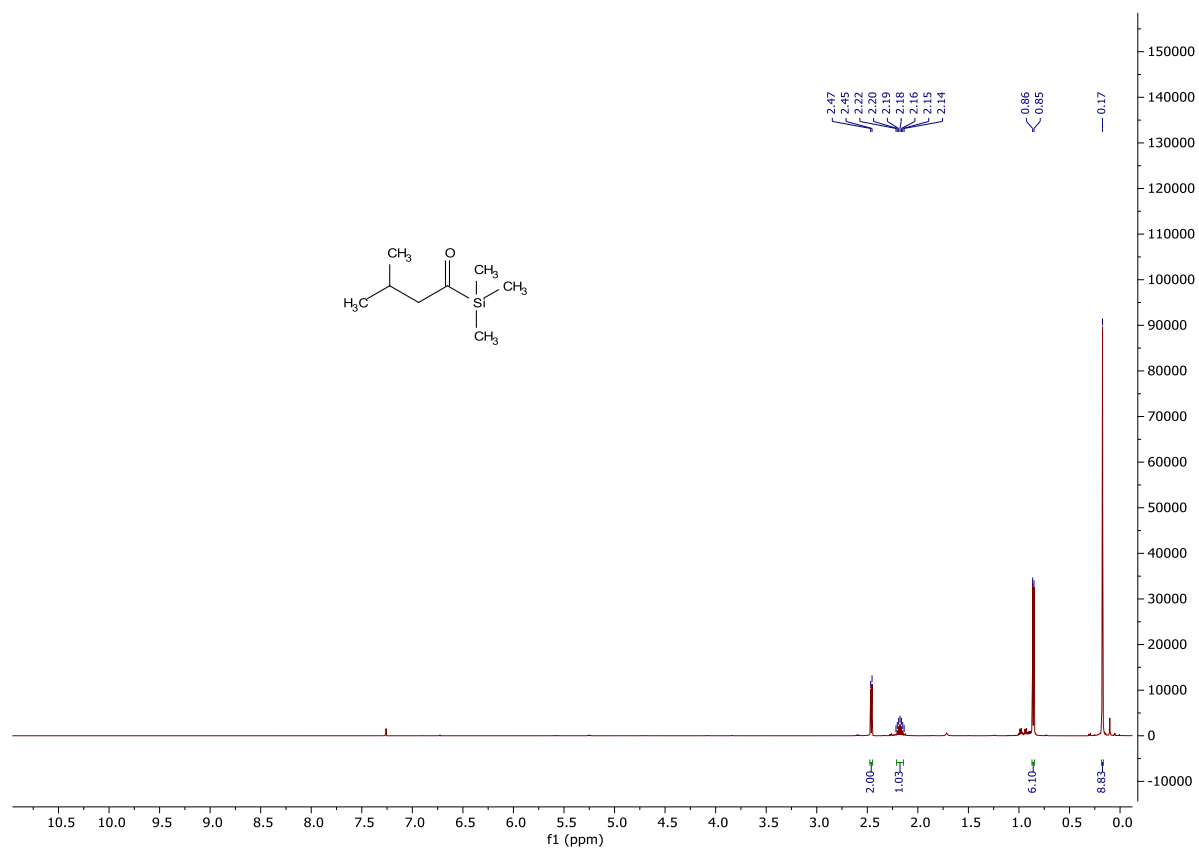
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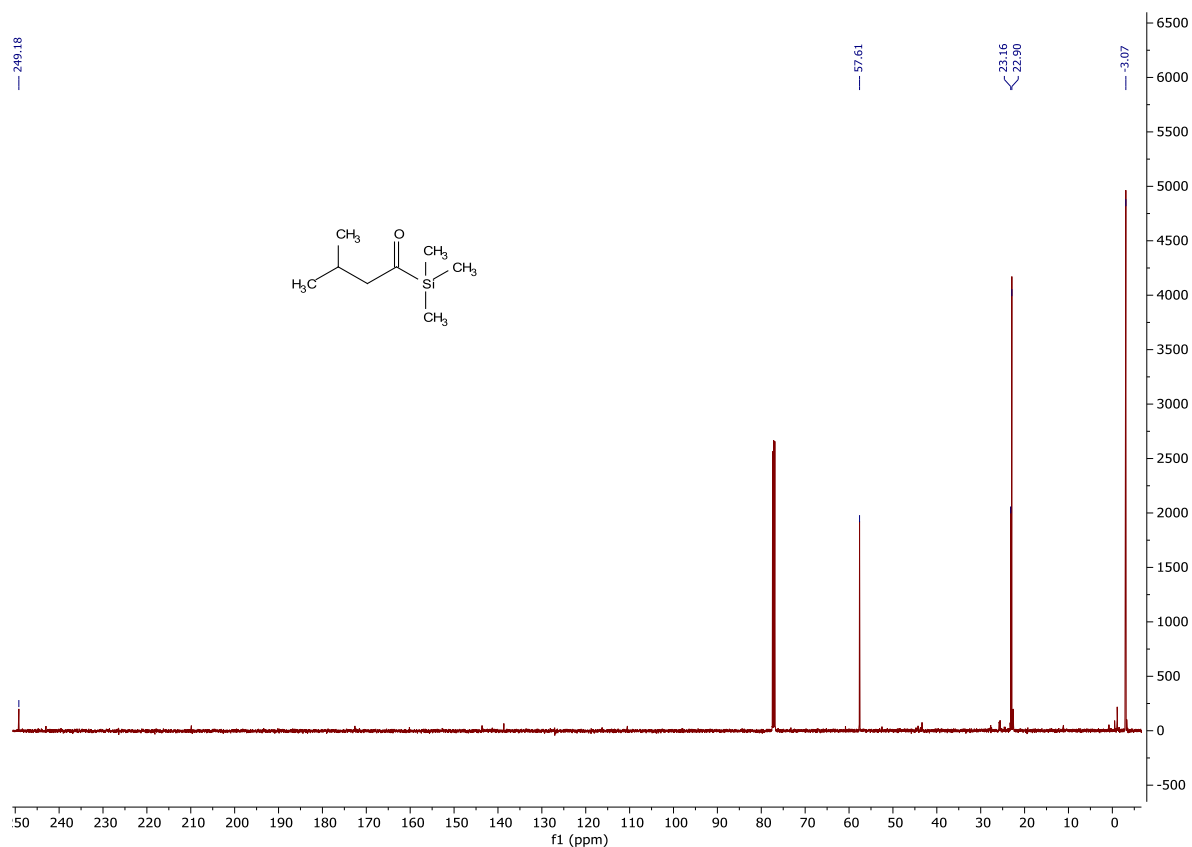
^{13}C NMR (126 MHz, CDCl_3) of 7a



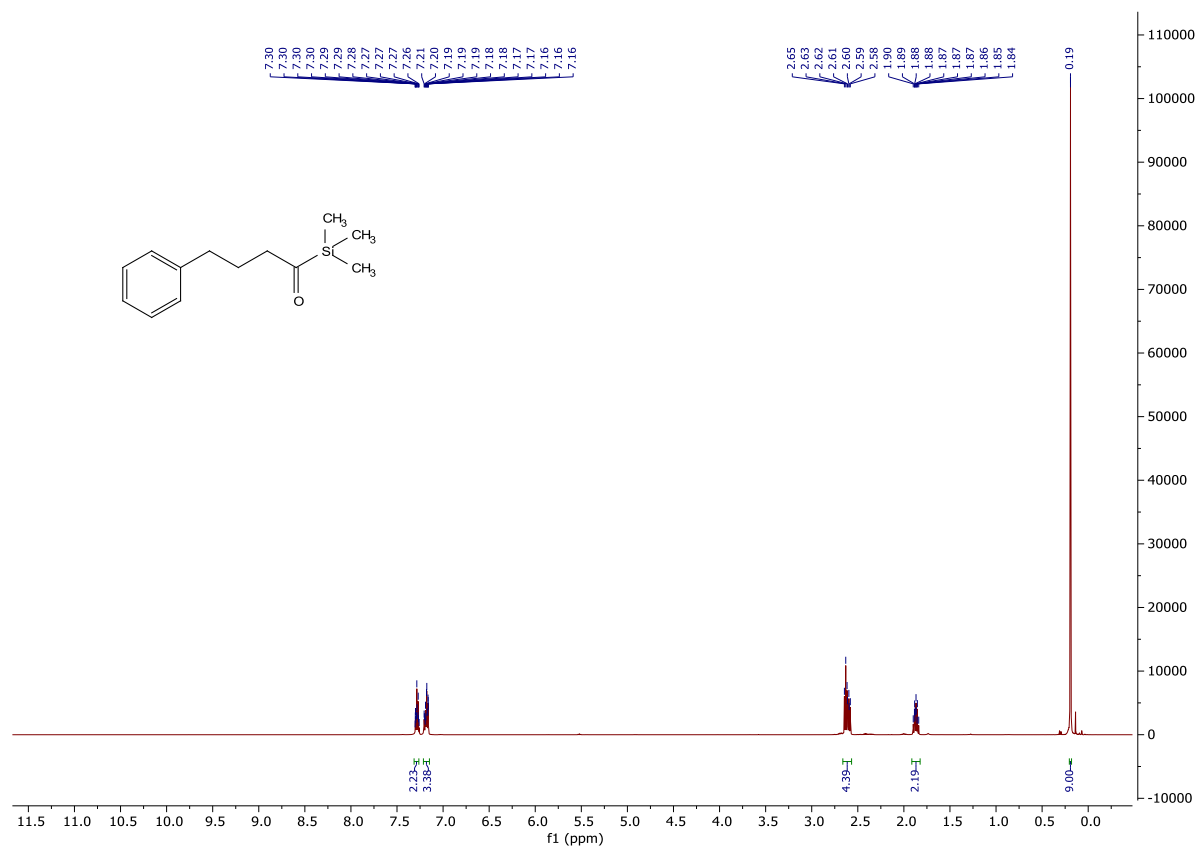
^1H NMR (500 MHz, CDCl_3) of 7b



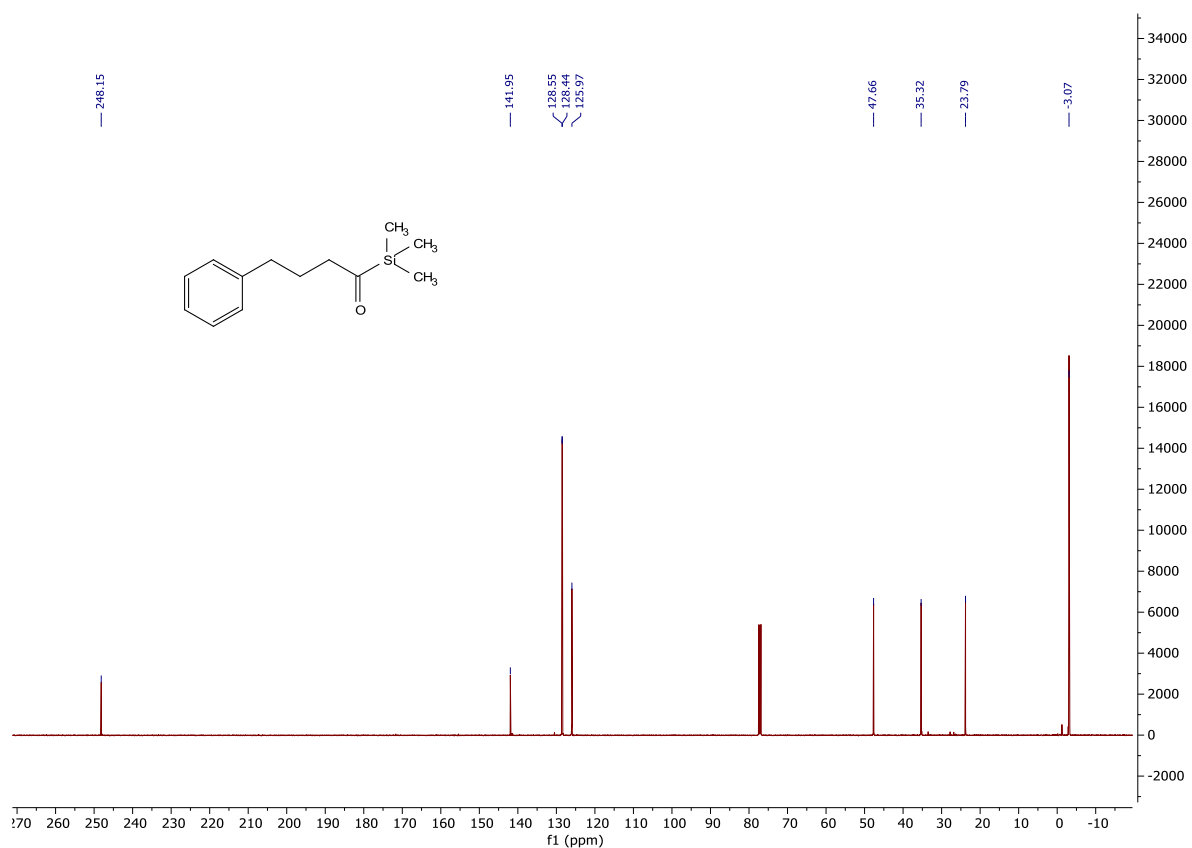
^{13}C NMR (126 MHz, CDCl_3) of **7b**



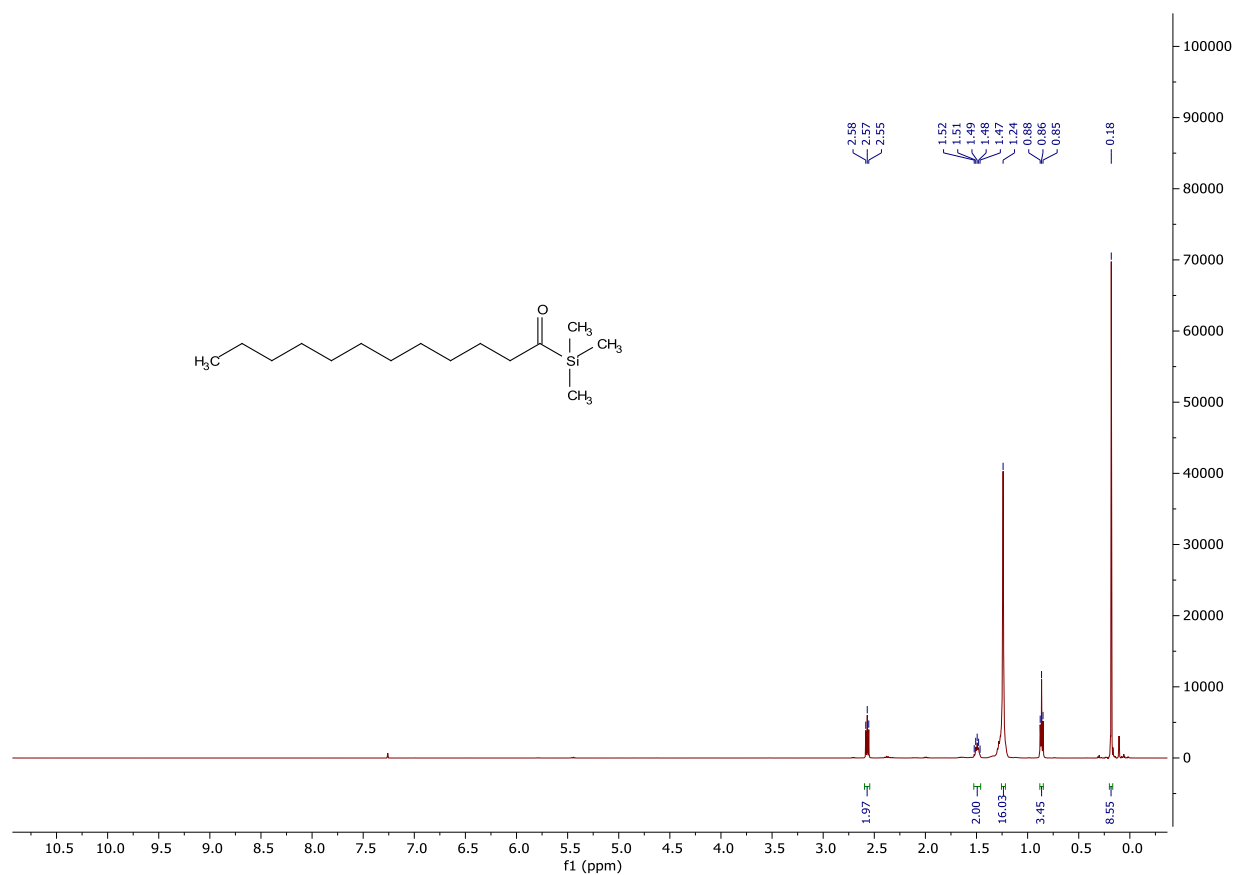
^1H NMR (500 MHz, CDCl_3) of **7c**



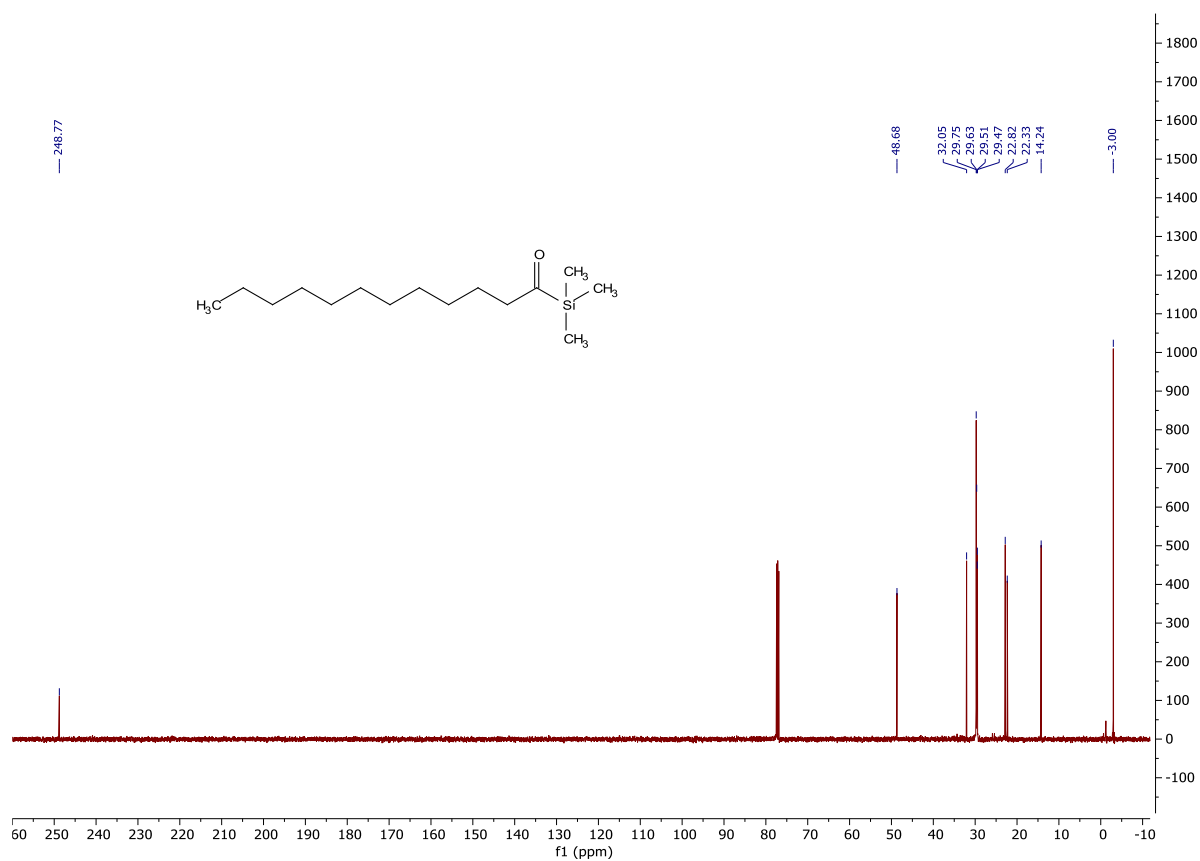
^{13}C NMR (126 MHz, CDCl_3) of 7c



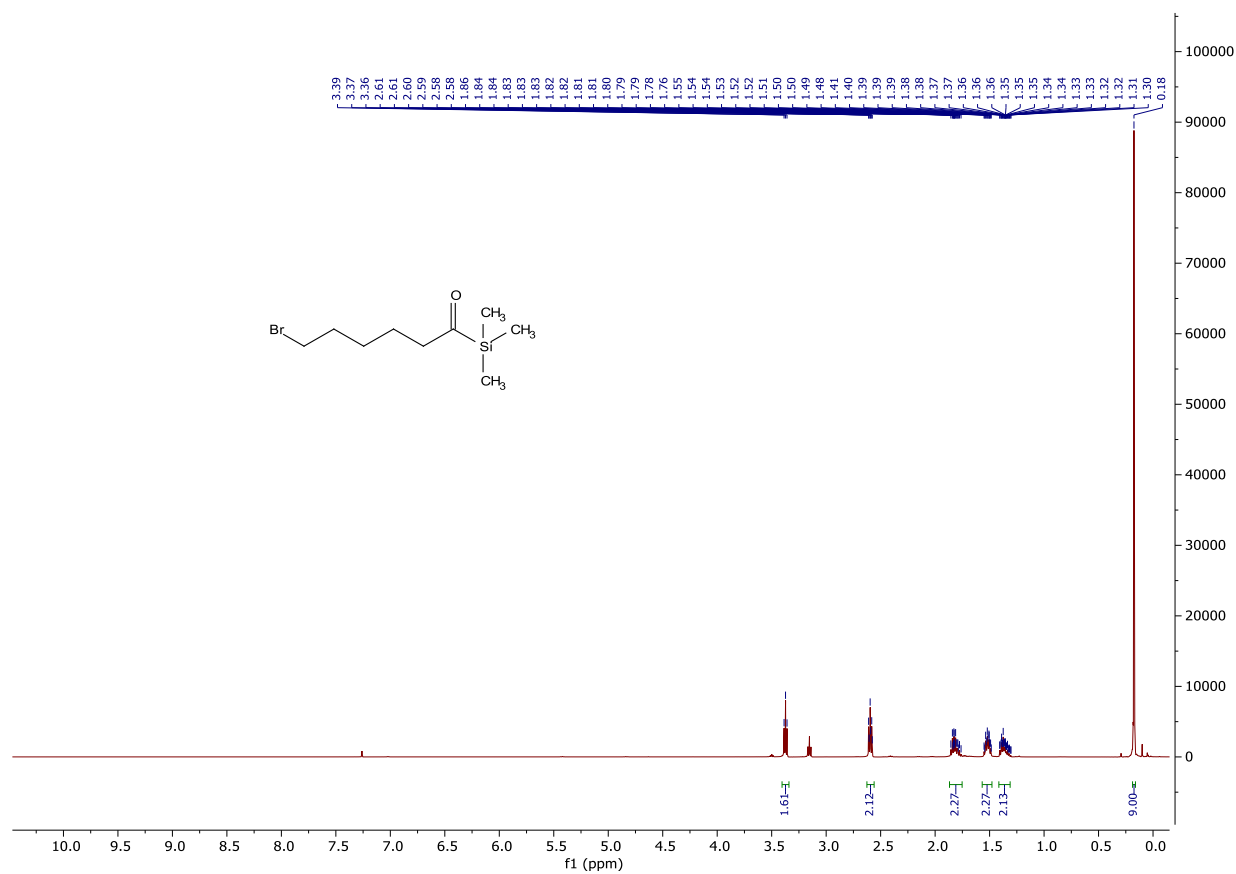
^1H NMR (500 MHz, CDCl_3) of 7d



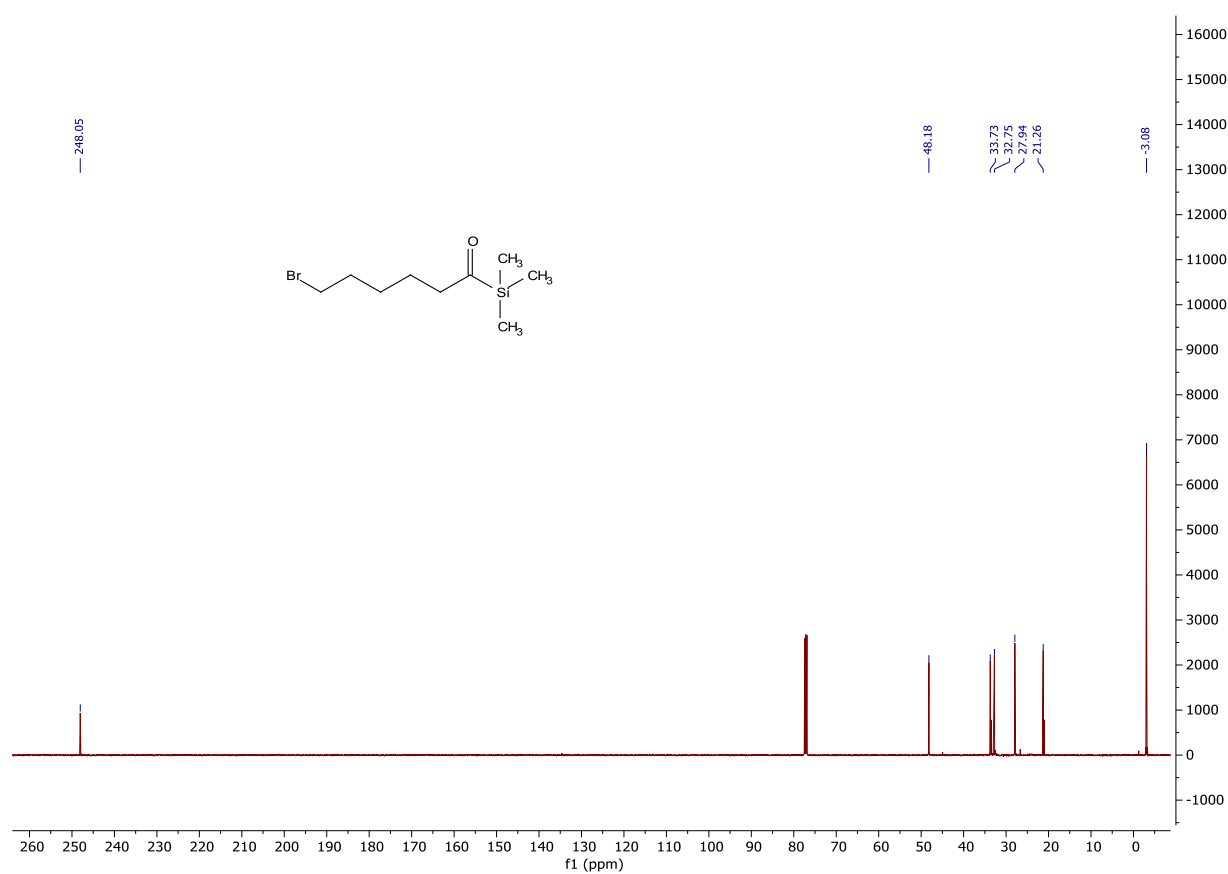
¹³C NMR (126 MHz, CDCl₃) of 7d



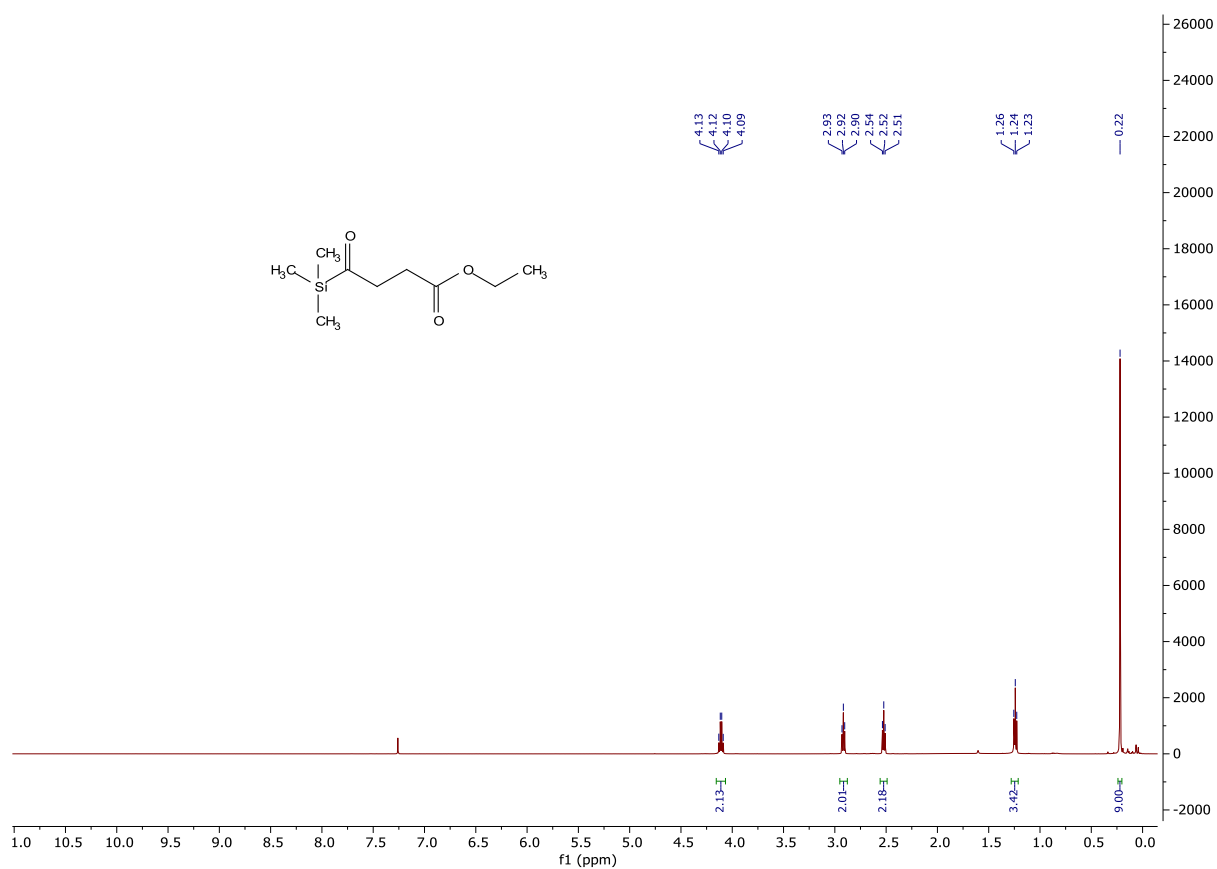
¹H NMR (500 MHz, CDCl₃) of 7e



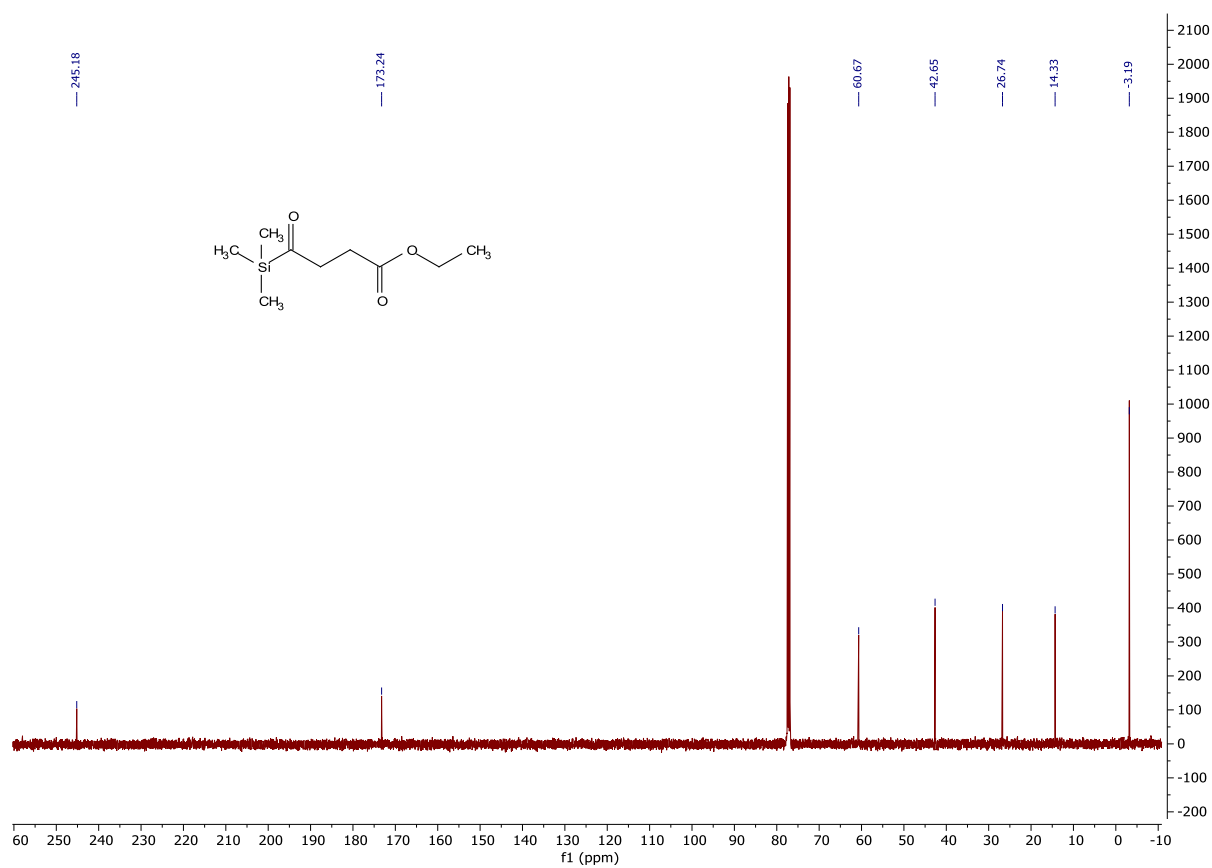
¹³C NMR (126 MHz, CDCl₃) of 7e



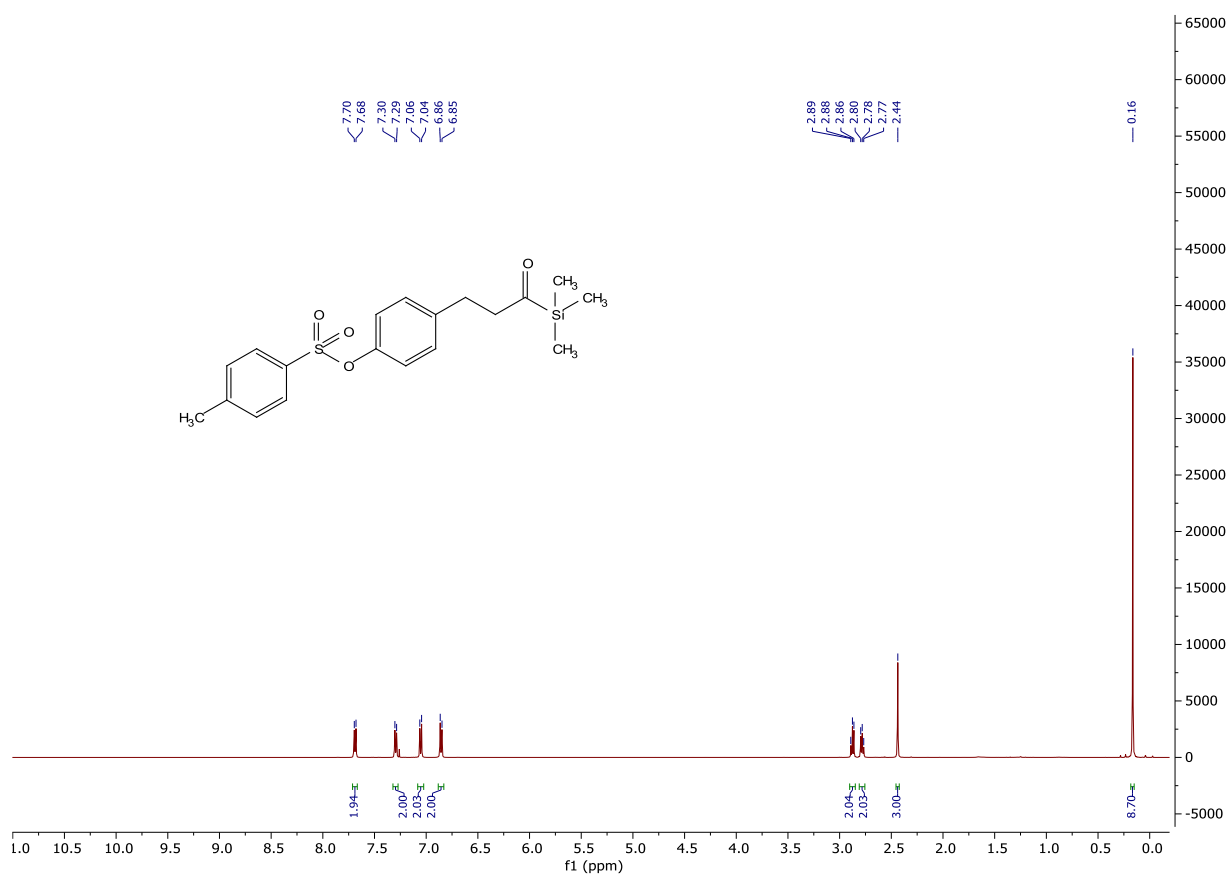
¹H NMR (500 MHz, CDCl₃) of 7f



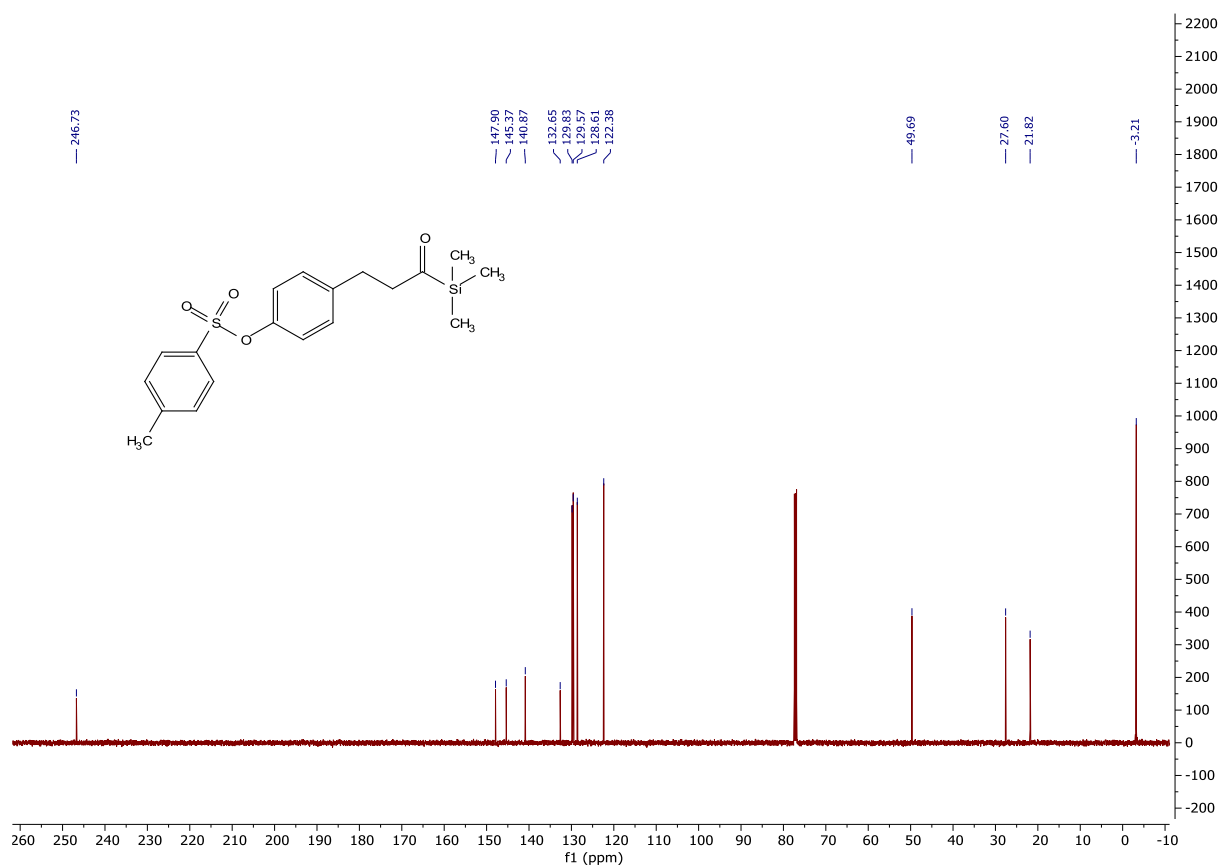
^{13}C NMR (126 MHz, CDCl_3) of **7f**



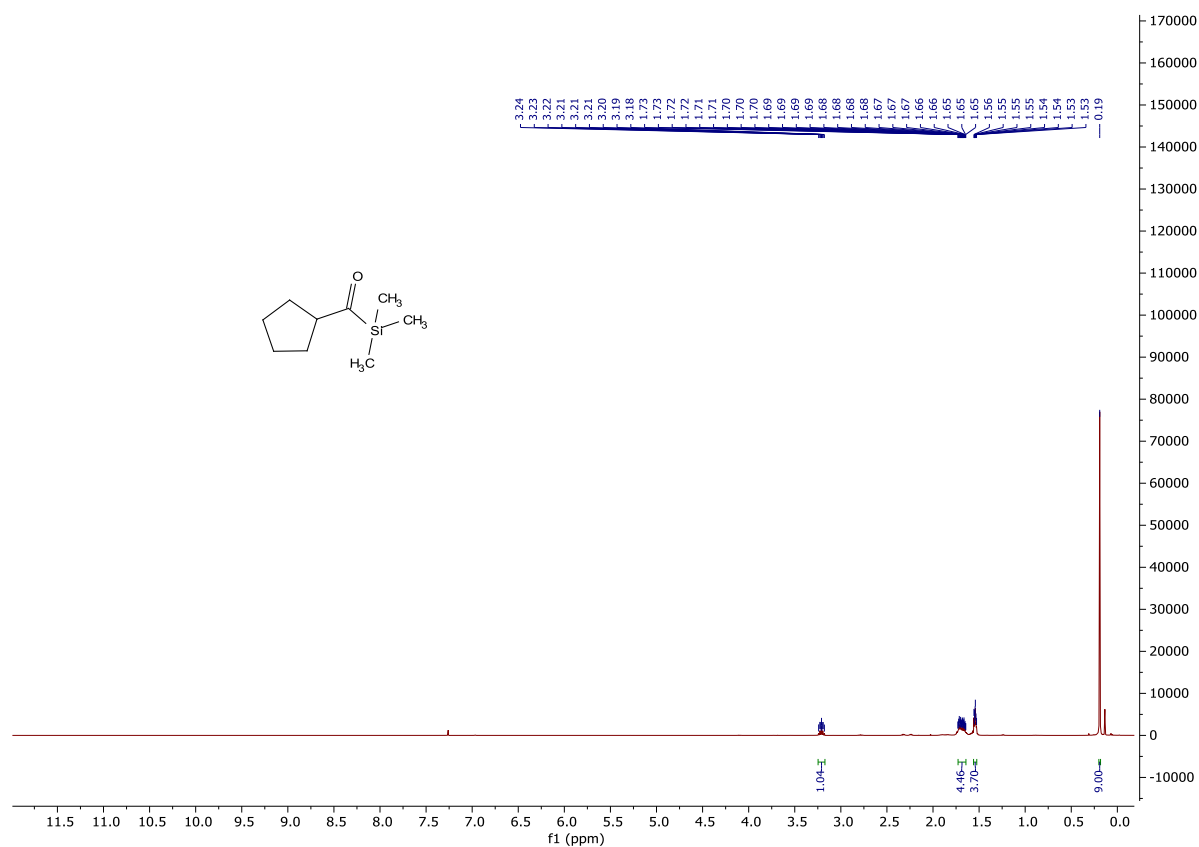
^1H NMR (500 MHz, CDCl_3) **7g**



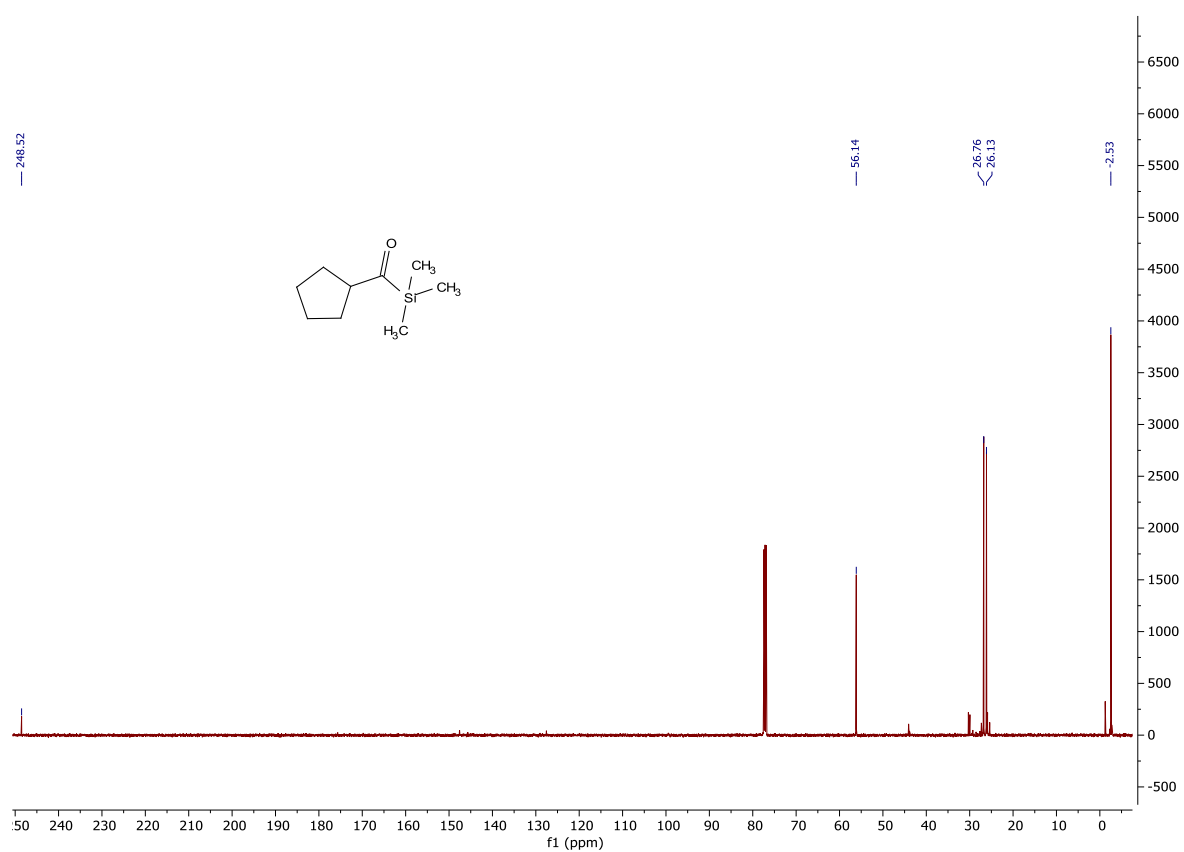
^{13}C NMR (126 MHz, CDCl_3) of **7g**



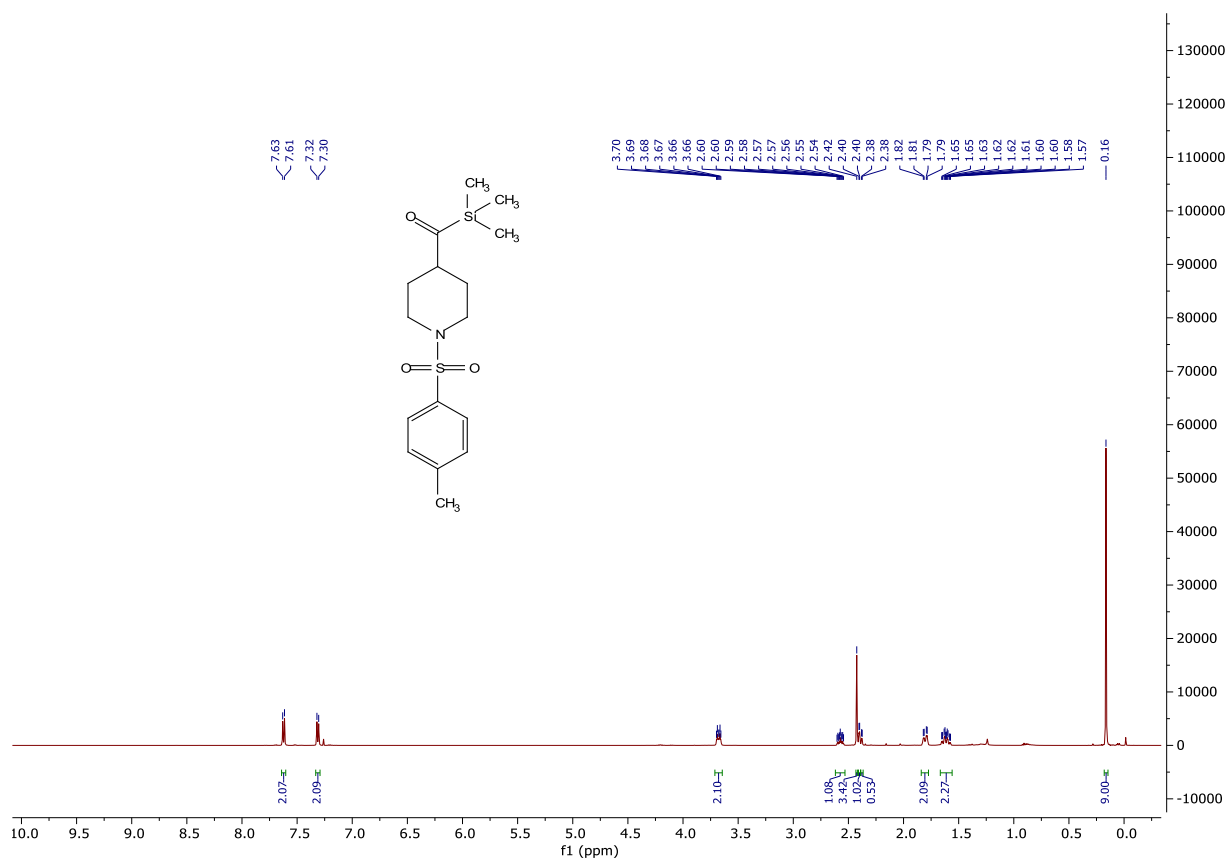
^1H NMR (500 MHz, CDCl_3) of **7h**



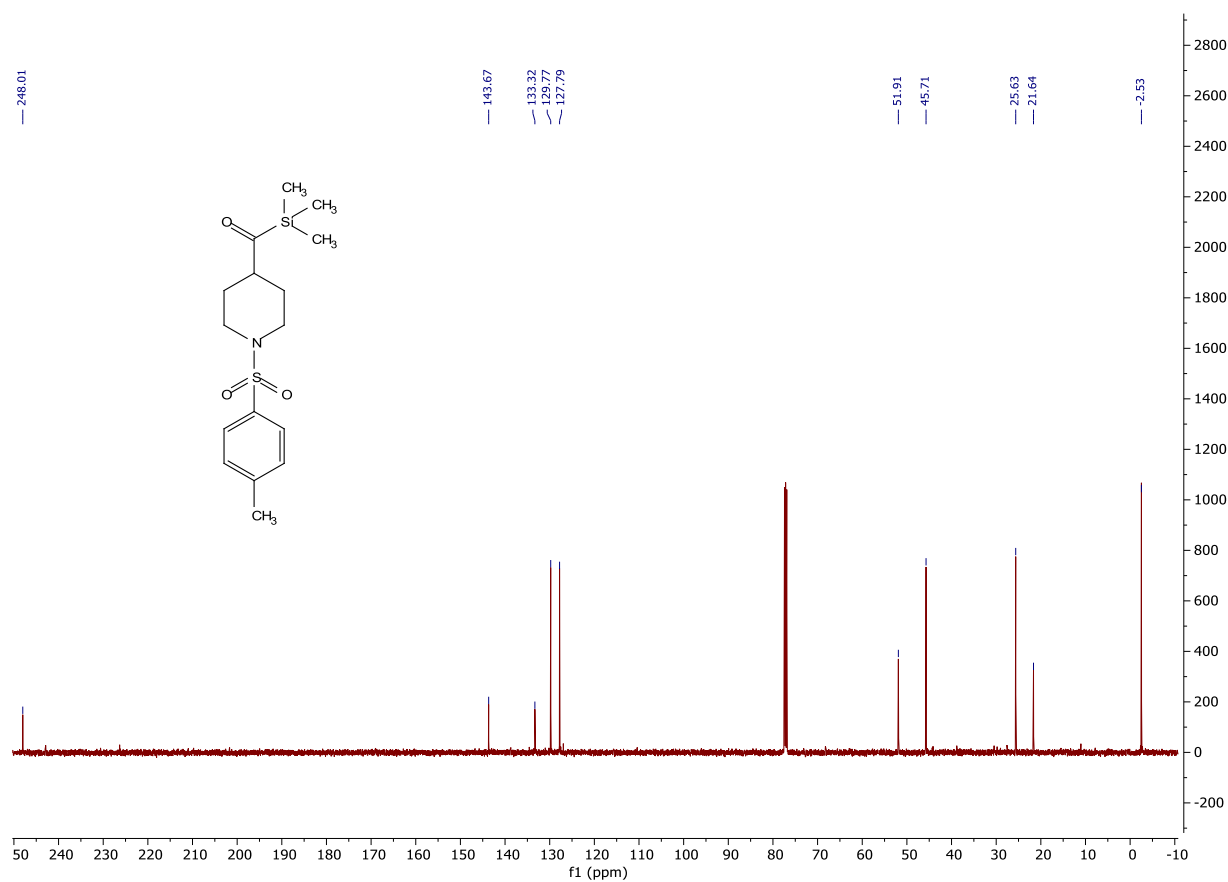
^{13}C NMR (126 MHz, CDCl_3) of **7h**



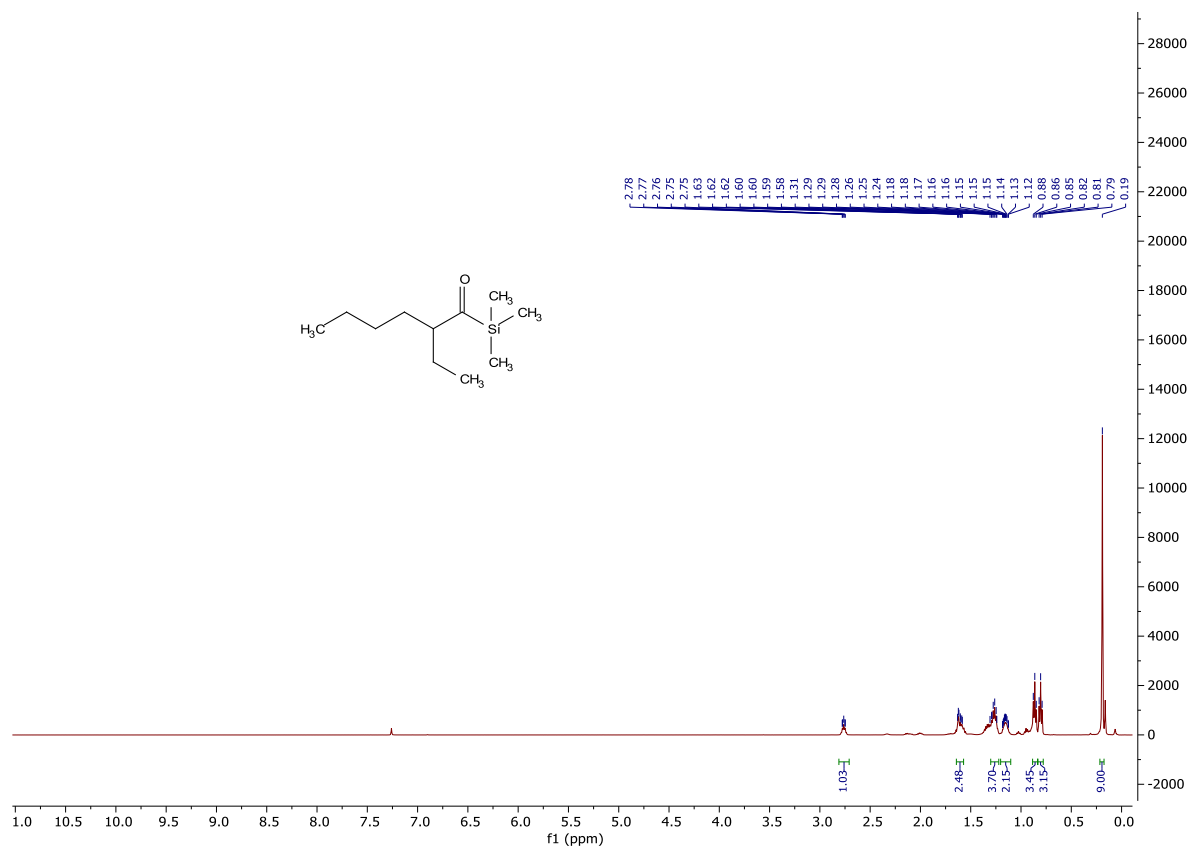
^1H NMR (500 MHz, CDCl_3) of **7hi**



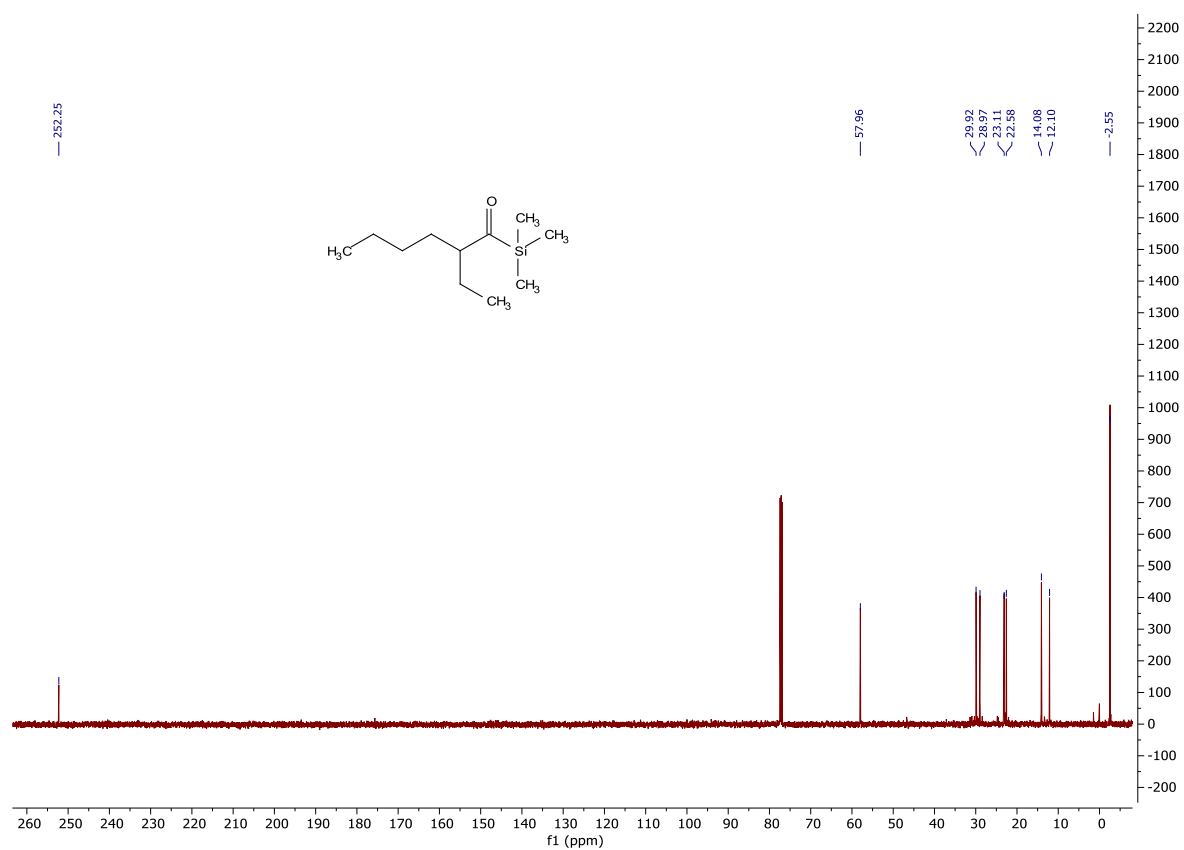
^{13}C NMR (126 MHz, CDCl_3) of **7hi**



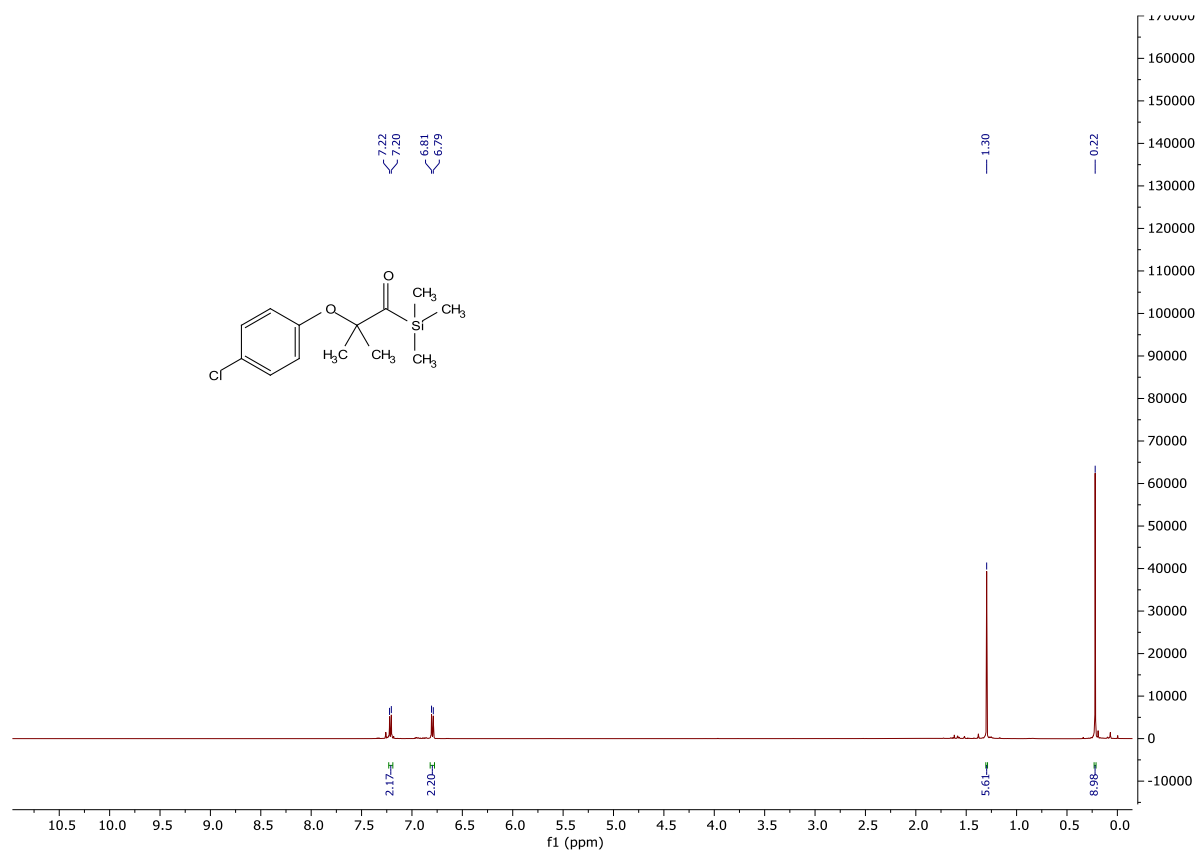
^1H NMR (500 MHz, CDCl_3) of **7i**



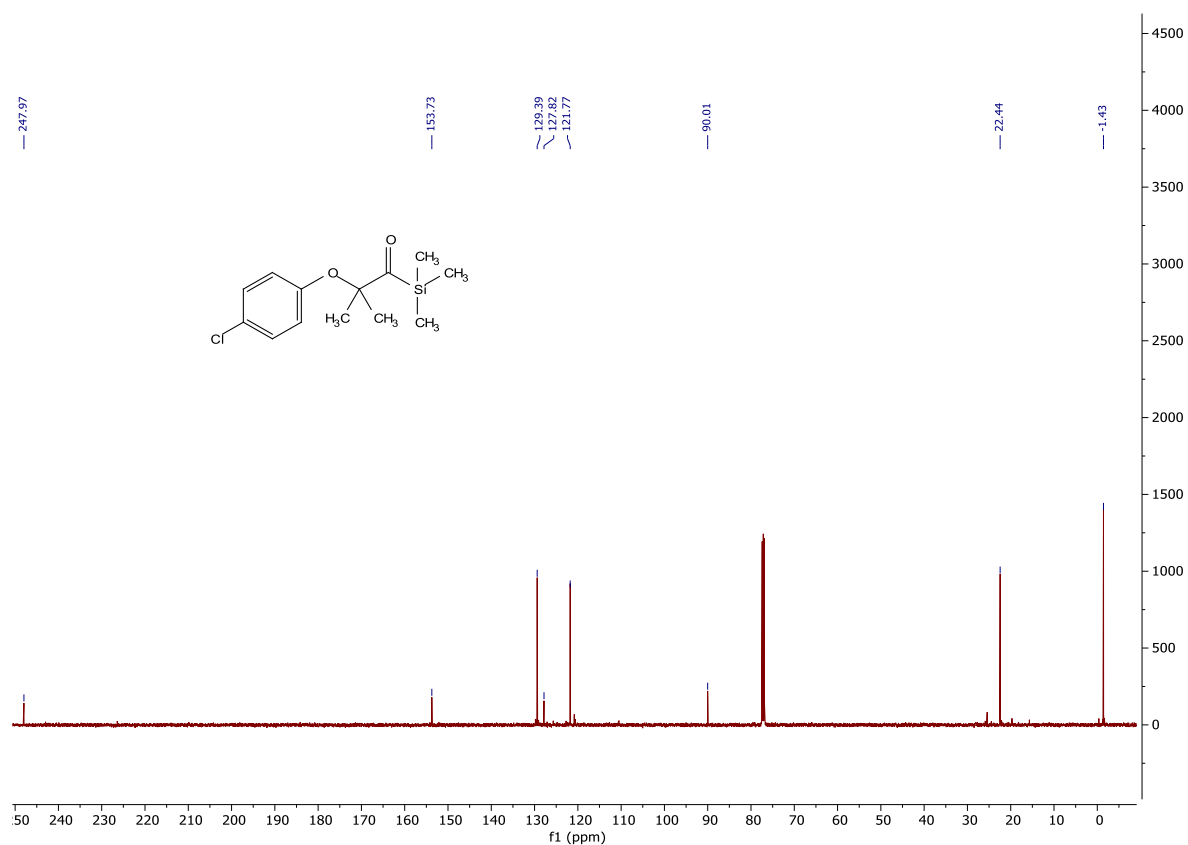
^{13}C NMR (126 MHz, CDCl_3) of **7i**



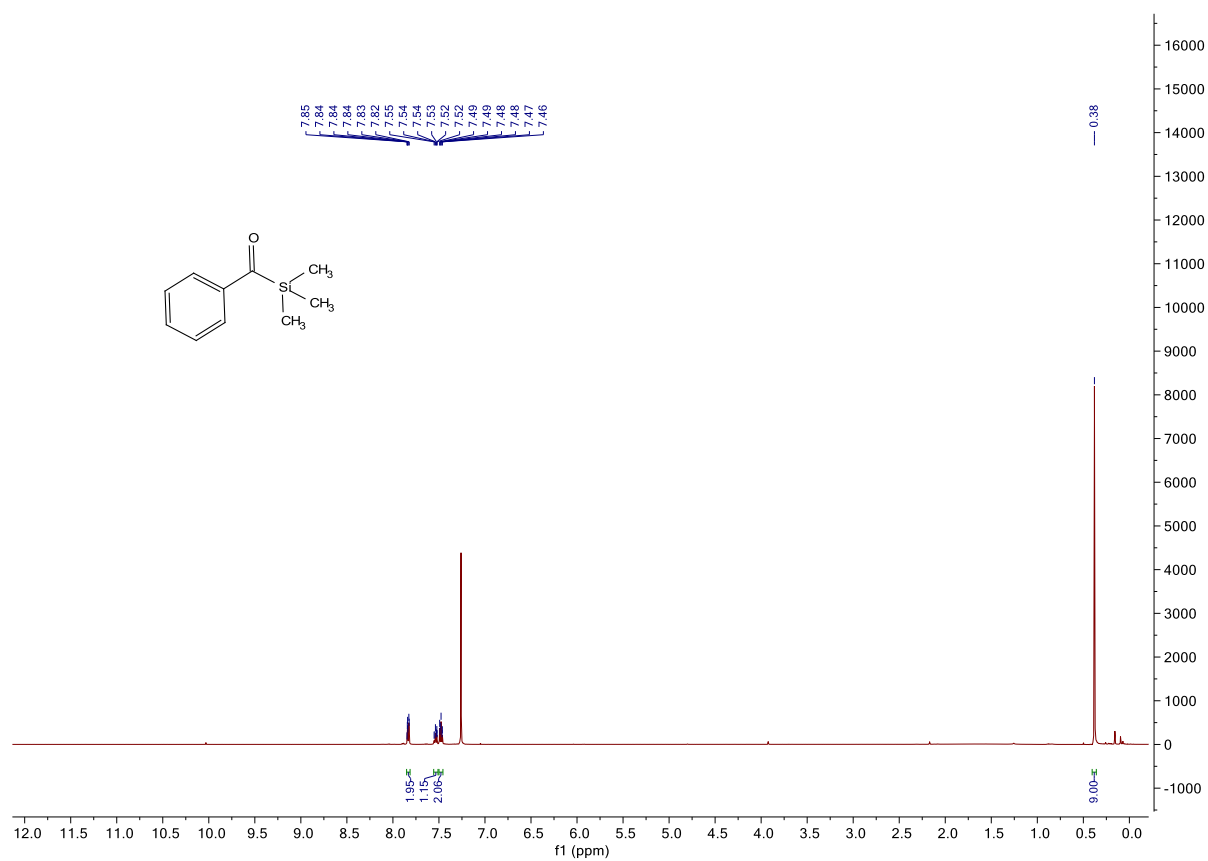
^1H NMR (500 MHz, CDCl_3) of **7ij**



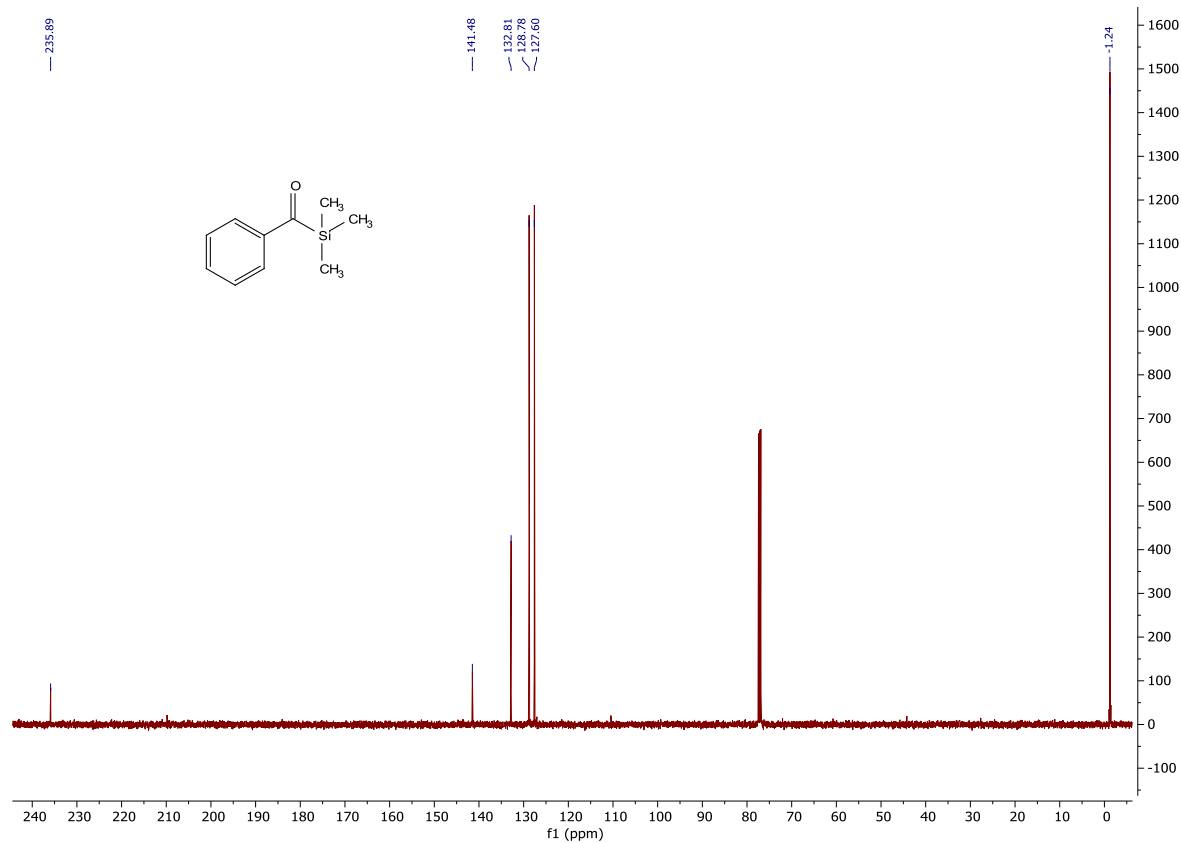
^{13}C NMR (126 MHz, CDCl_3) of **7ij**



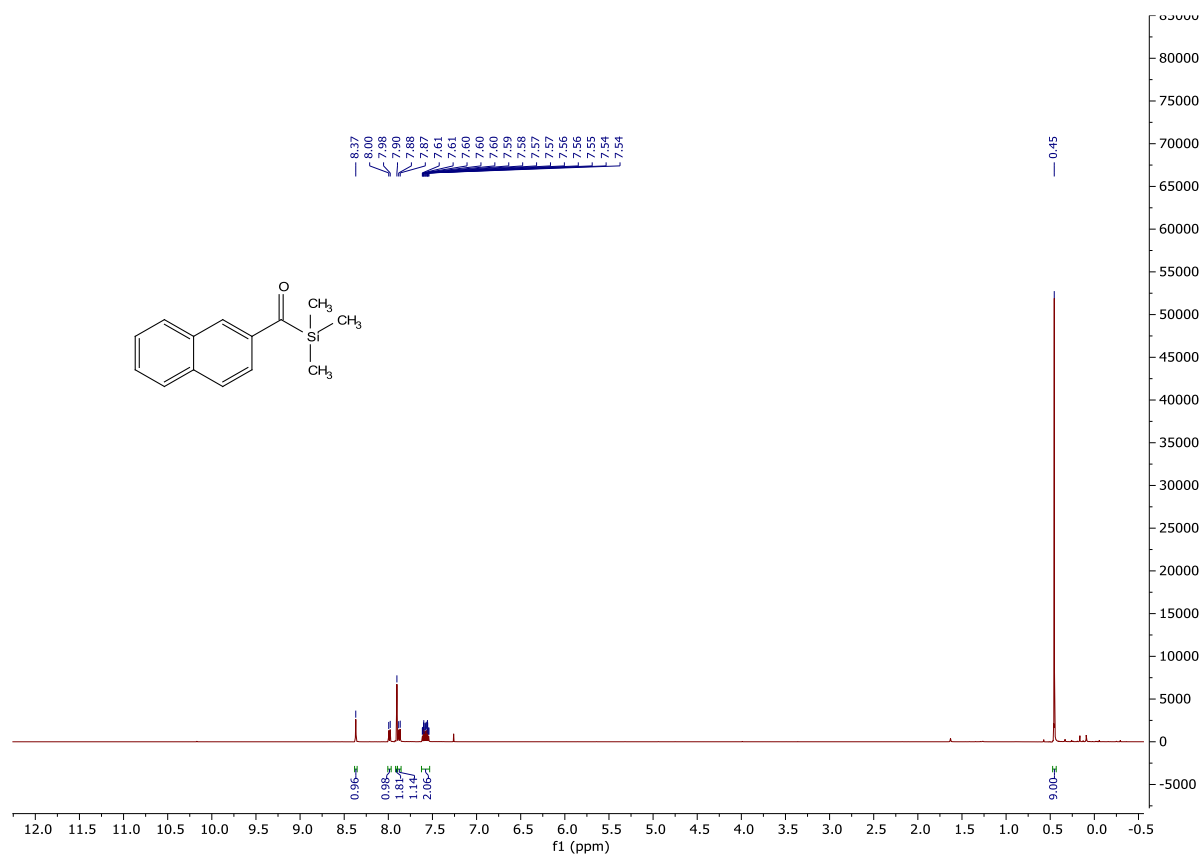
^1H NMR (500 MHz, CDCl_3) of **7j**



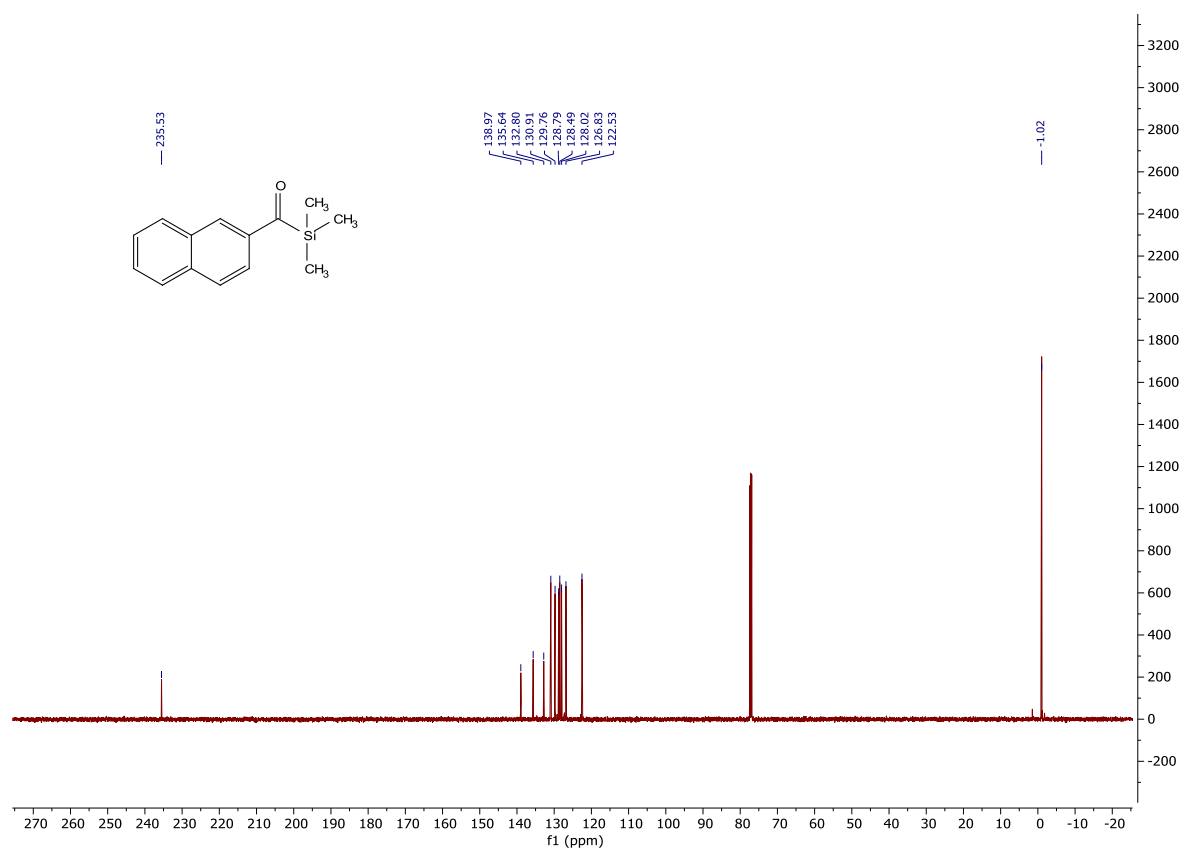
^{13}C NMR (126 MHz, CDCl_3) of **7j**



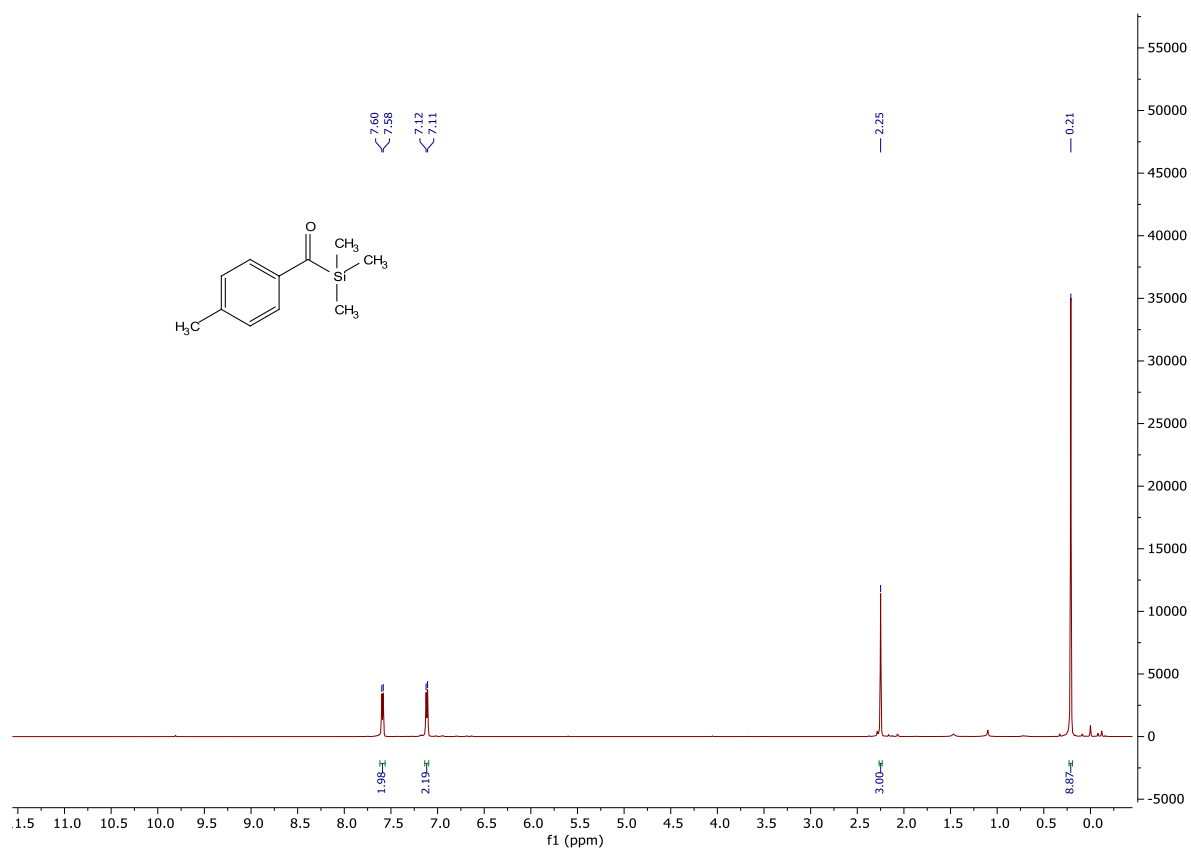
^1H NMR (500 MHz, CDCl_3) of **7k**



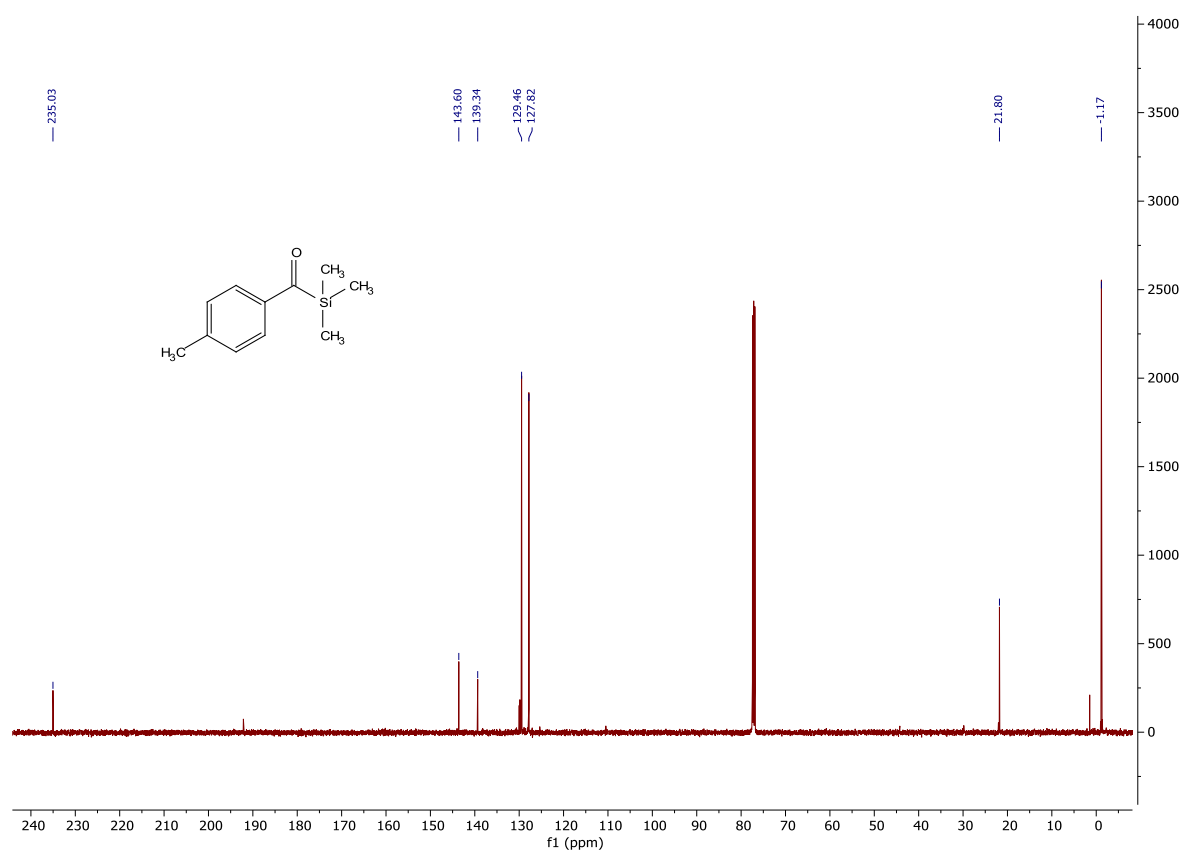
^{13}C NMR (126 MHz, CDCl_3) of **7k**



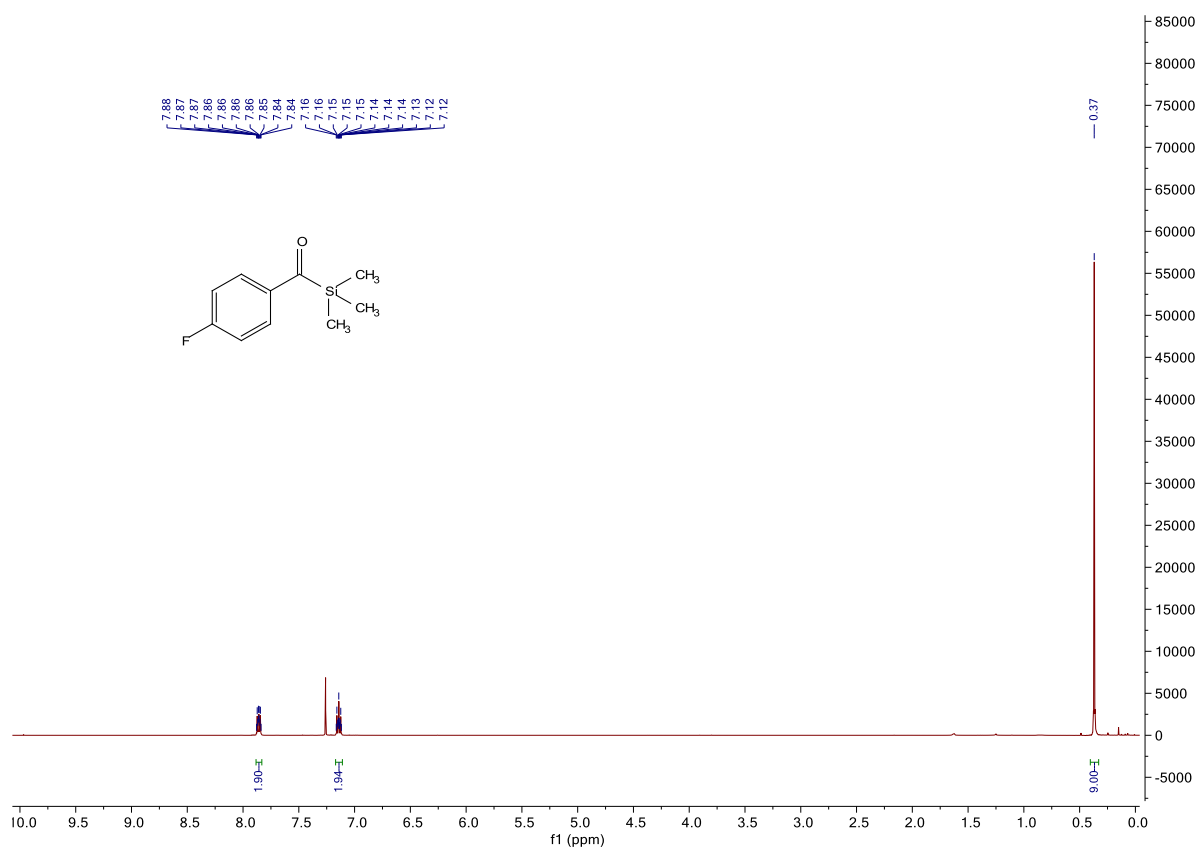
^1H NMR (500 MHz, CDCl_3) of **7l**



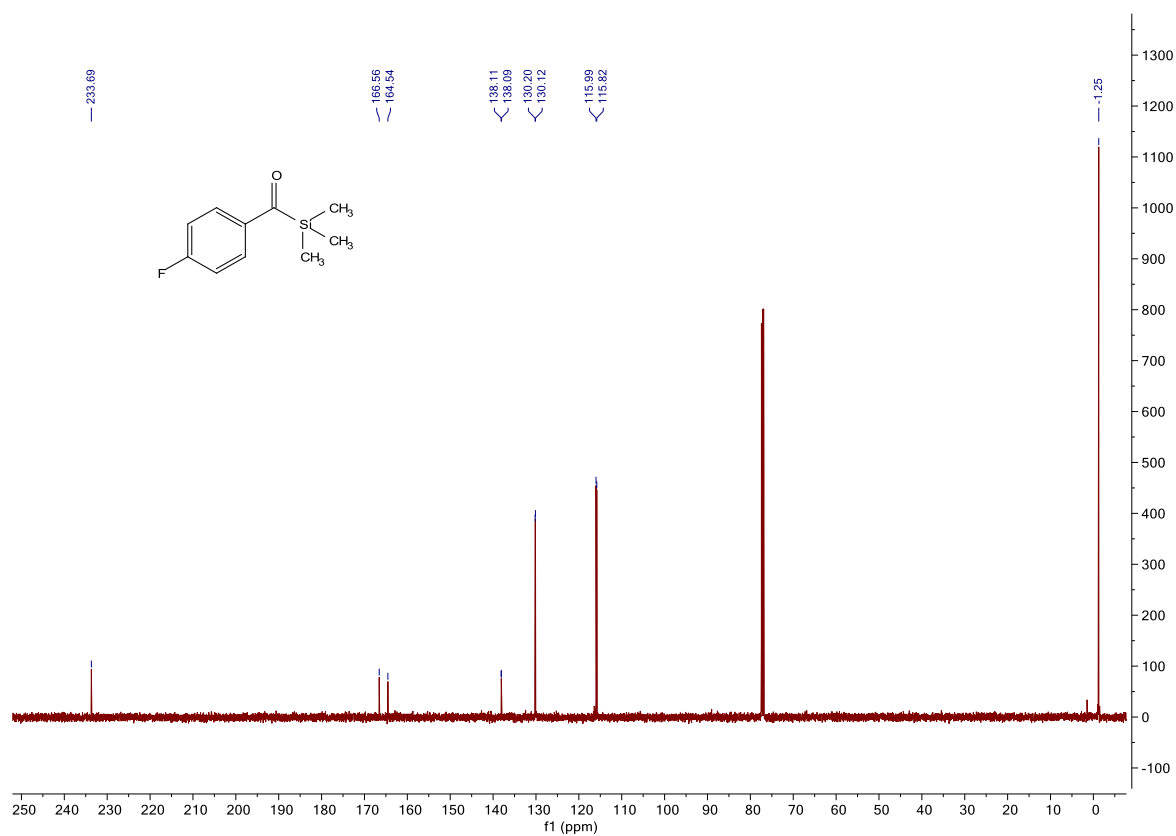
^{13}C NMR (126 MHz, CDCl_3) of **7l**



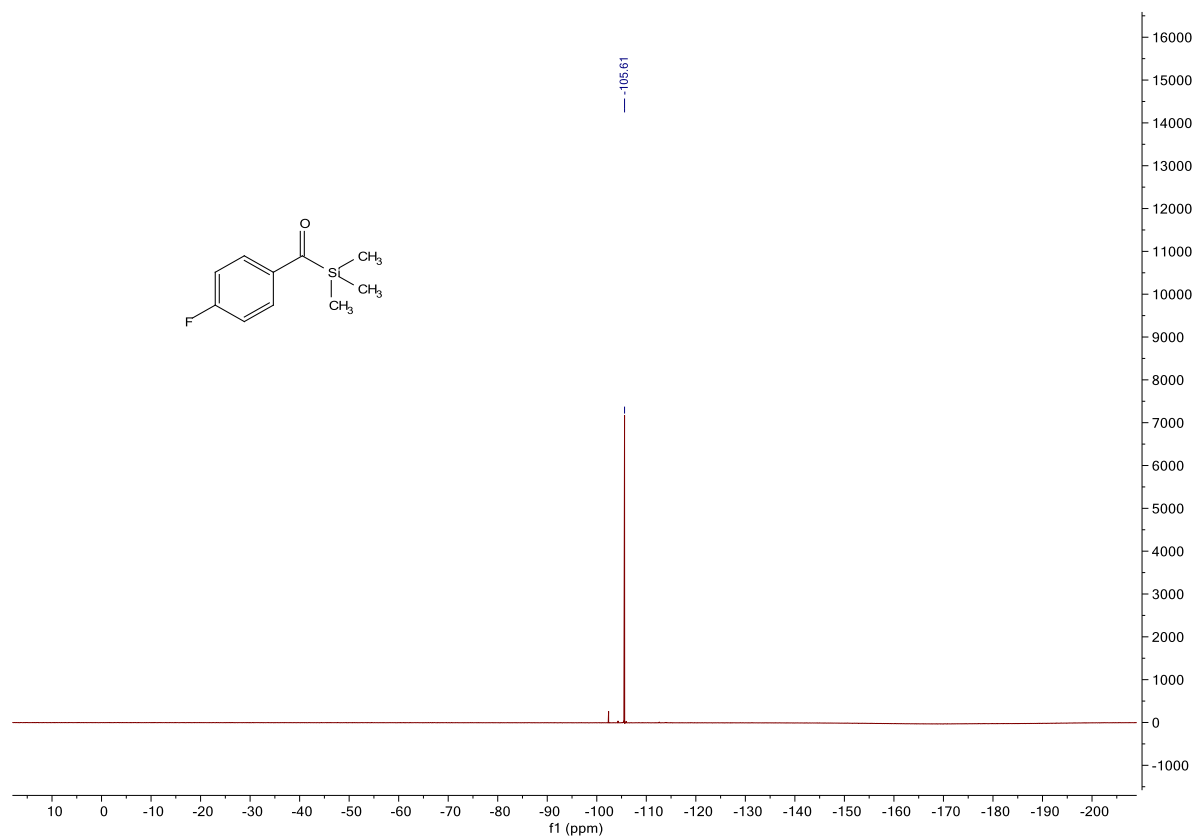
^1H NMR (500 MHz, CDCl_3) of **7m**



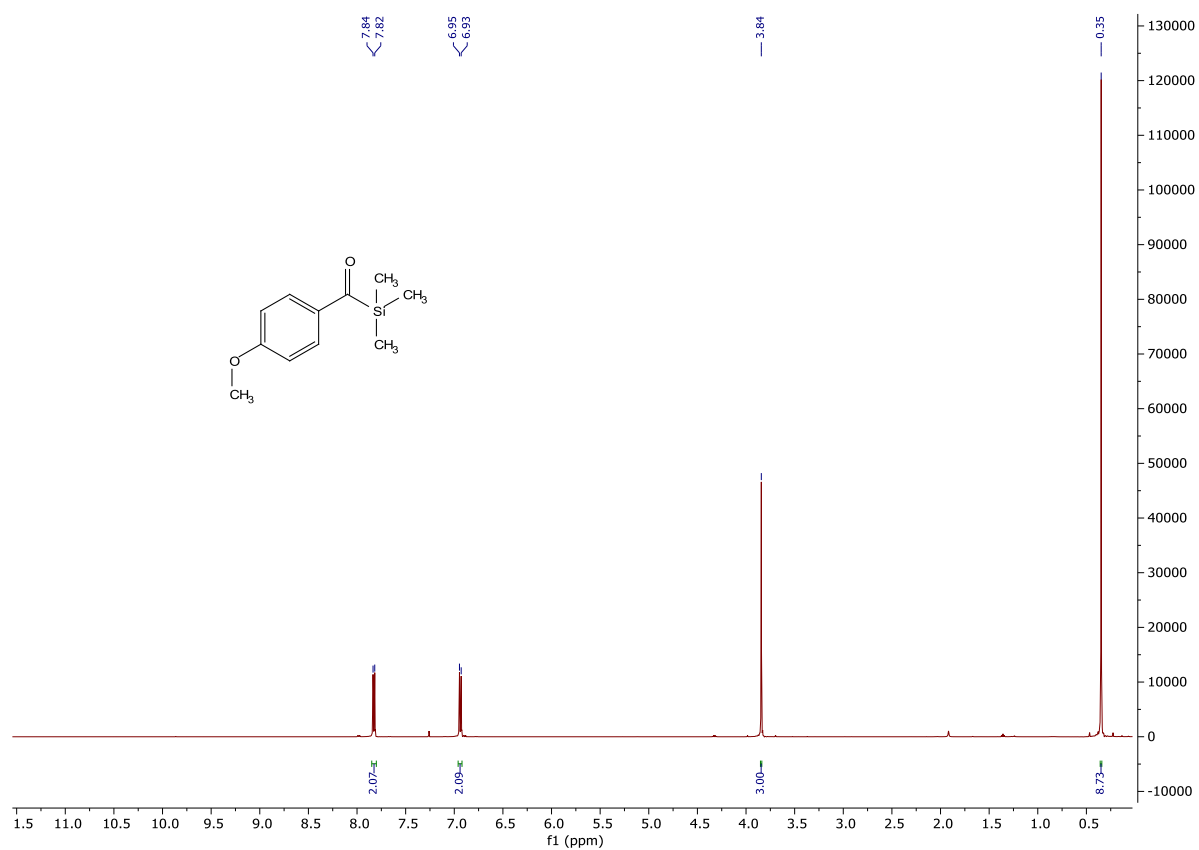
¹³C NMR (126 MHz, CDCl₃) of 7m



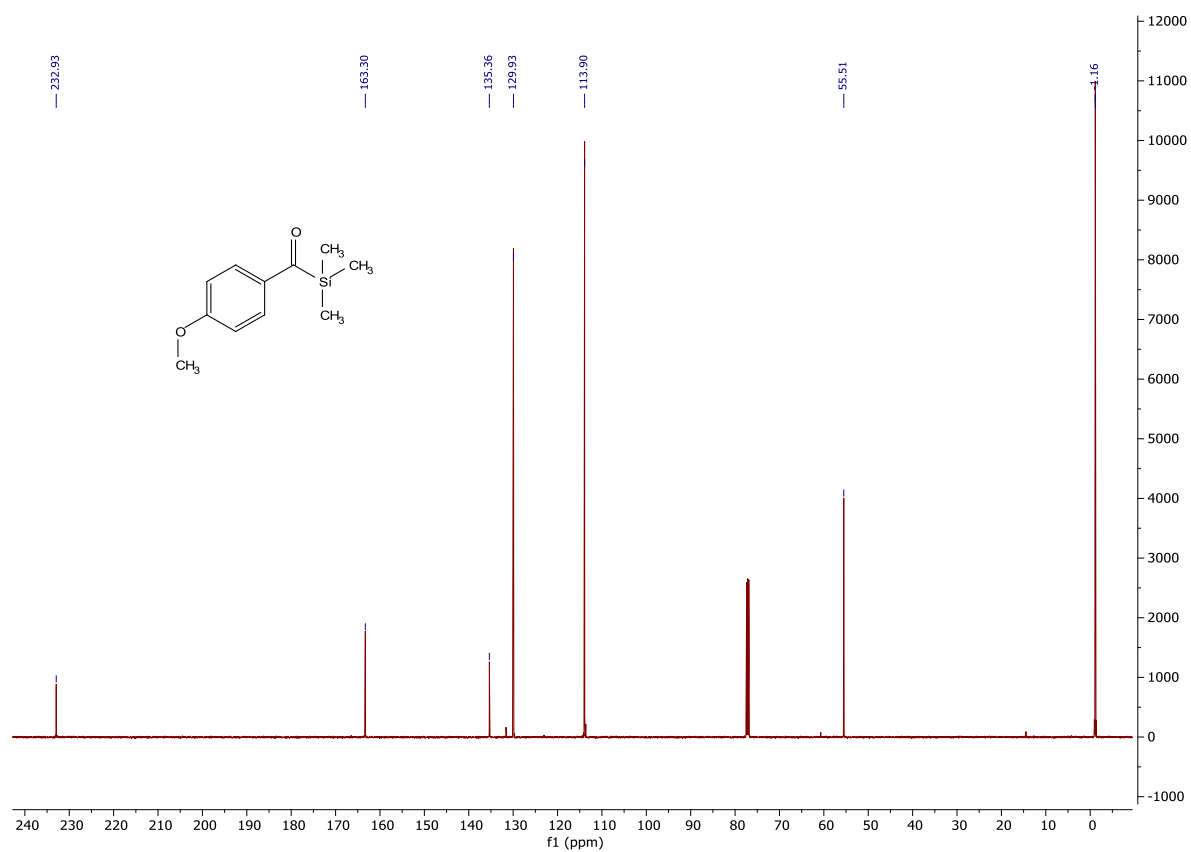
¹⁹F NMR (471 MHz, CDCl₃) of 7m



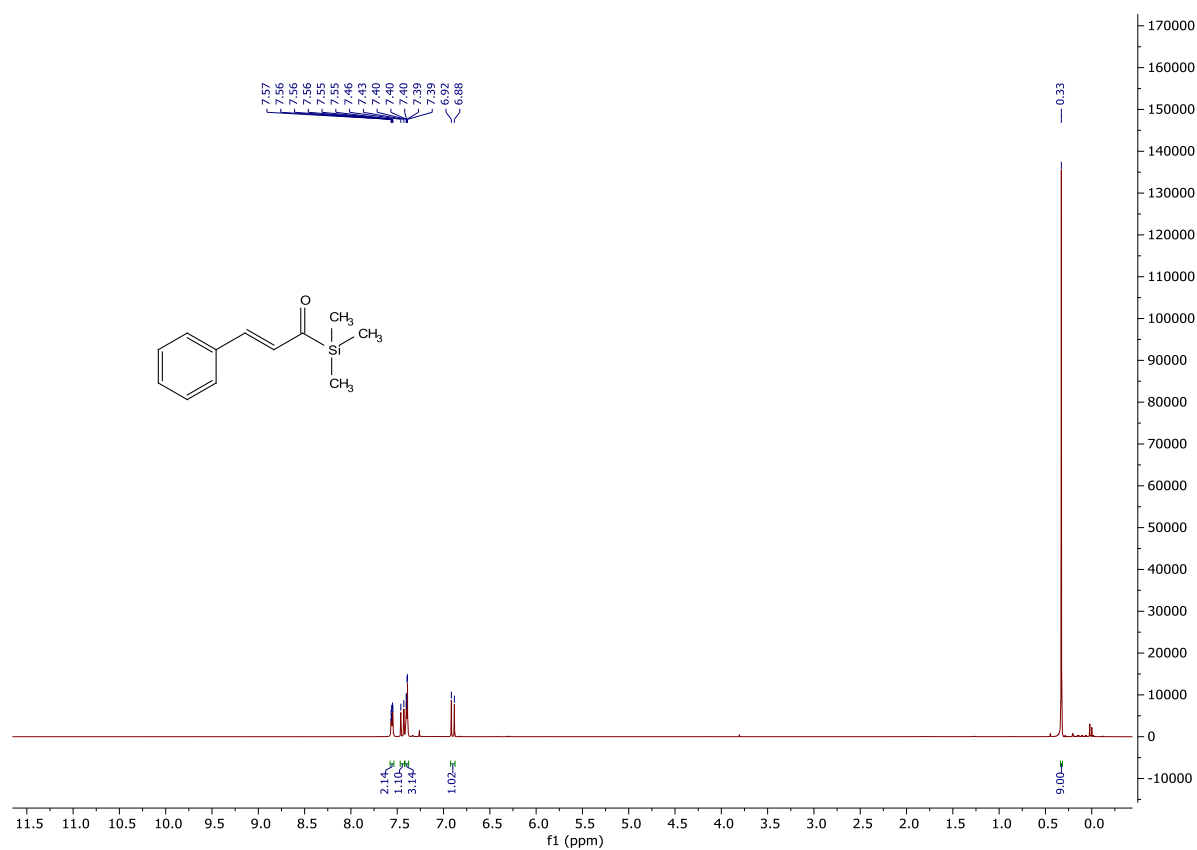
^1H NMR (500 MHz, CDCl_3) of **7n**



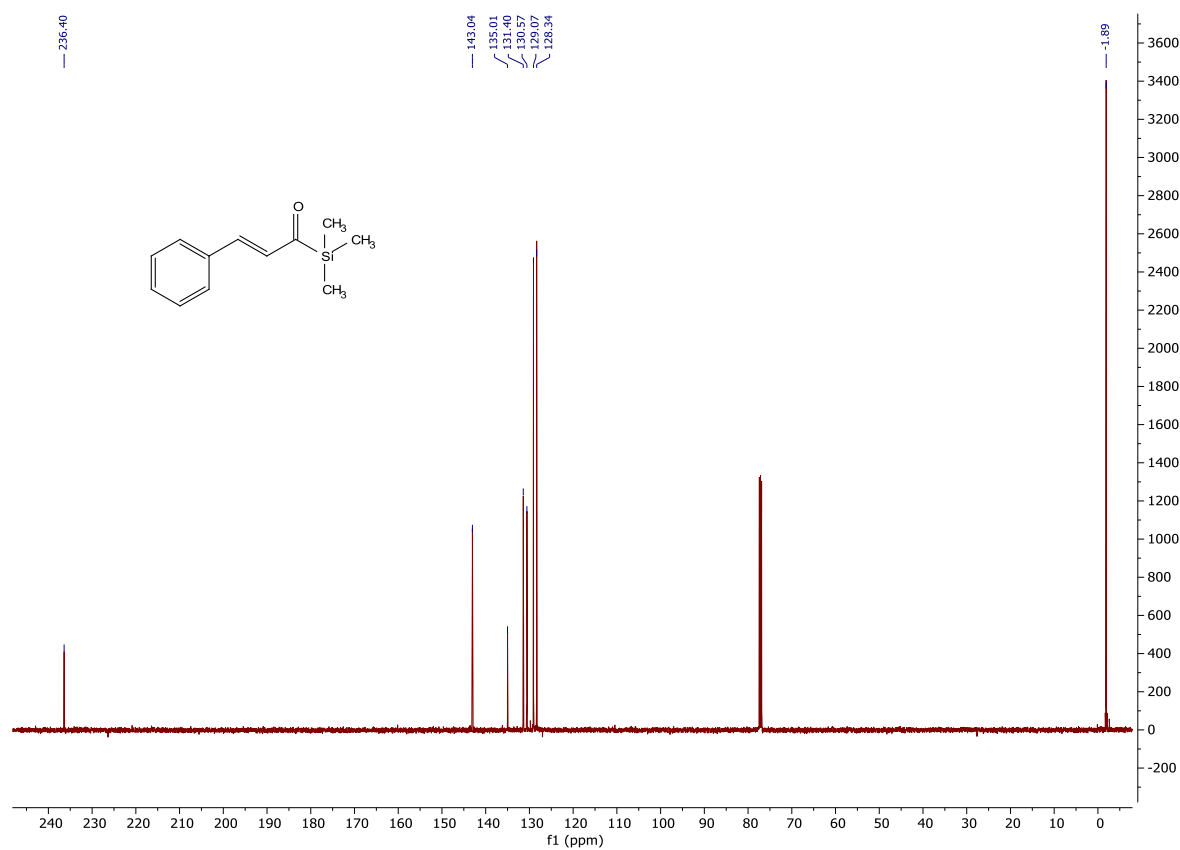
^{13}C NMR (126 MHz, CDCl_3) of **7n**



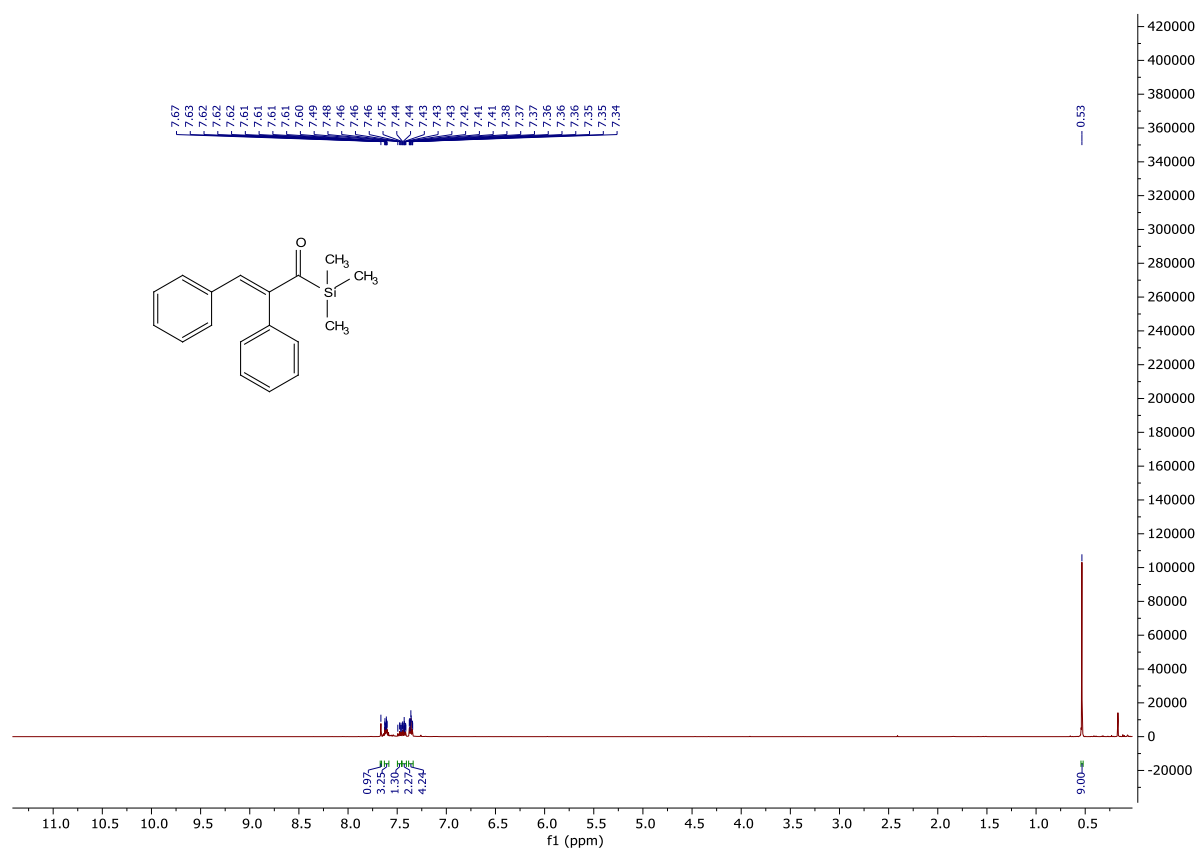
¹H NMR (500 MHz, CDCl₃) of 7o



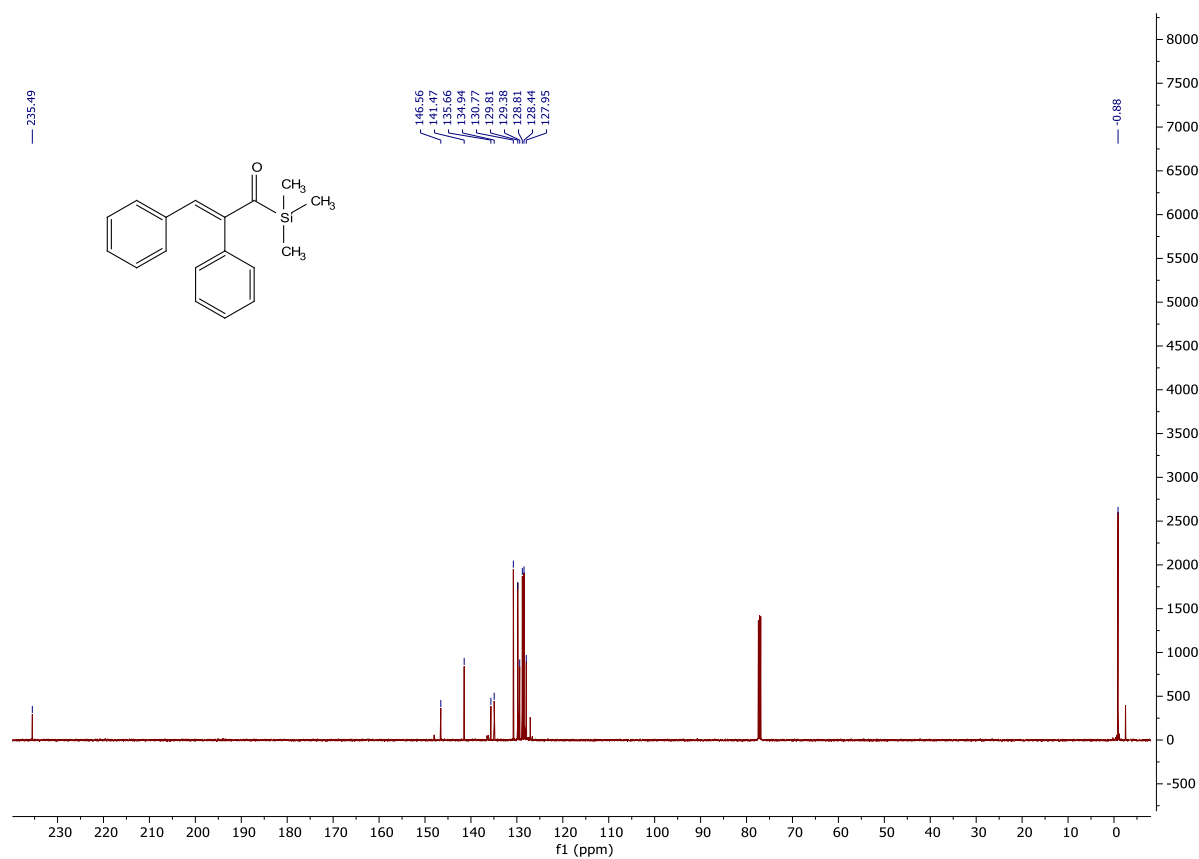
¹³C NMR (126 MHz, CDCl₃) of 7o



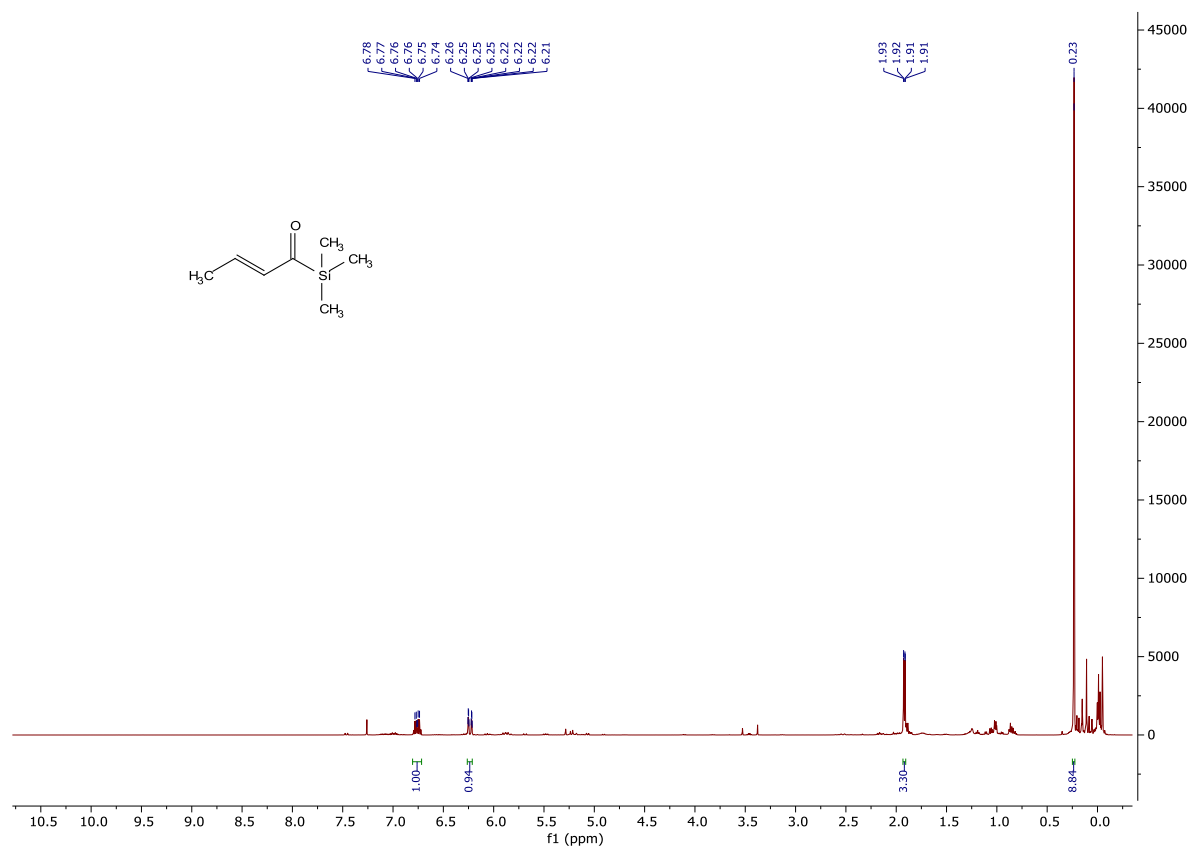
^1H NMR (500 MHz, CDCl_3) of 7p



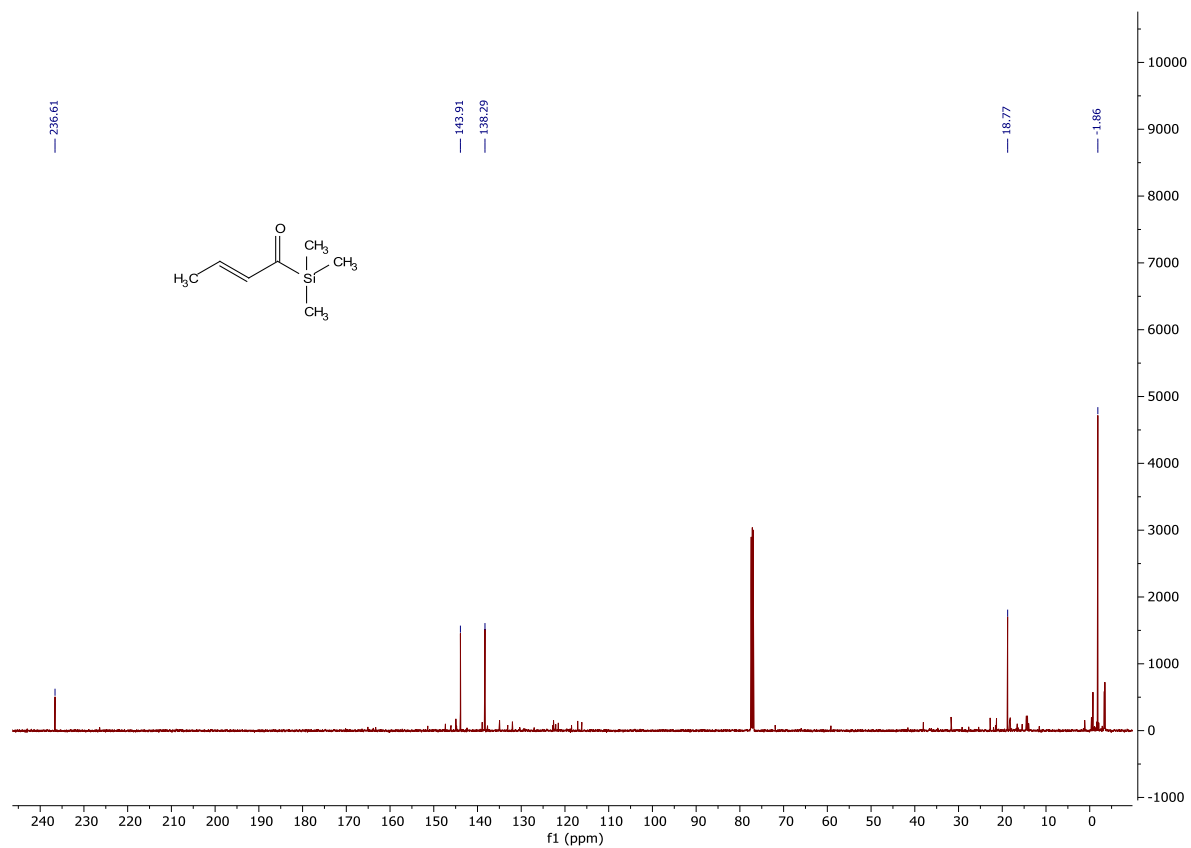
^{13}C NMR (126 MHz, CDCl_3) of 7p



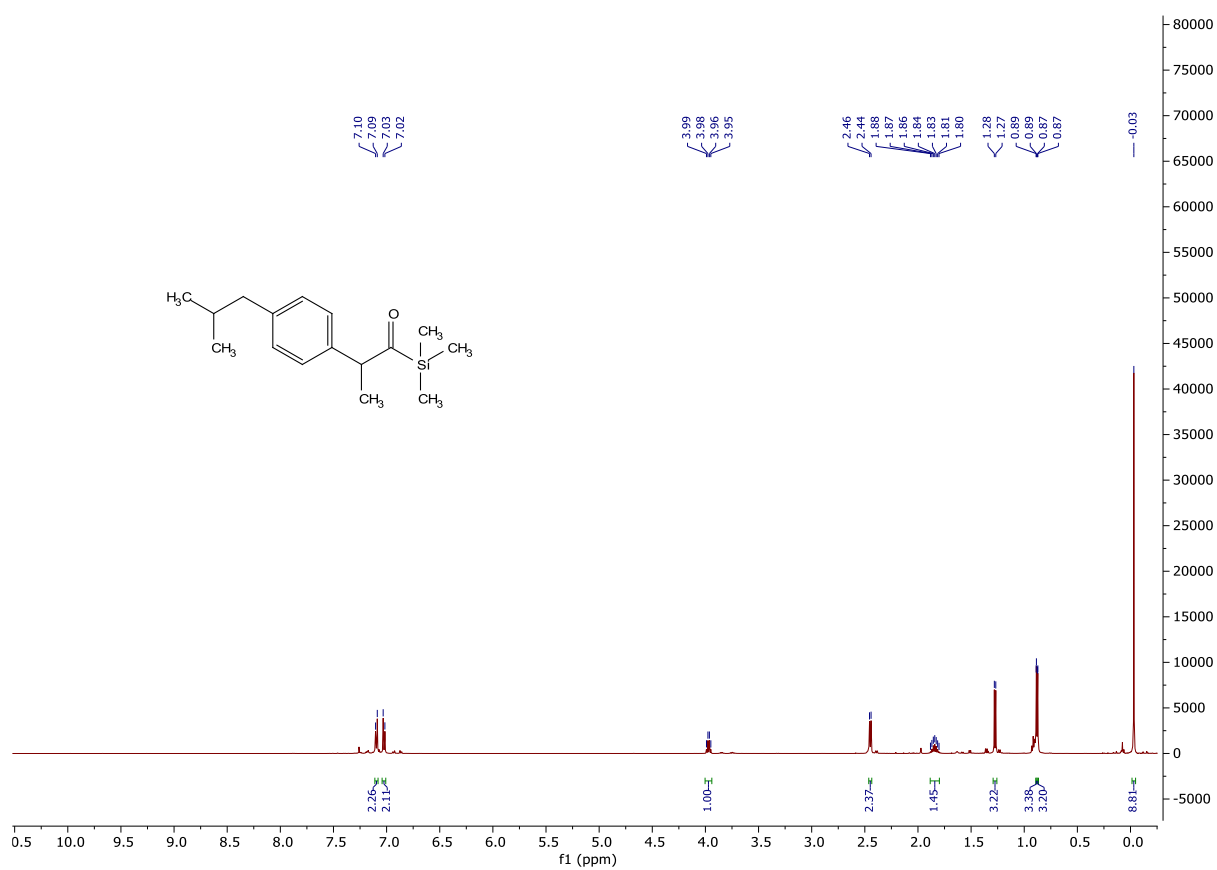
¹H NMR (500 MHz, CDCl₃) of 7q (impure)



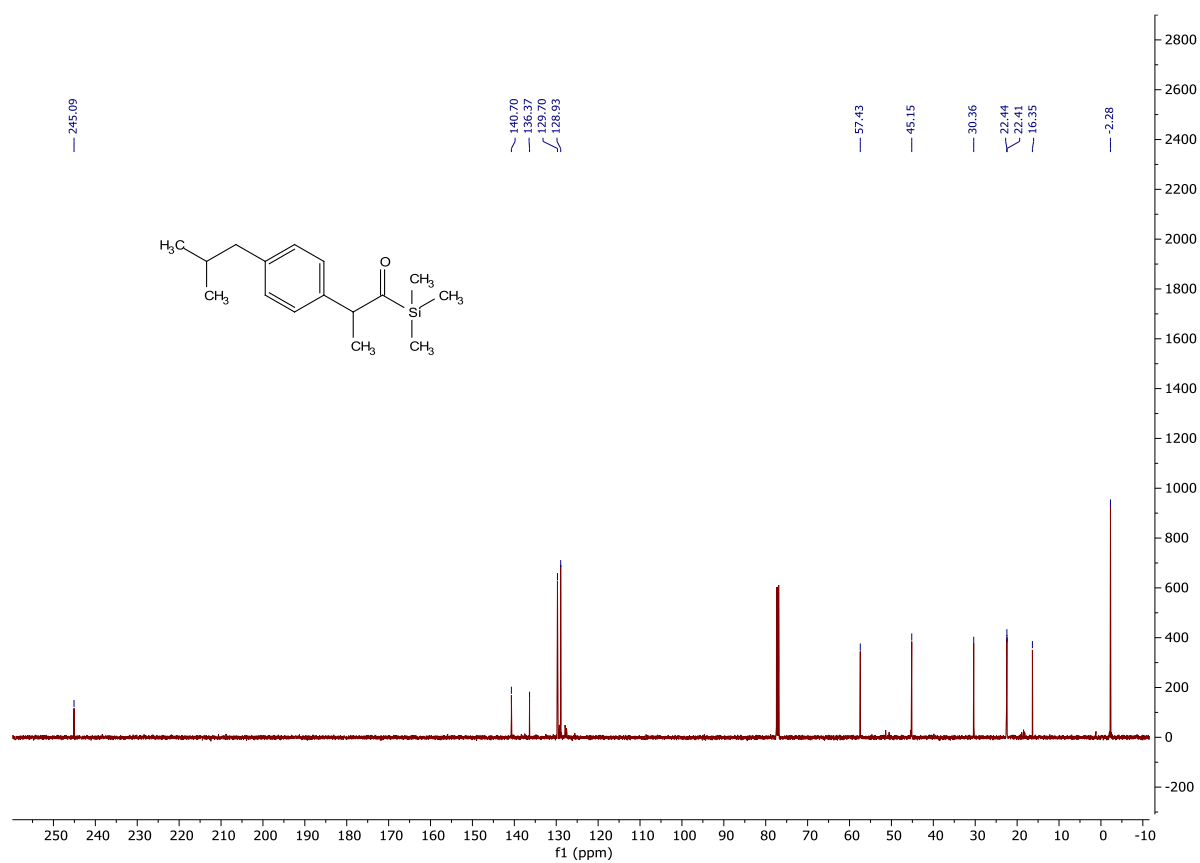
¹³C NMR (126 MHz, CDCl₃) of 7q (impure)



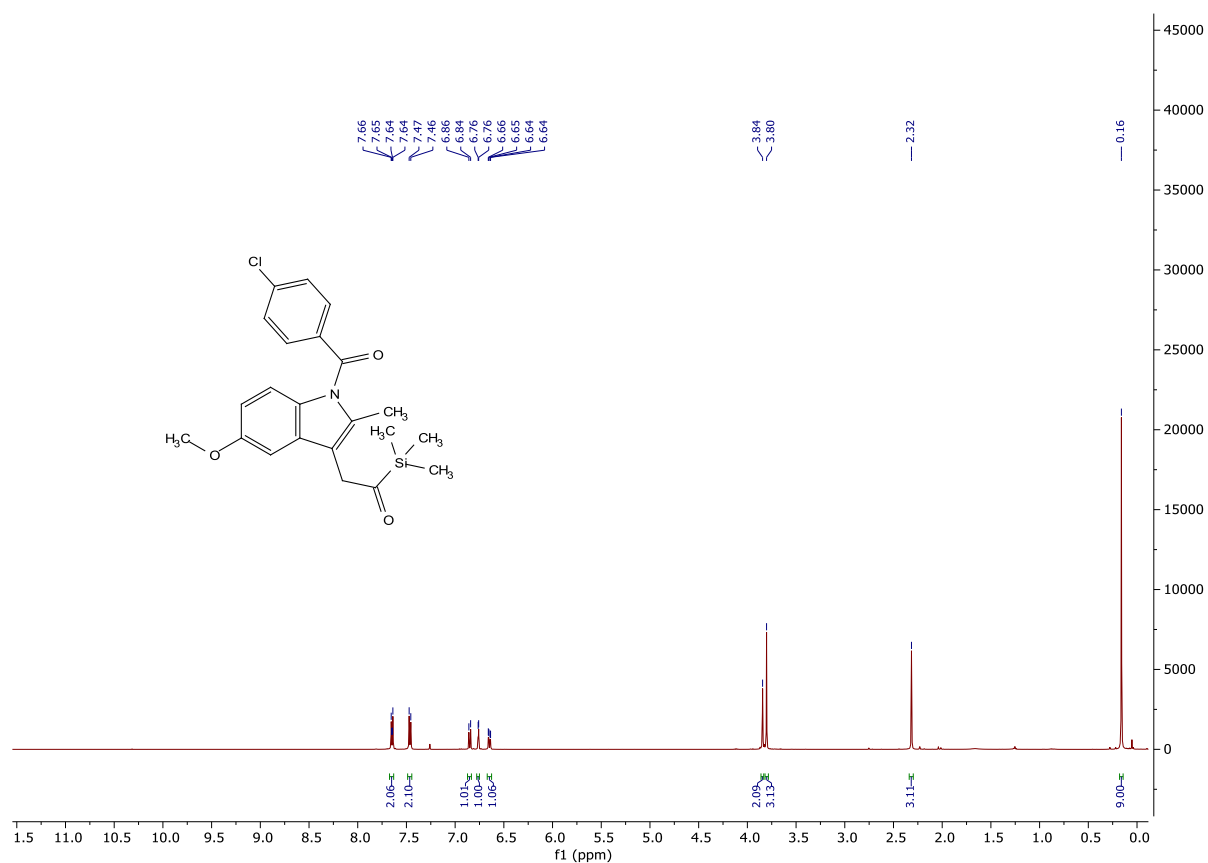
^1H NMR (500 MHz, CDCl_3) of **7r**



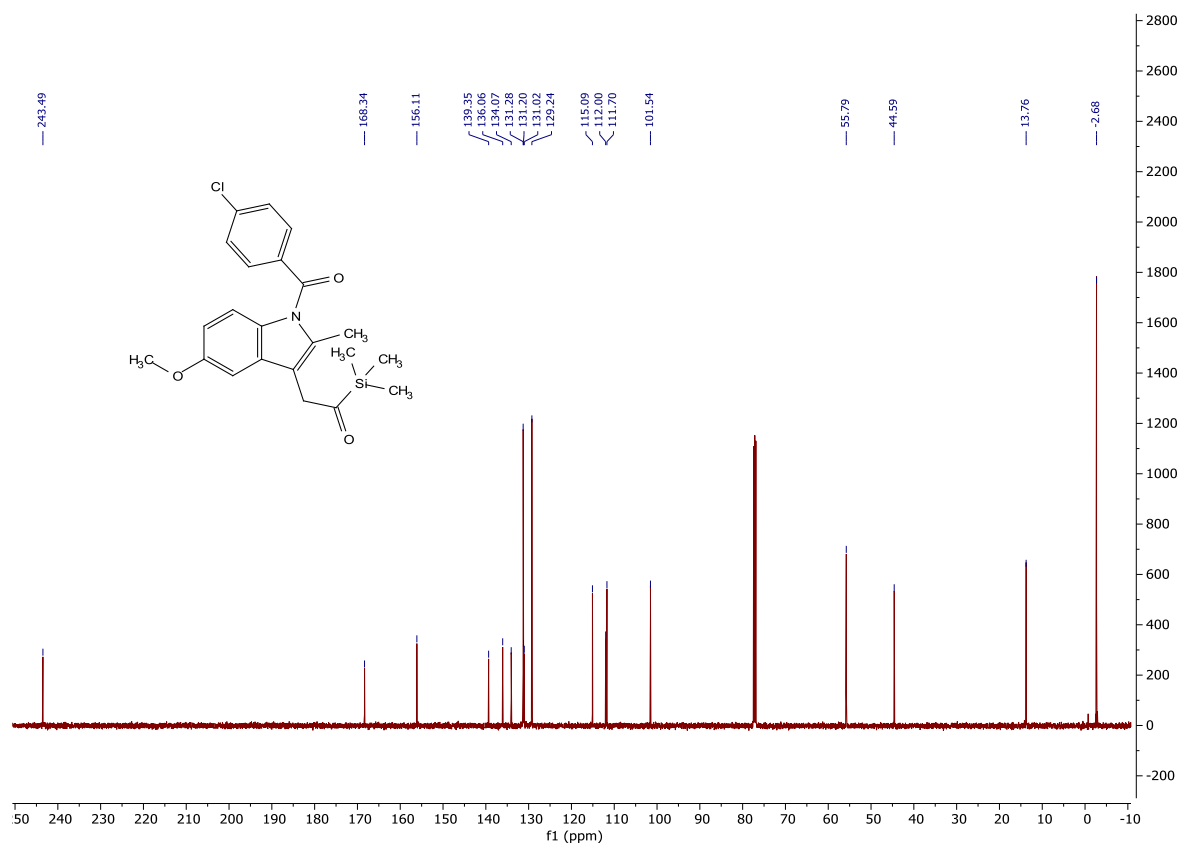
^{13}C NMR (126 MHz, CDCl_3) of **7r**



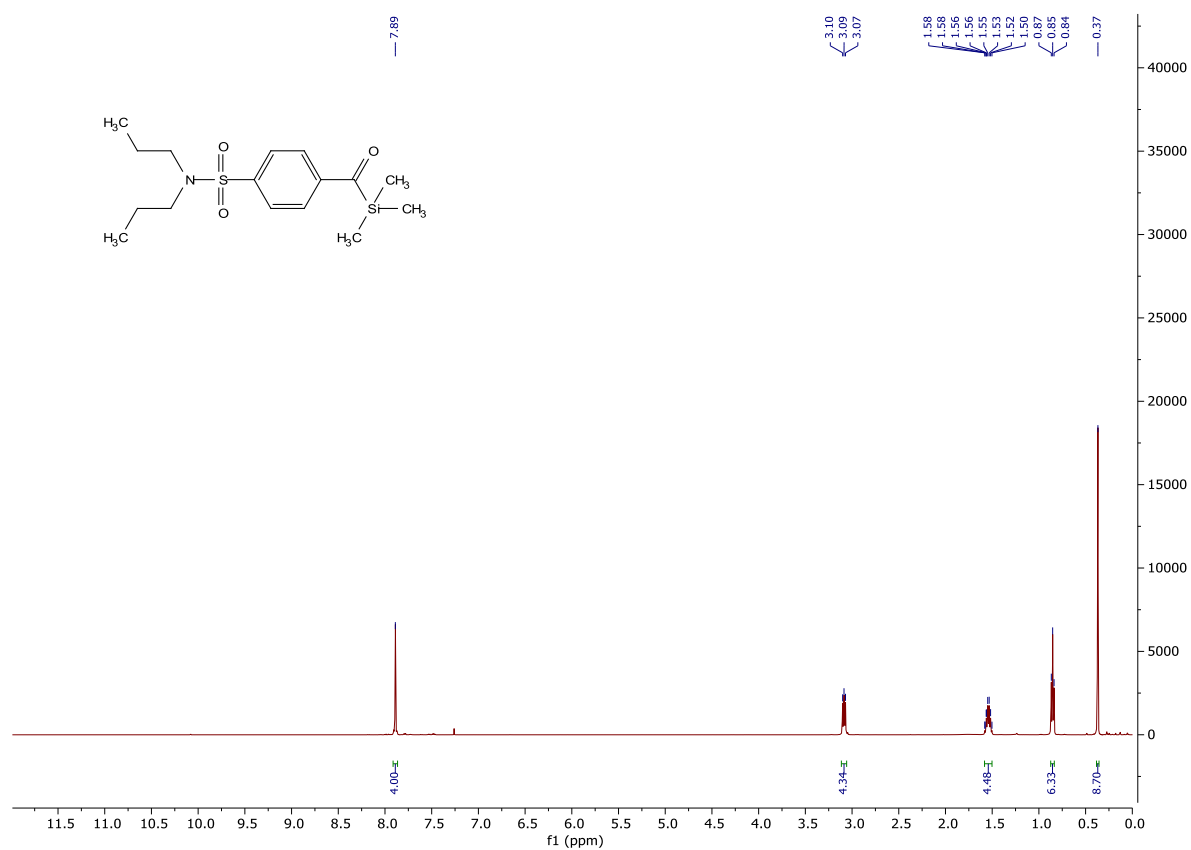
^1H NMR (500 MHz, CDCl_3) of **7s**



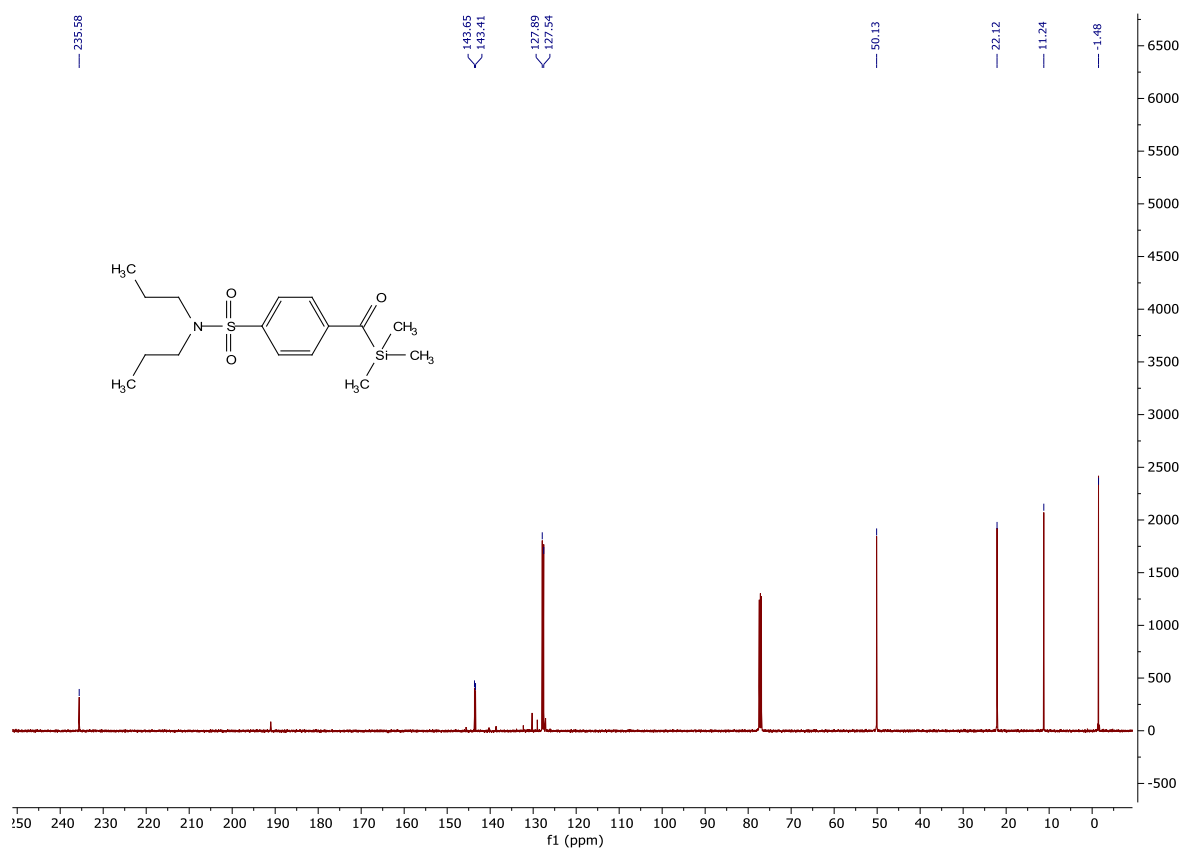
^{13}C NMR (126 MHz, CDCl_3) of **7s**



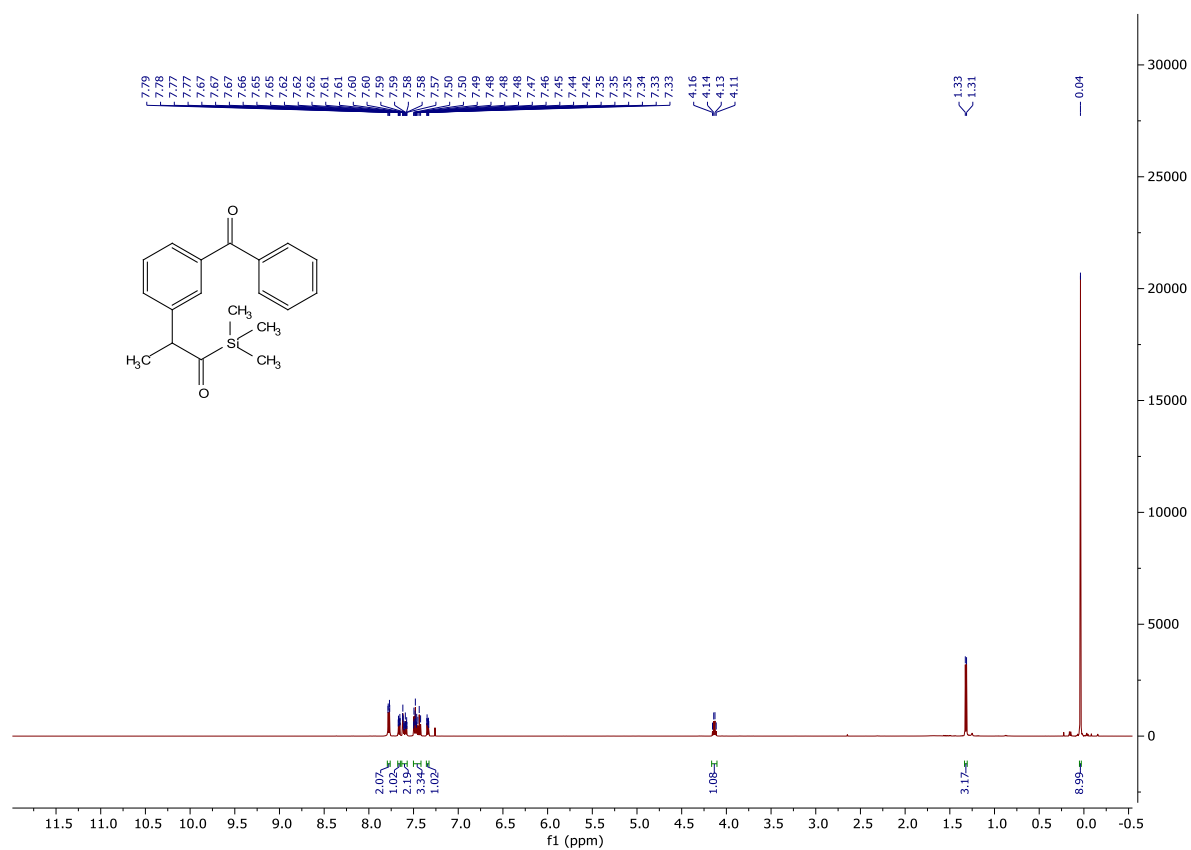
^1H NMR (500 MHz, CDCl_3) of **7t**



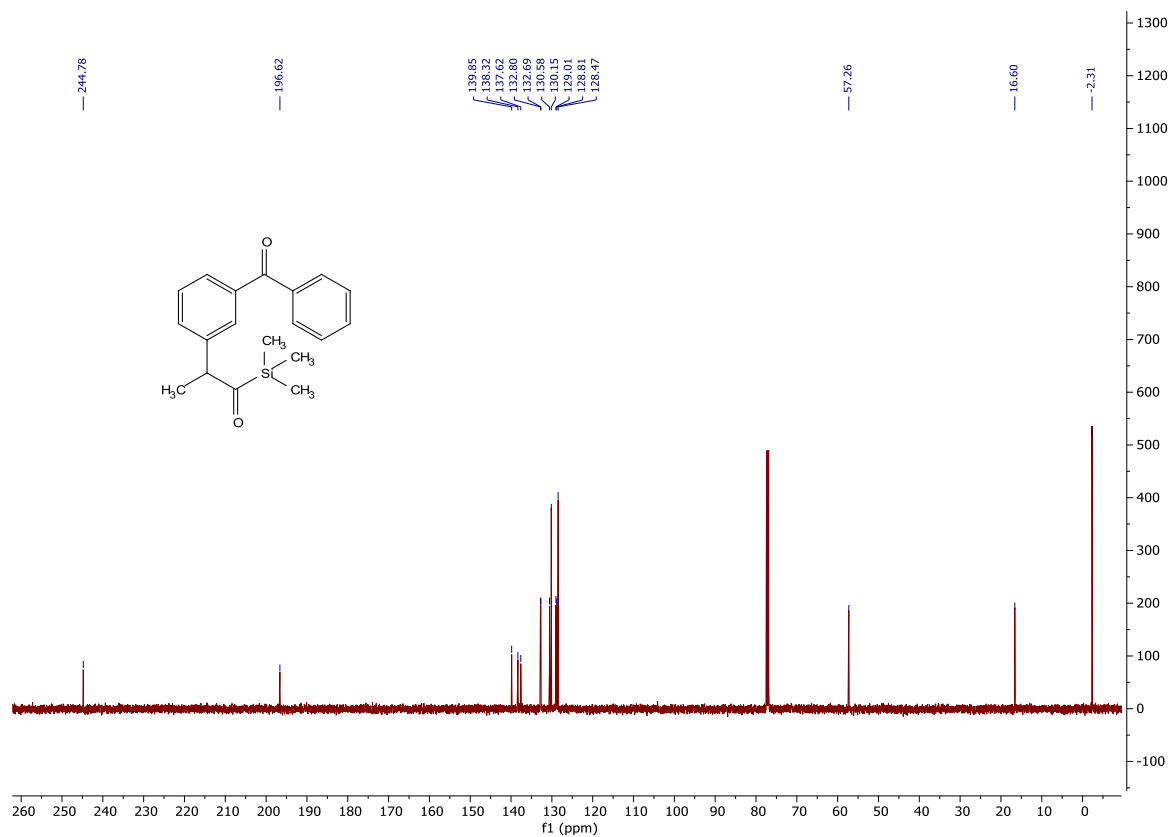
^{13}C NMR (126 MHz, CDCl_3) of **7t**



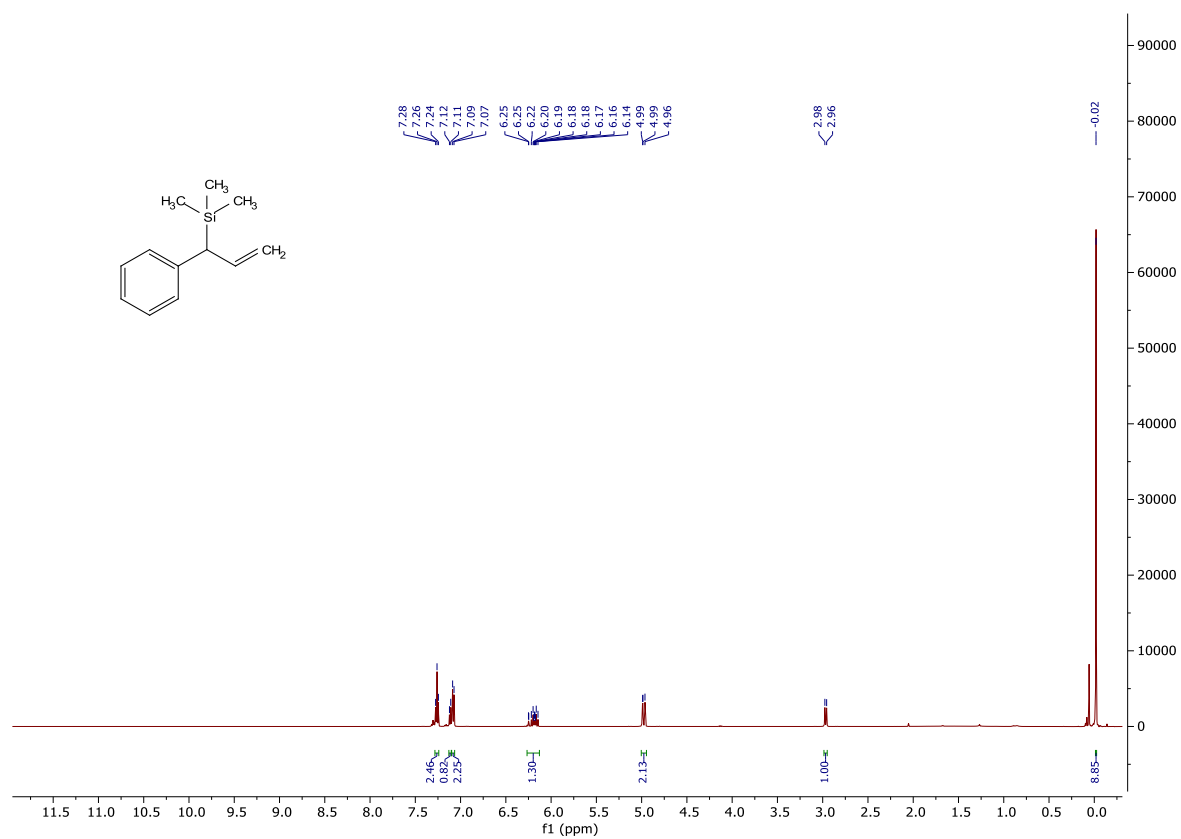
^1H NMR (500 MHz, CDCl_3) of **7u**



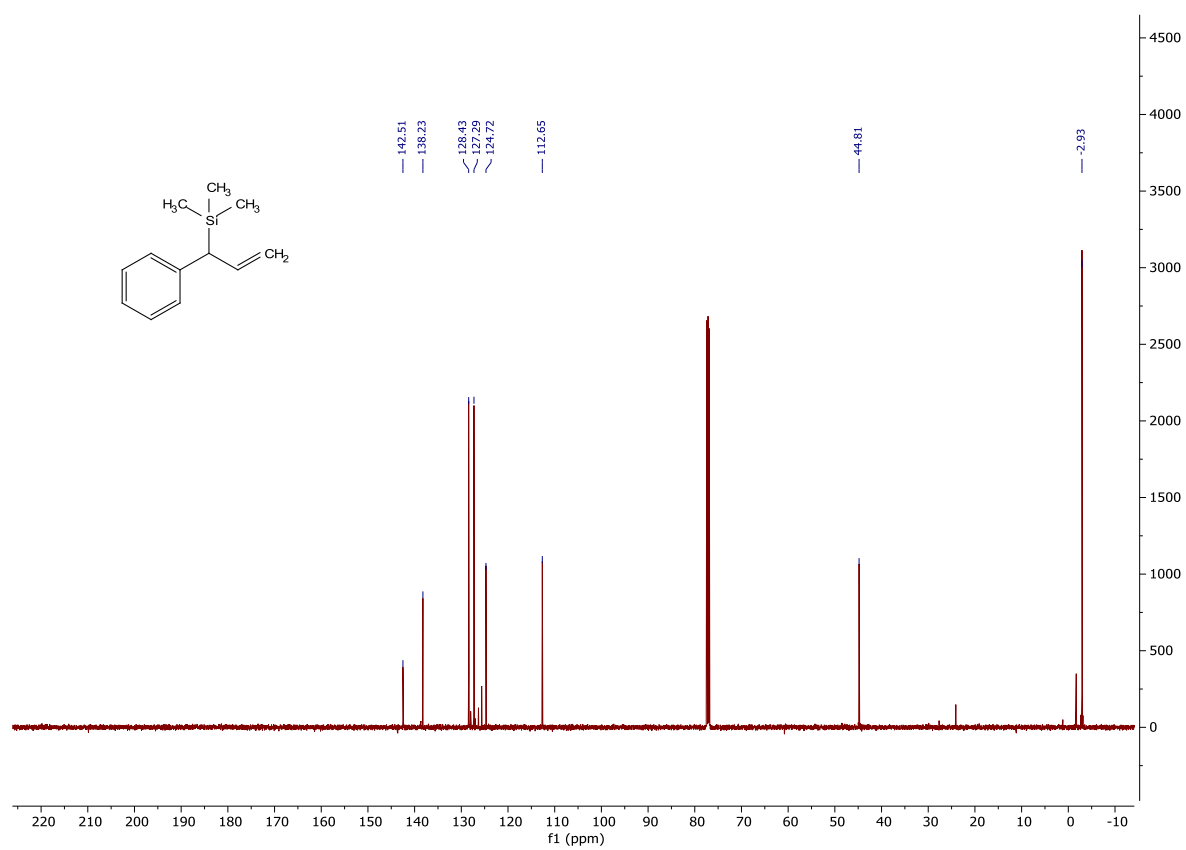
^{13}C NMR (126 MHz, CDCl_3) of **7u**



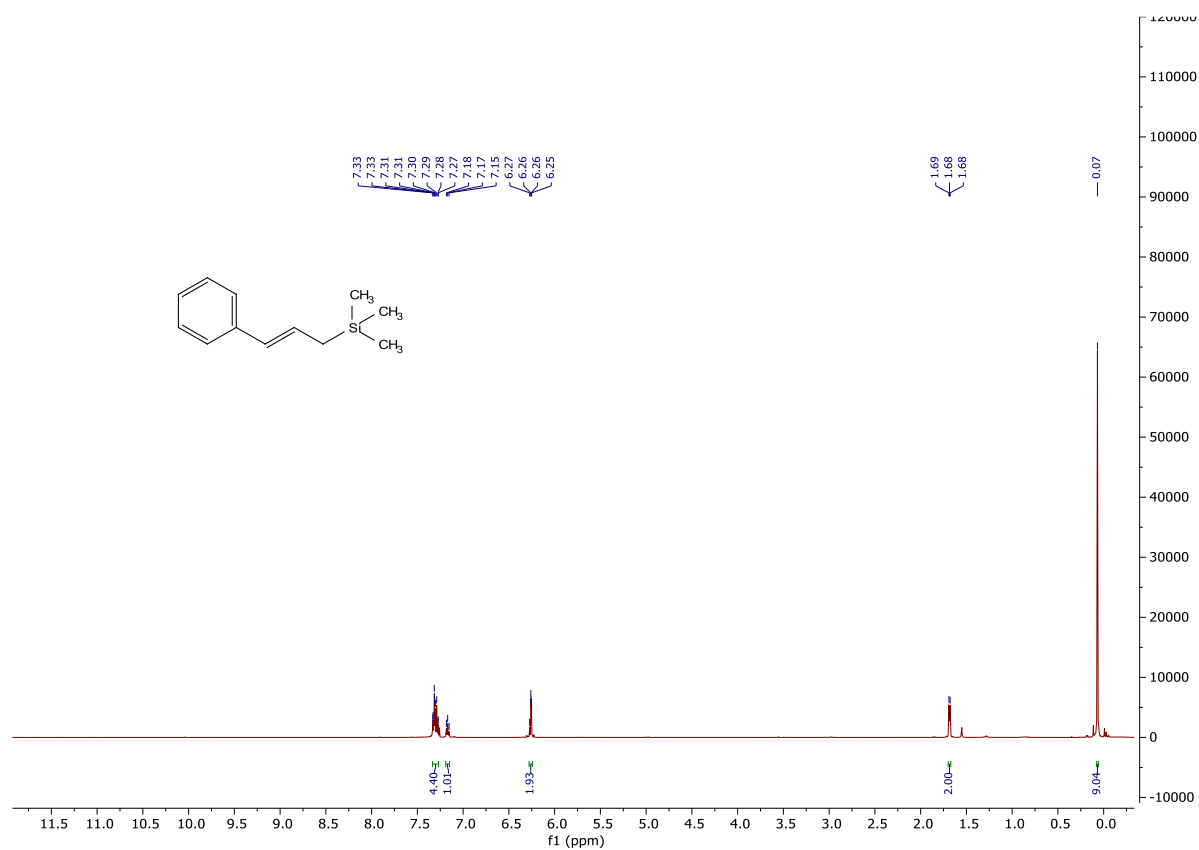
^1H NMR (500 MHz, CDCl_3) of **8b (mixture of linear isomer)**



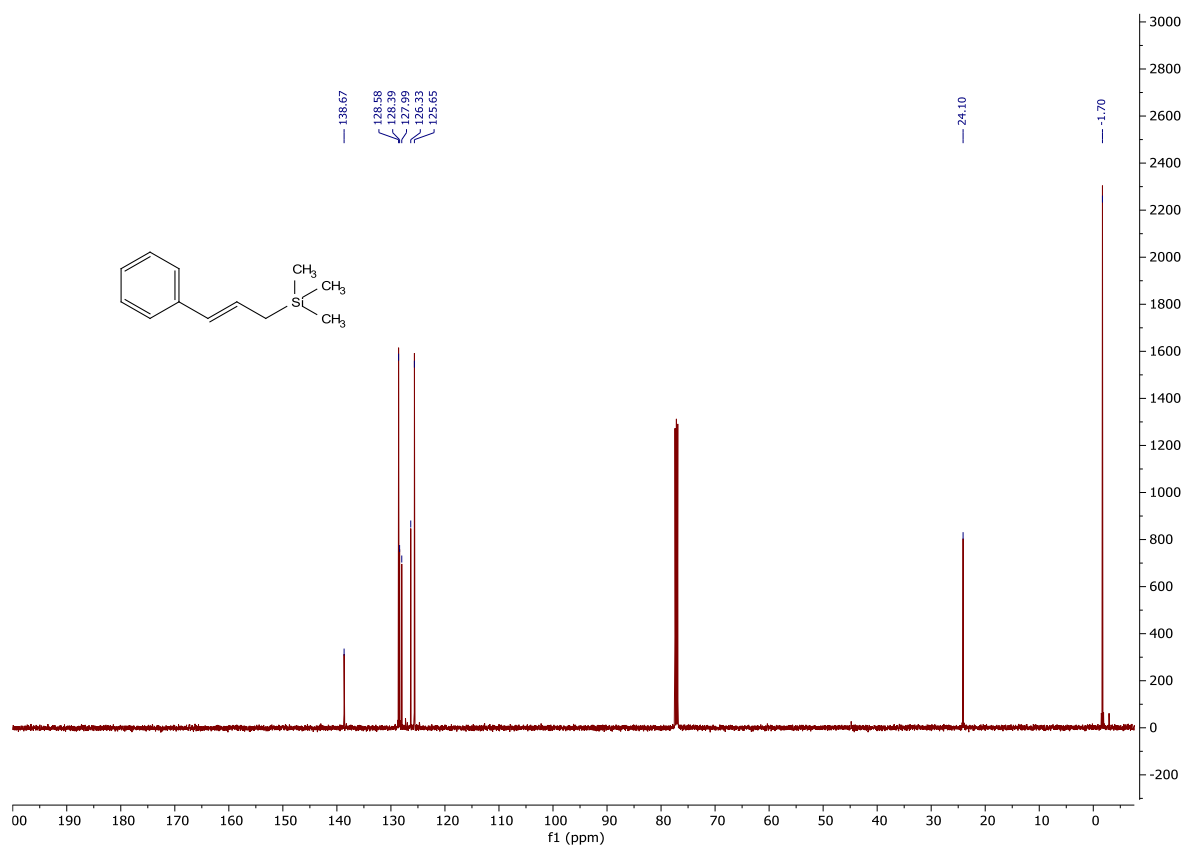
^{13}C NMR (126 MHz, CDCl_3) of **8b (mixture of linear isomer)**



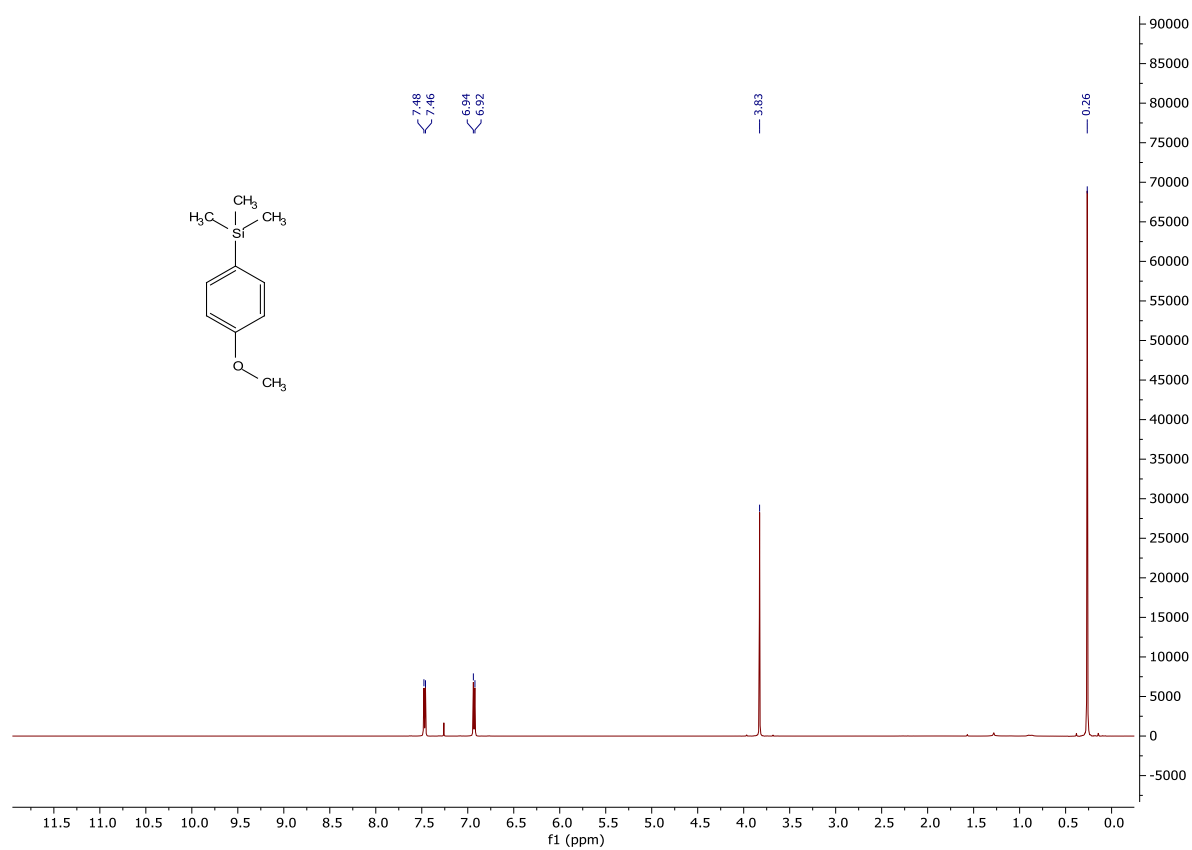
^1H NMR (500 MHz, CDCl_3) of **9b**



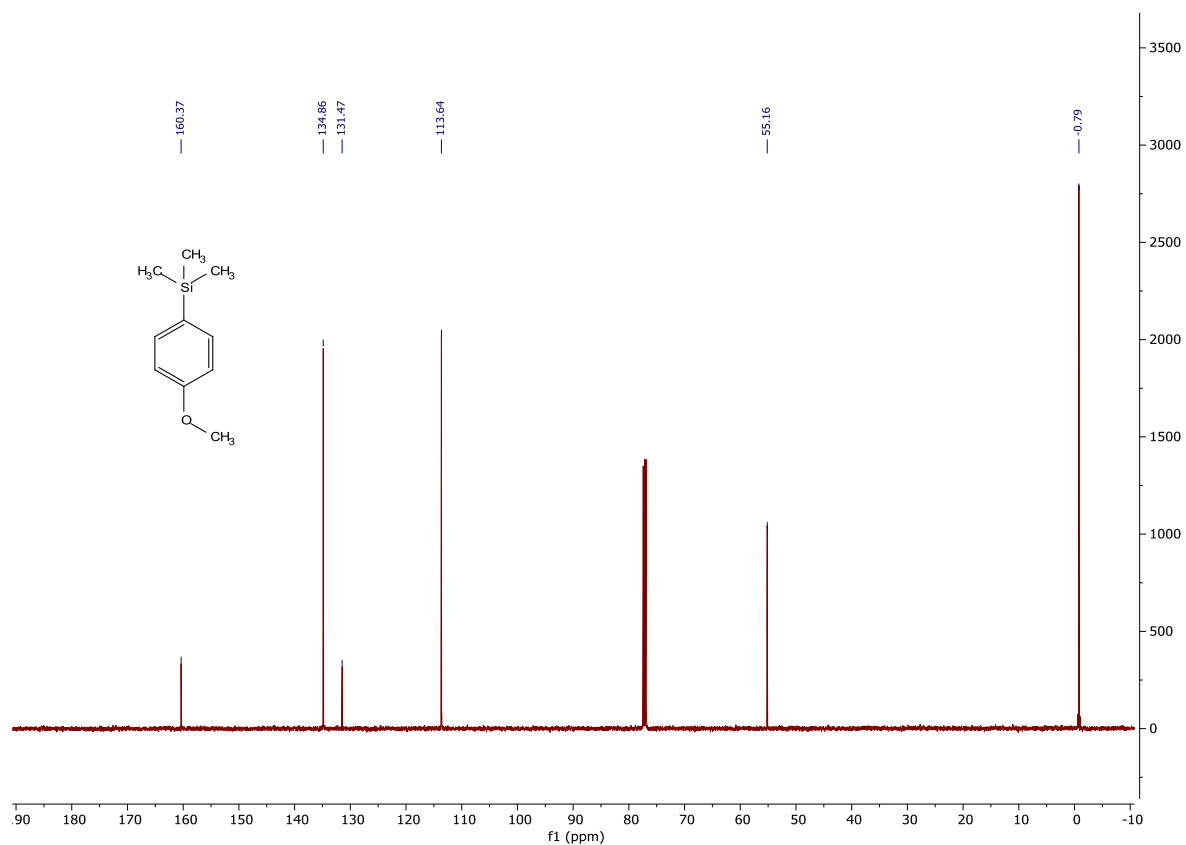
^{13}C NMR (126 MHz, CDCl_3) of **9b**



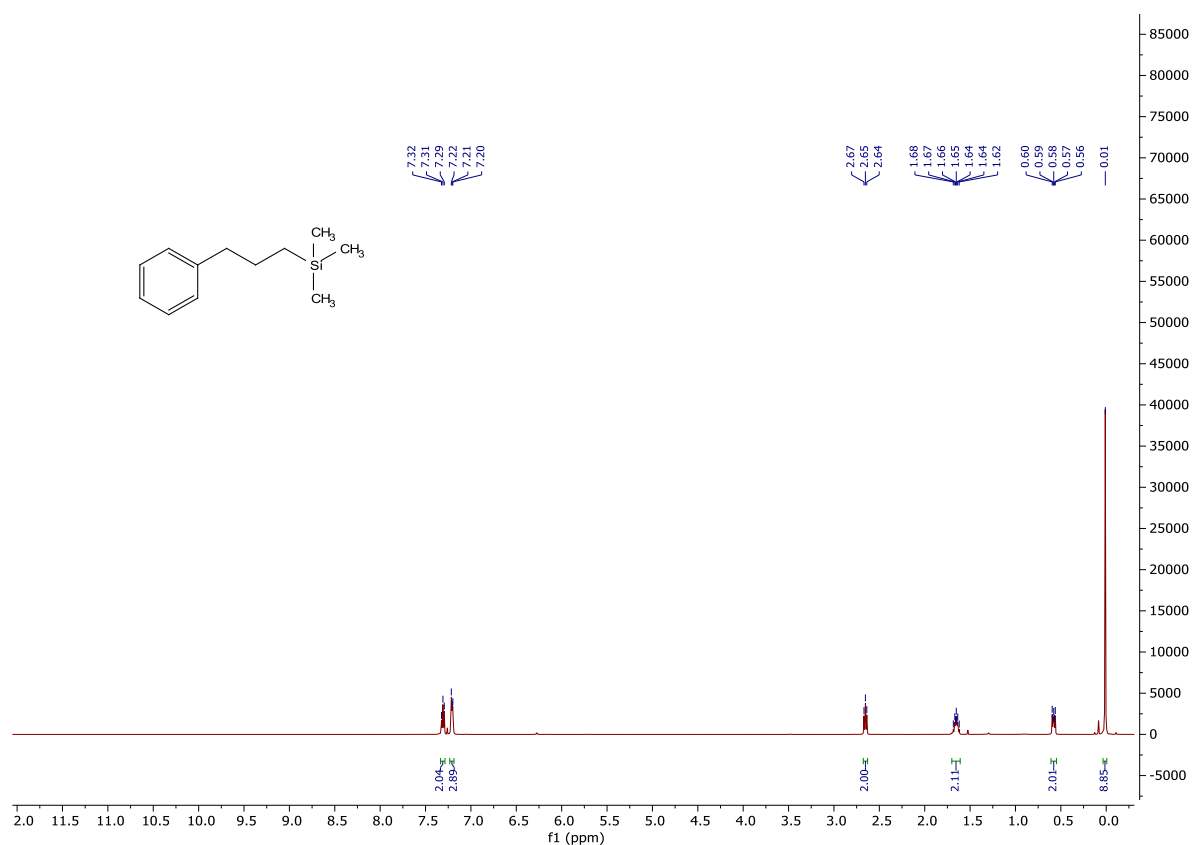
¹H NMR (500 MHz, CDCl₃) of 10b



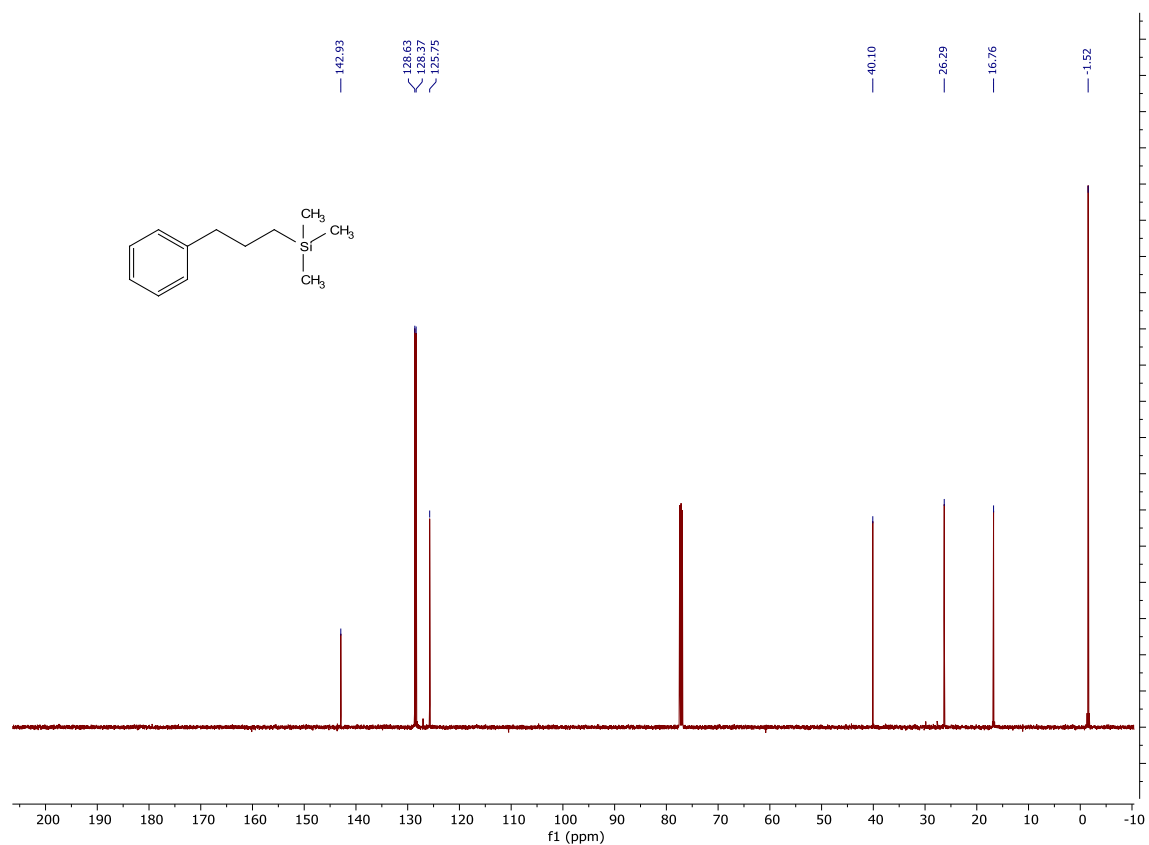
¹³C NMR (126 MHz, CDCl₃) of 10b



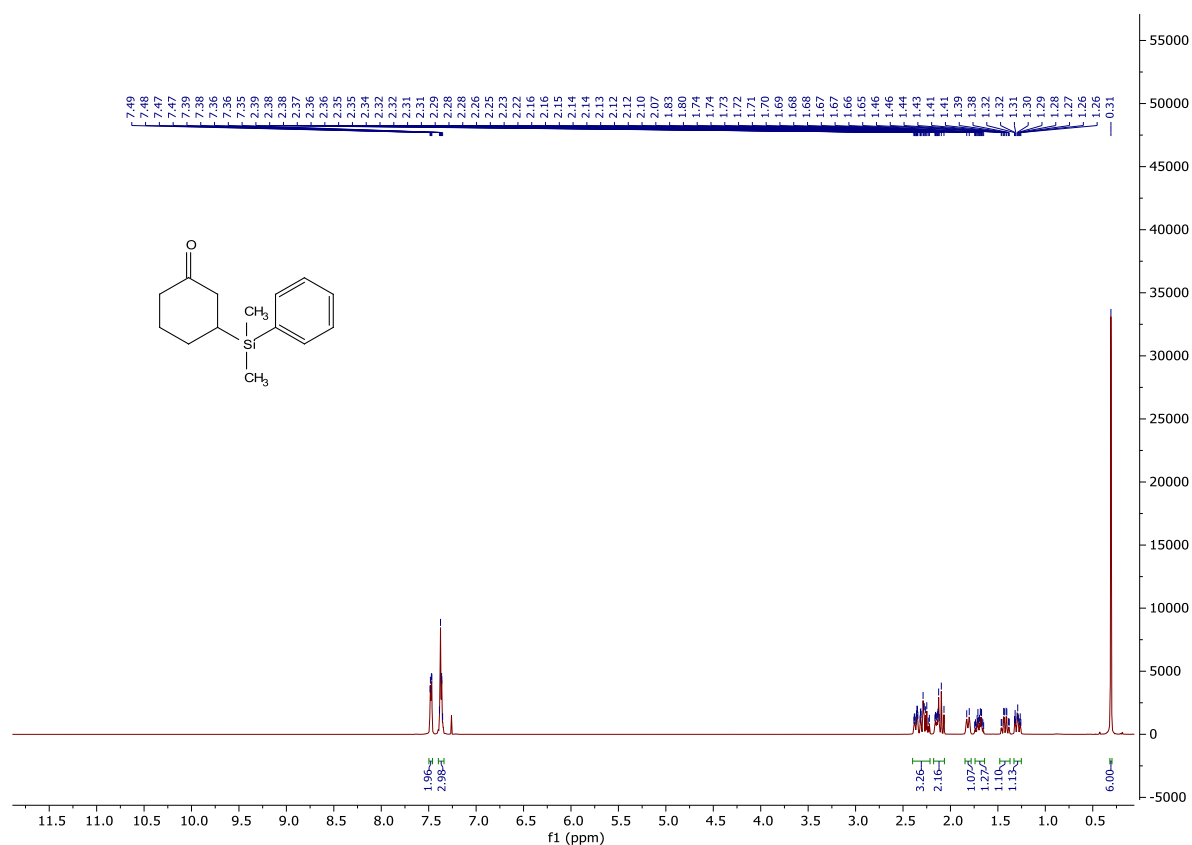
^1H NMR (500 MHz, CDCl_3) of **11b**



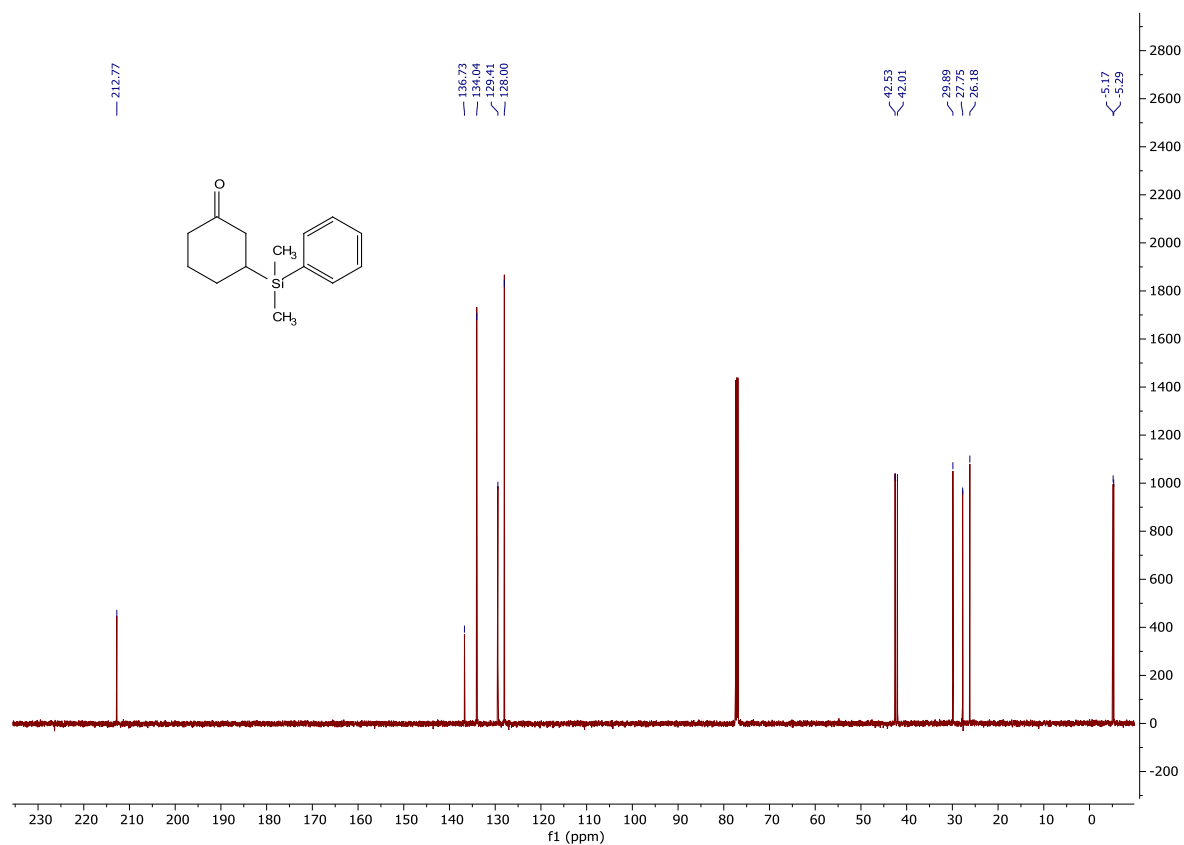
^{13}C NMR (126 MHz, CDCl_3) of **11b**



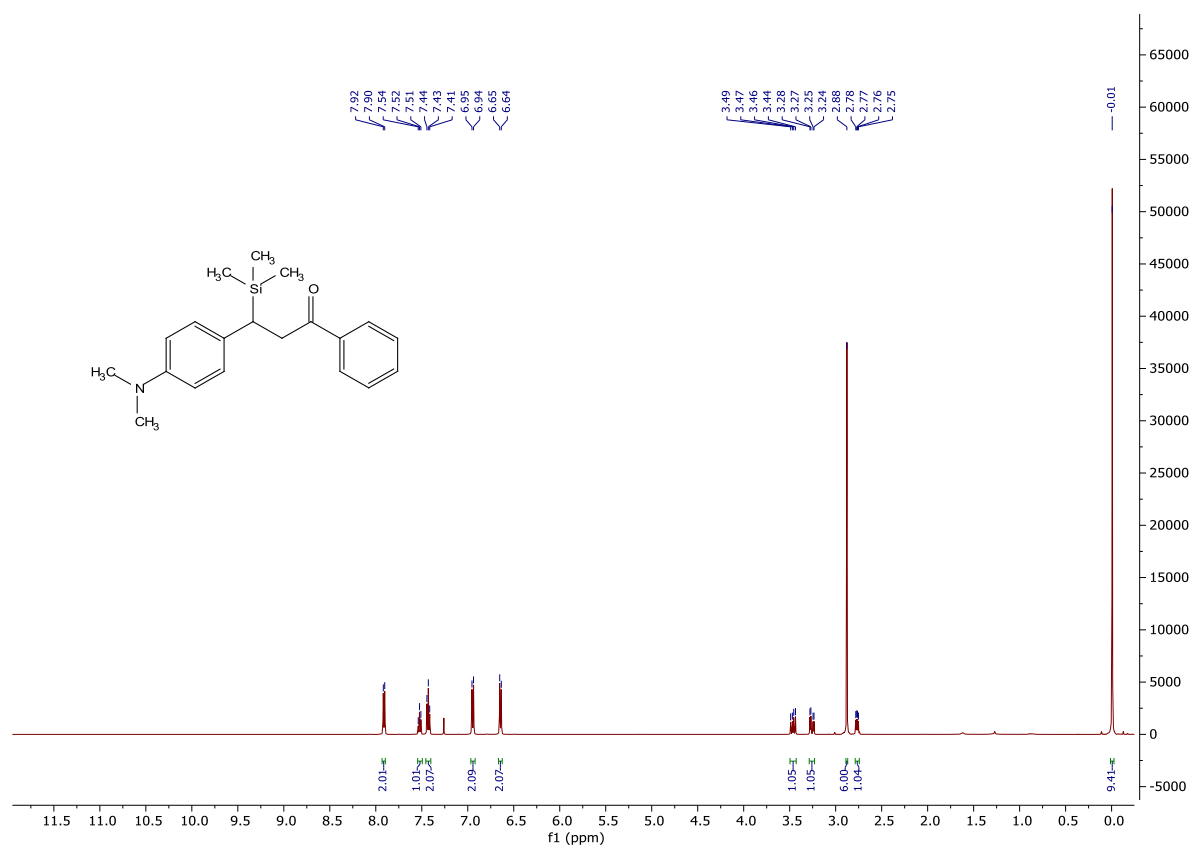
^1H NMR (500 MHz, CDCl_3) of **12b**



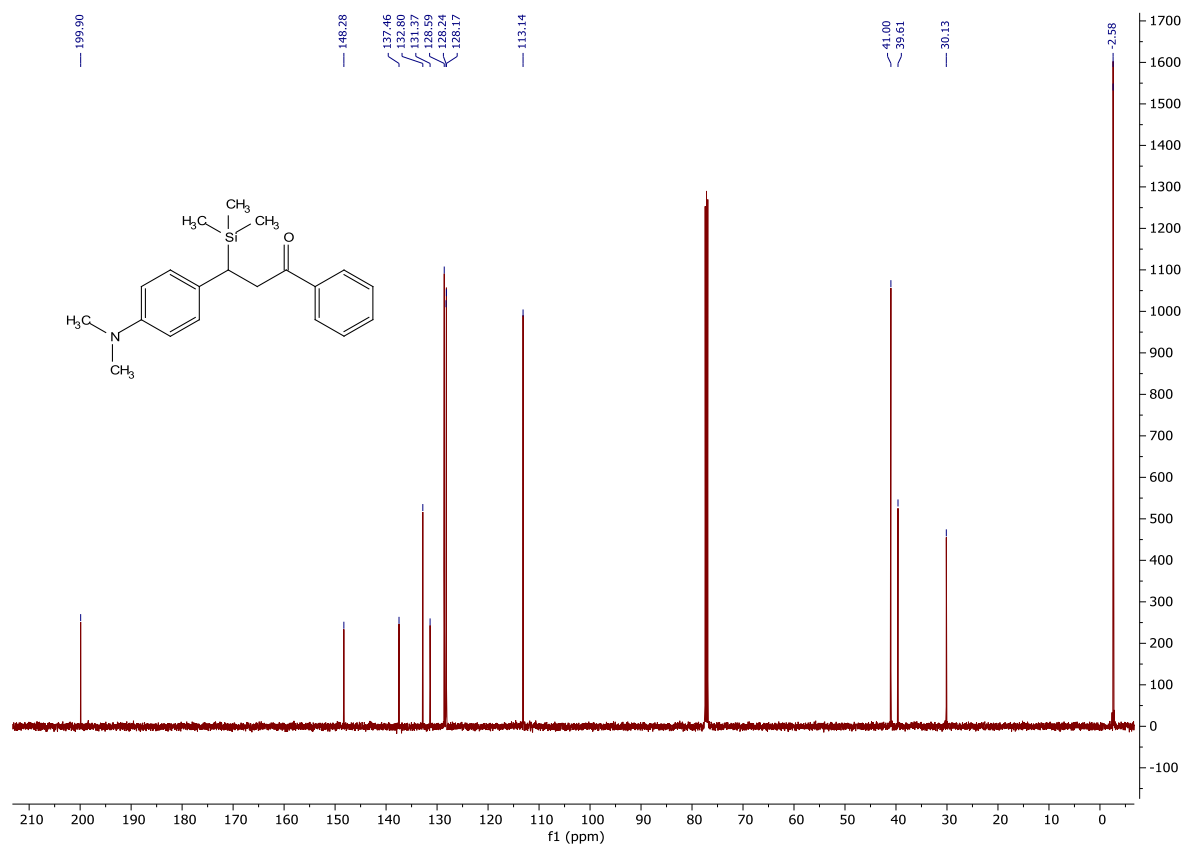
^{13}C NMR (126 MHz, CDCl_3) of **12b**



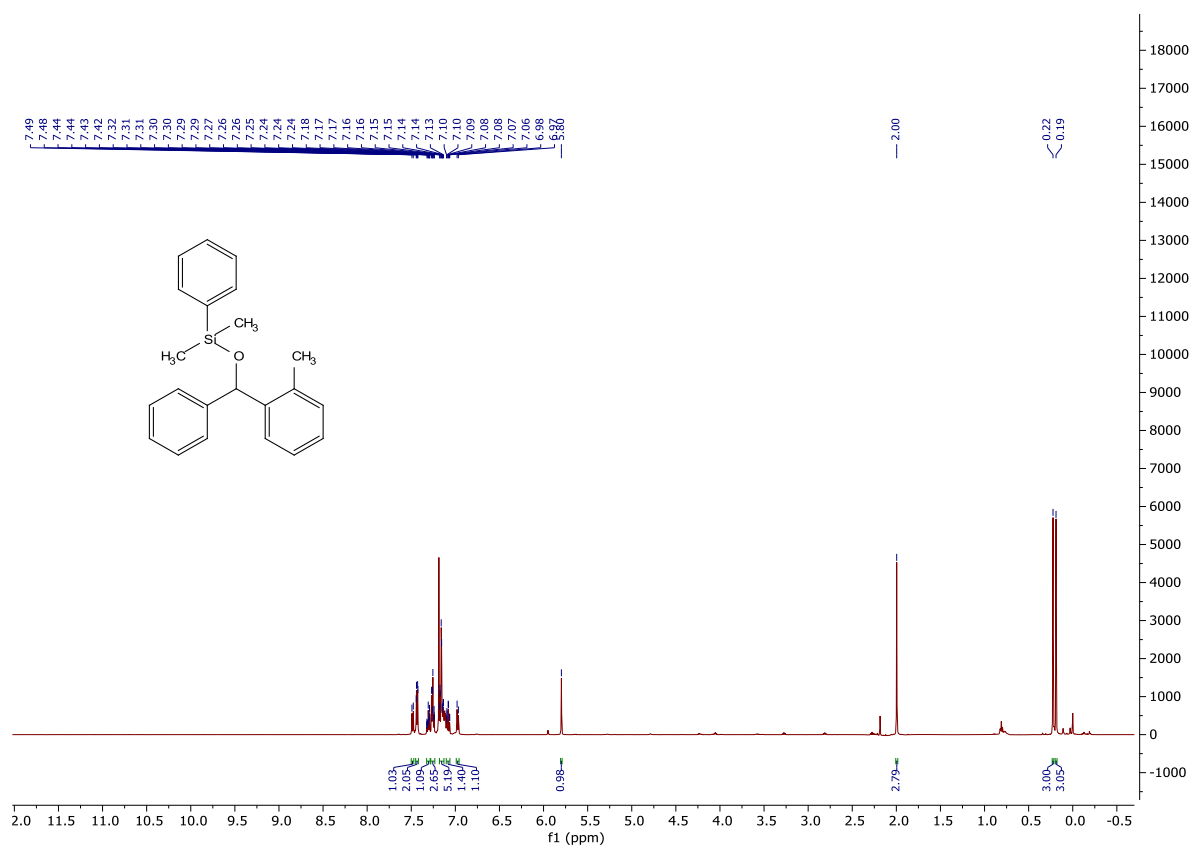
^1H NMR (500 MHz, CDCl_3) of **13b**



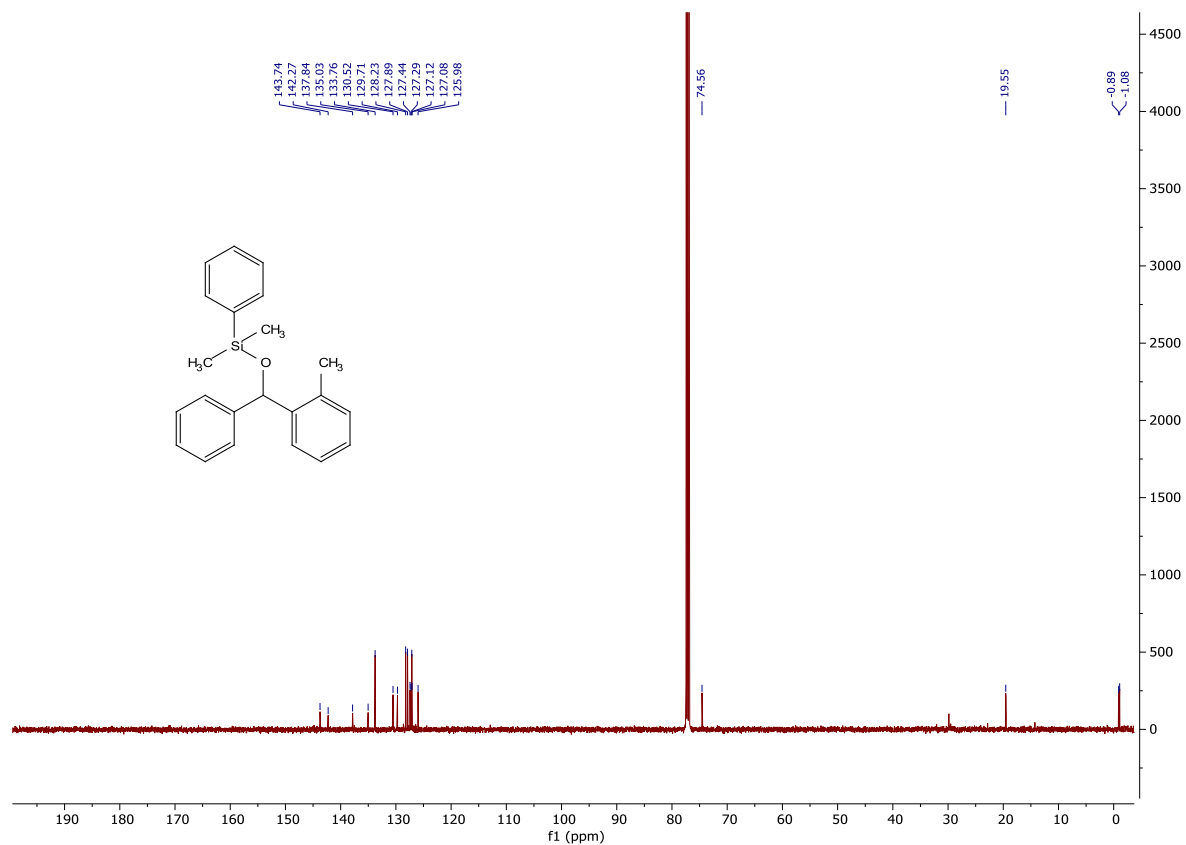
^{13}C NMR (126 MHz, CDCl_3) of **13b**



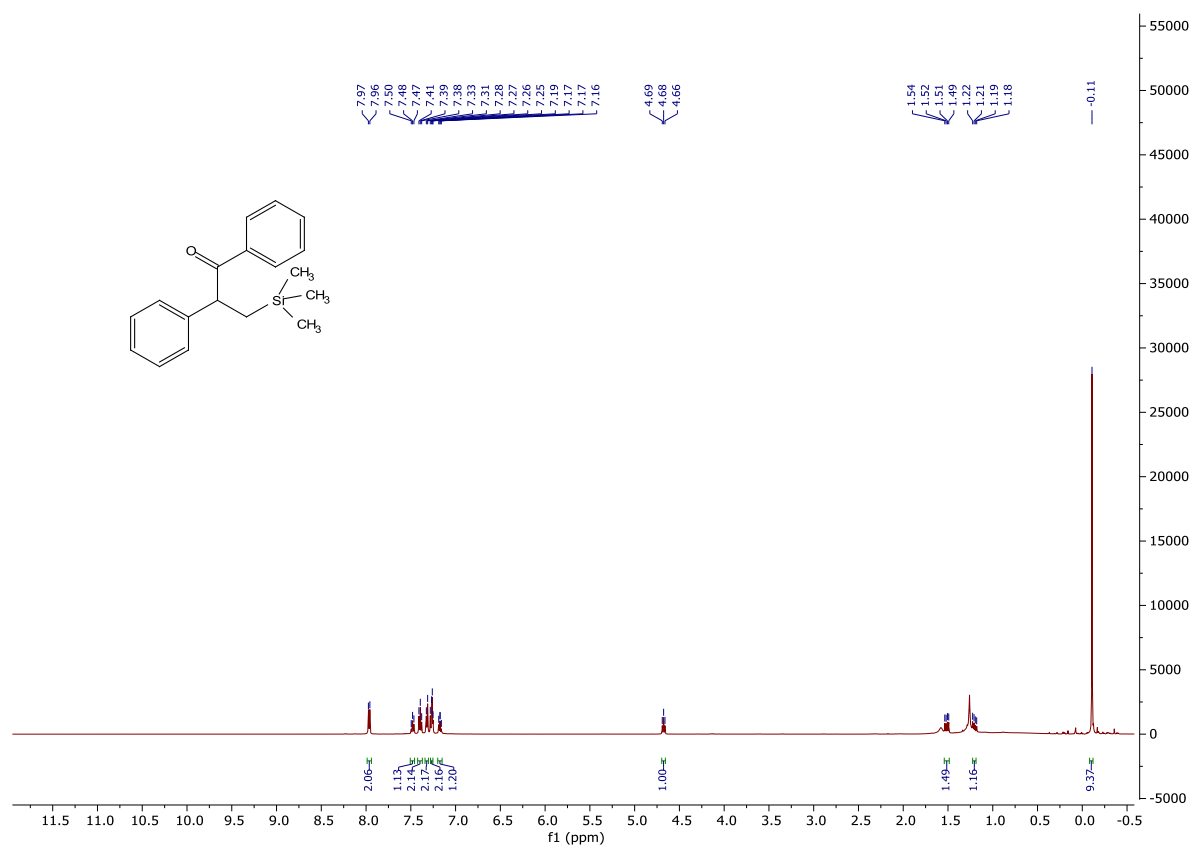
¹H NMR (500 MHz, CDCl₃) of **14b** (impure)



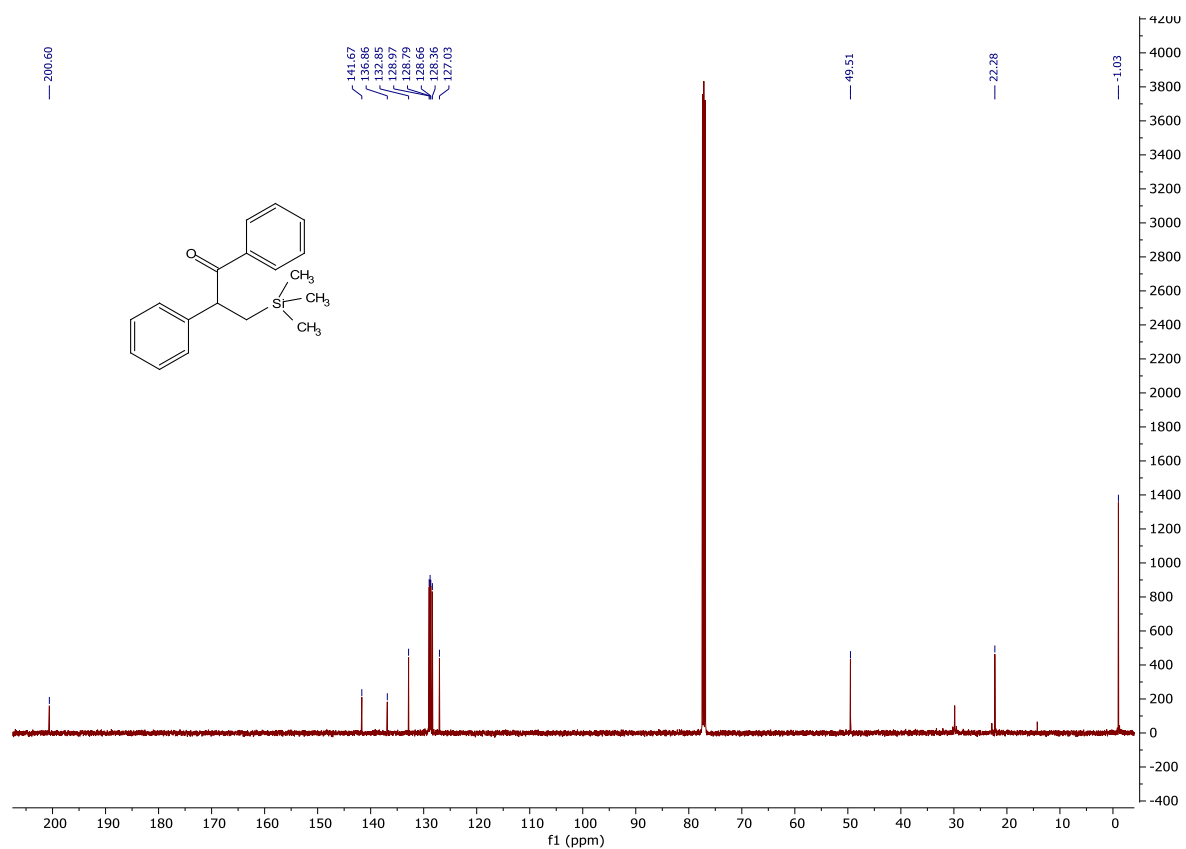
¹³C NMR (126 MHz, CDCl₃) of **14b** (impure)



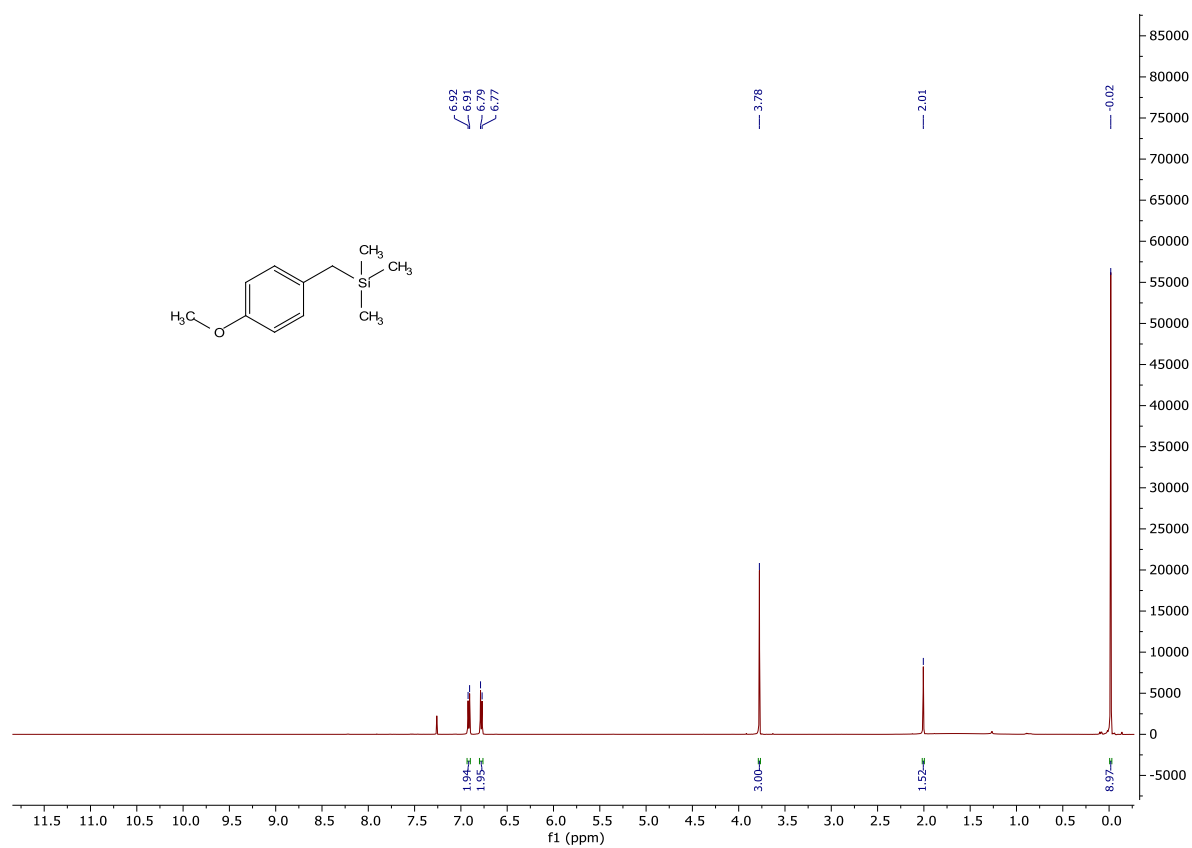
¹H NMR (500 MHz, CDCl₃) of 15b (impure)



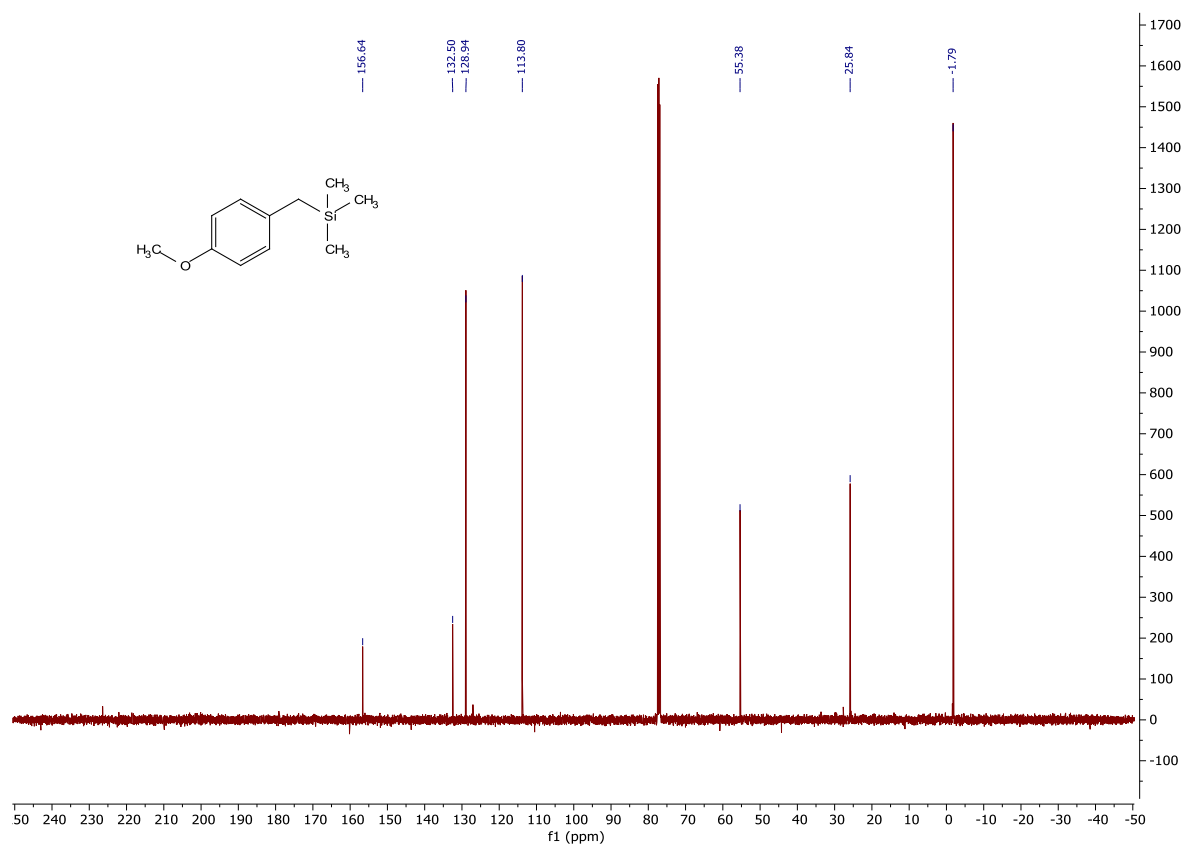
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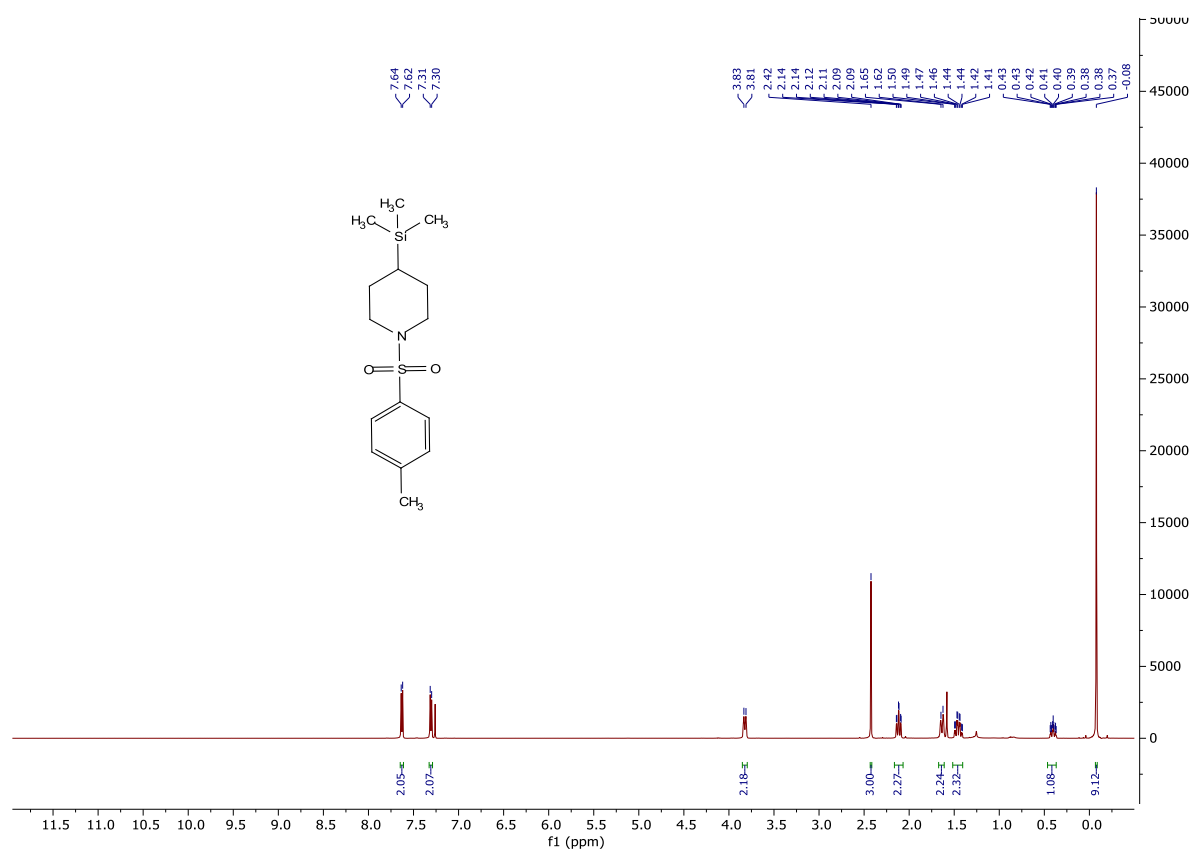
^1H NMR (500 MHz, CDCl_3) of **16b**



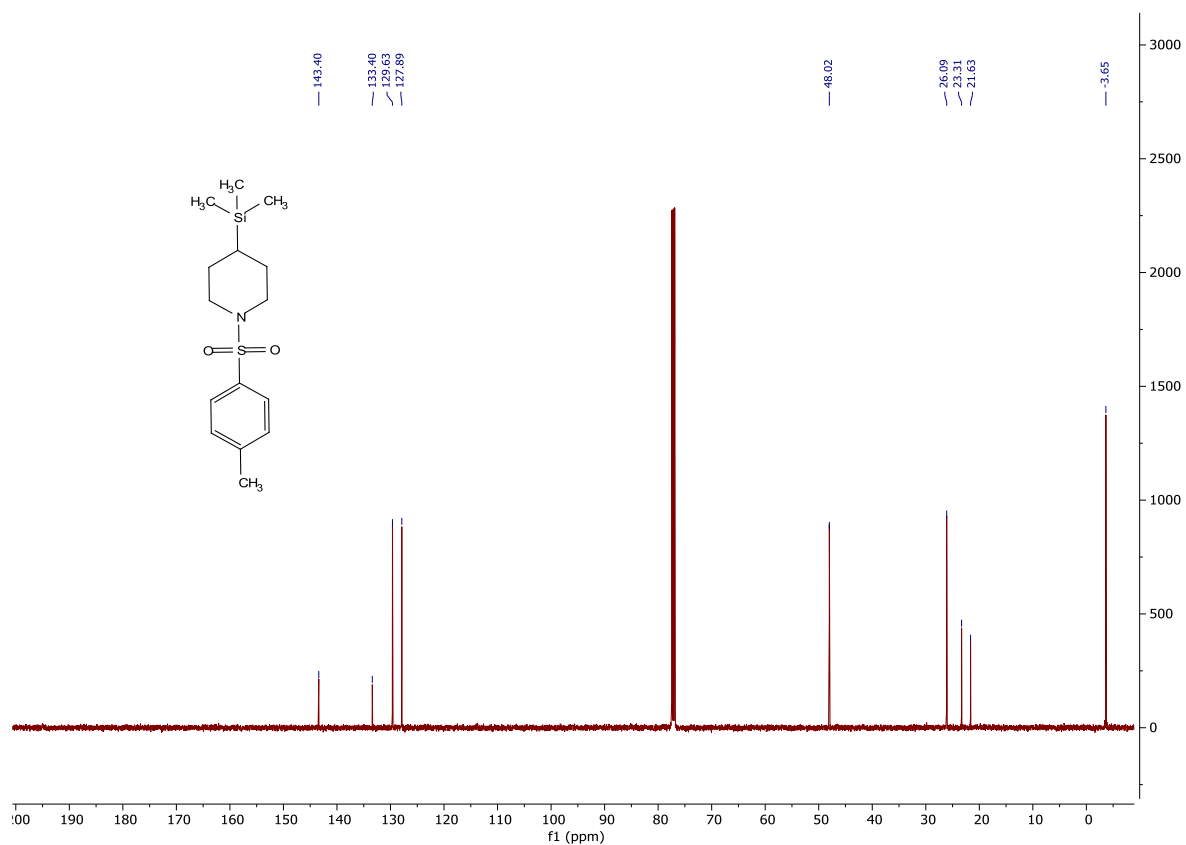
^{13}C NMR (126 MHz, CDCl_3) of **16b**



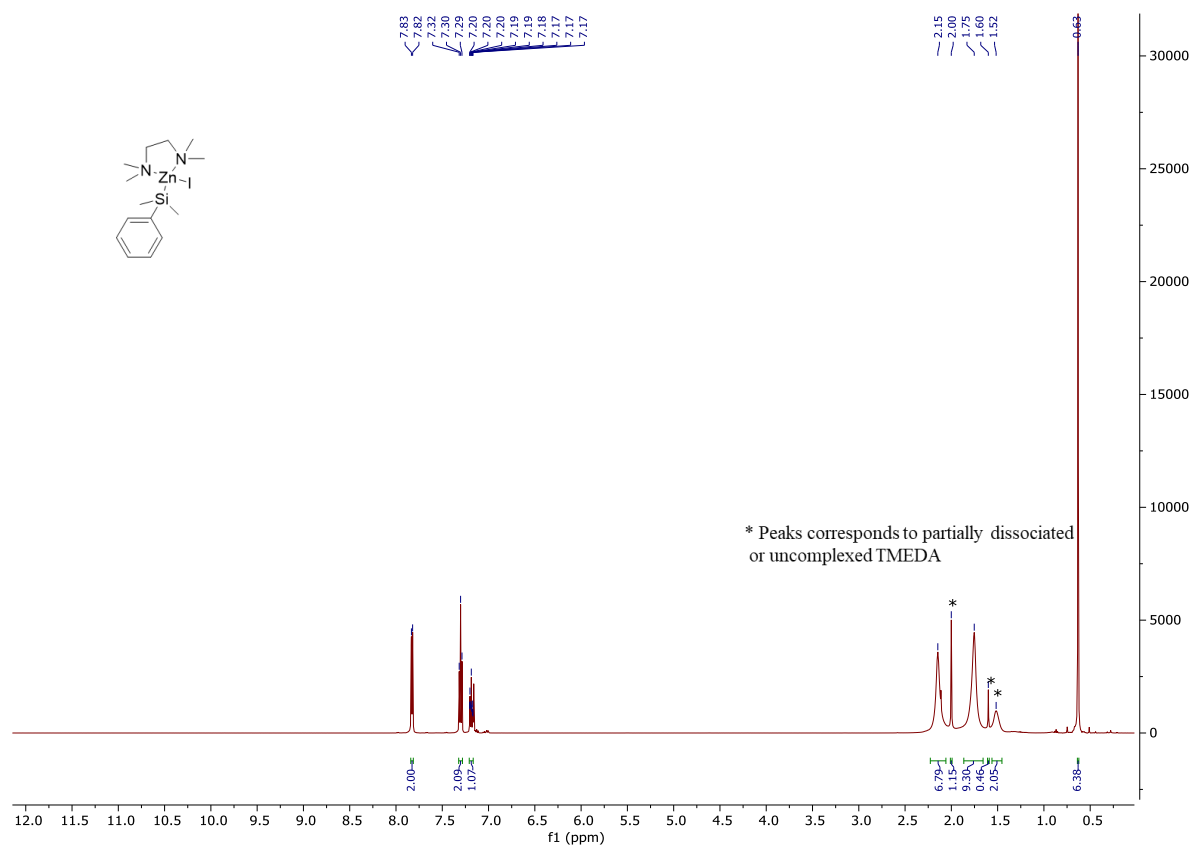
¹H NMR (500 MHz, CDCl₃) of 17b



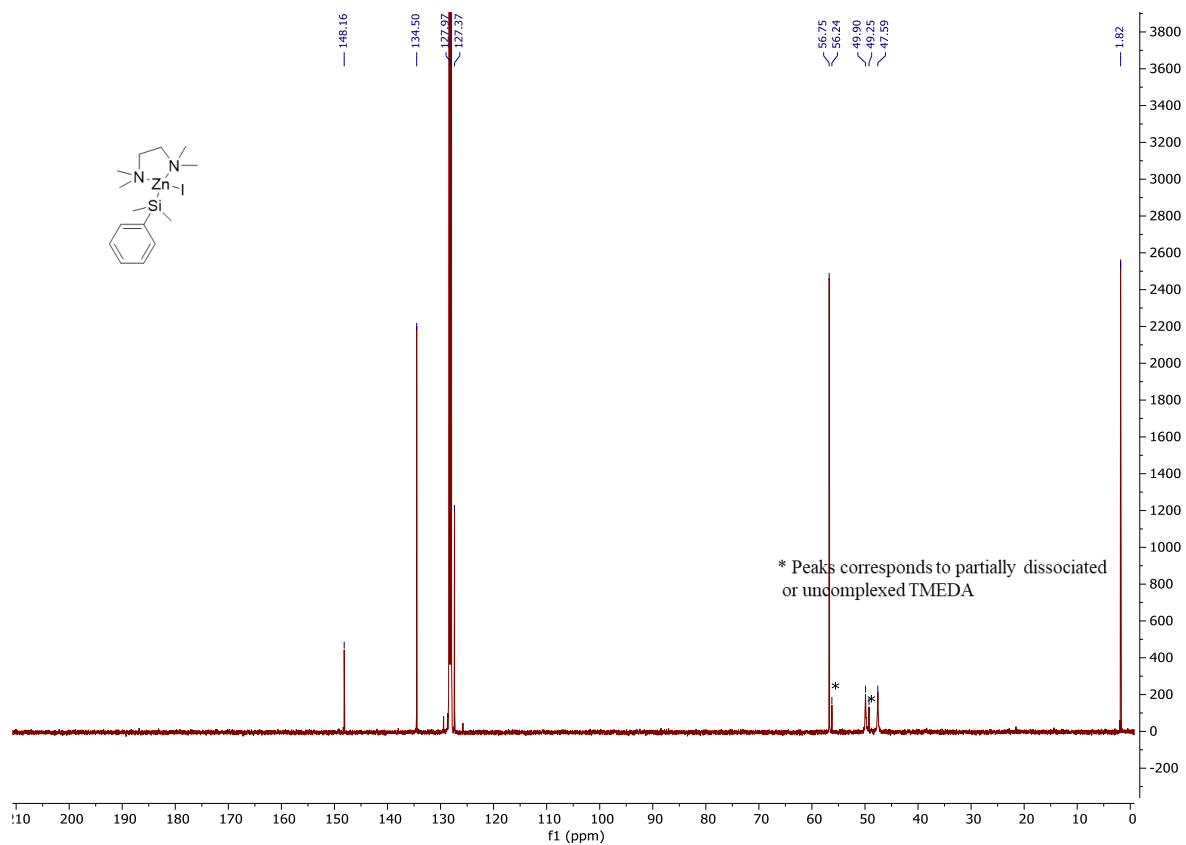
¹³C NMR (126 MHz, CDCl₃) of 17b



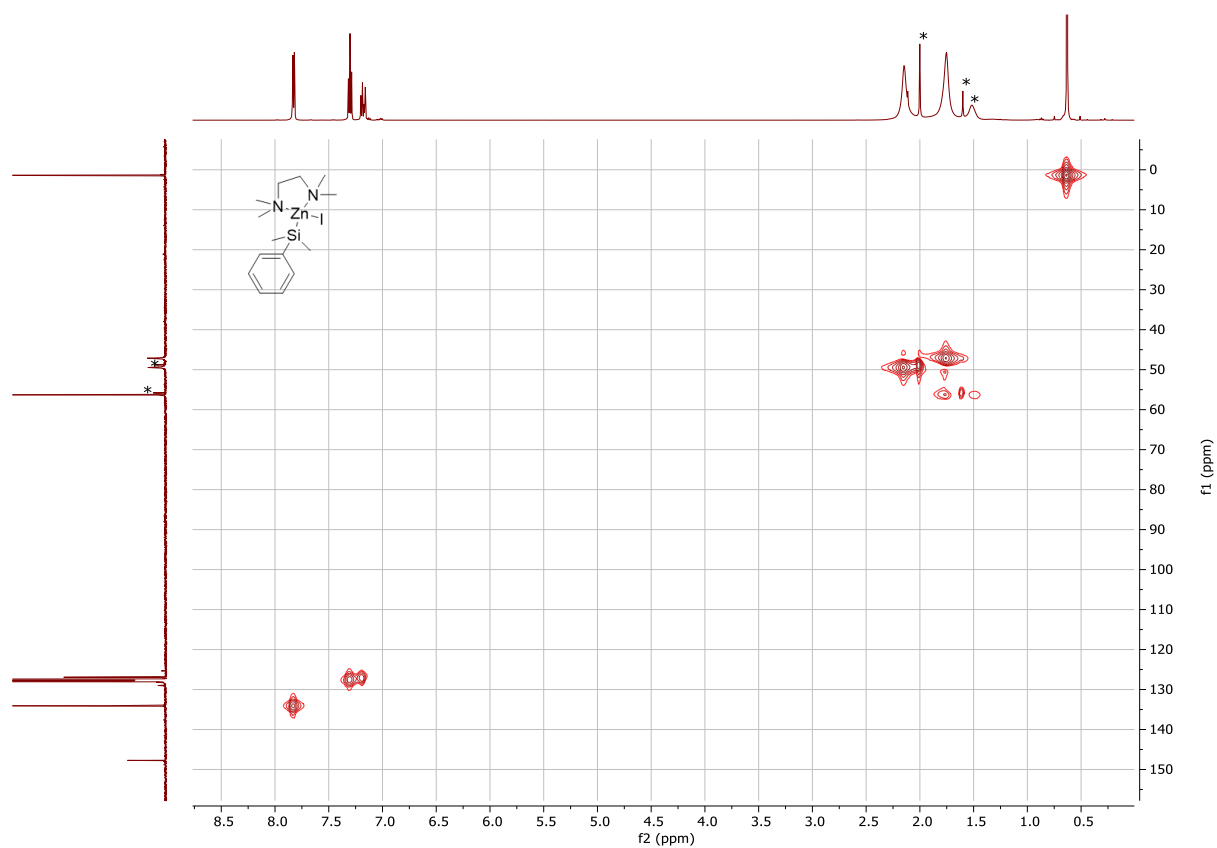
¹H NMR (500 MHz, C₆D₆) of 2a



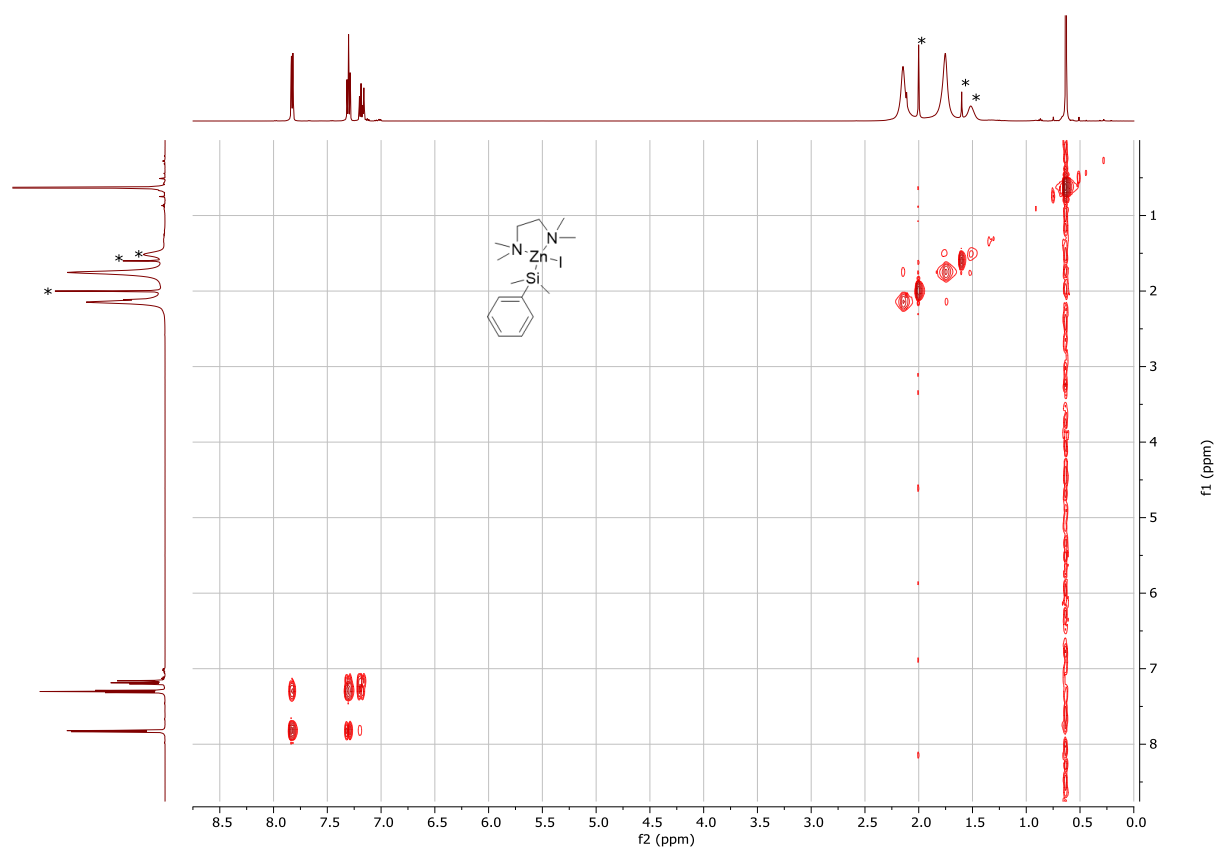
¹³C NMR (126 MHz, C₆D₆) of 2a



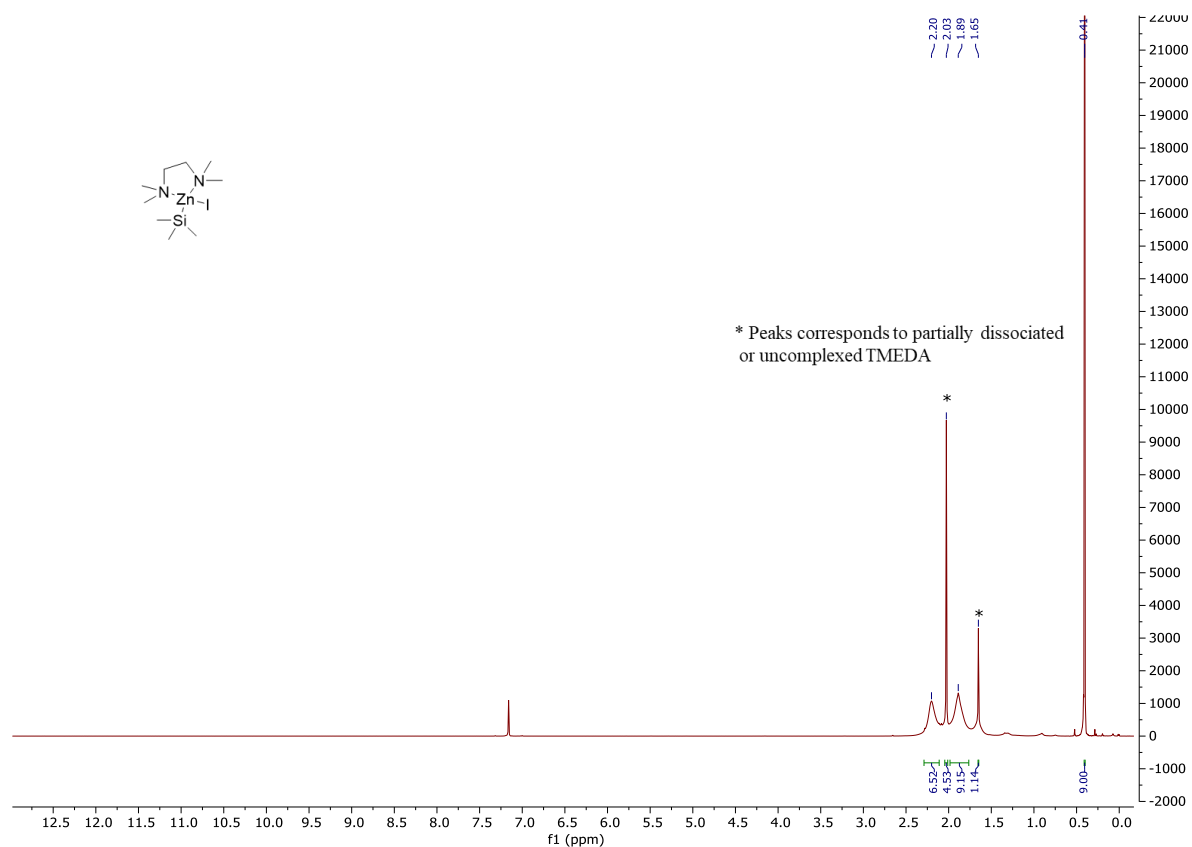
$^1\text{H}/^{13}\text{C}$ HMQC of 2a



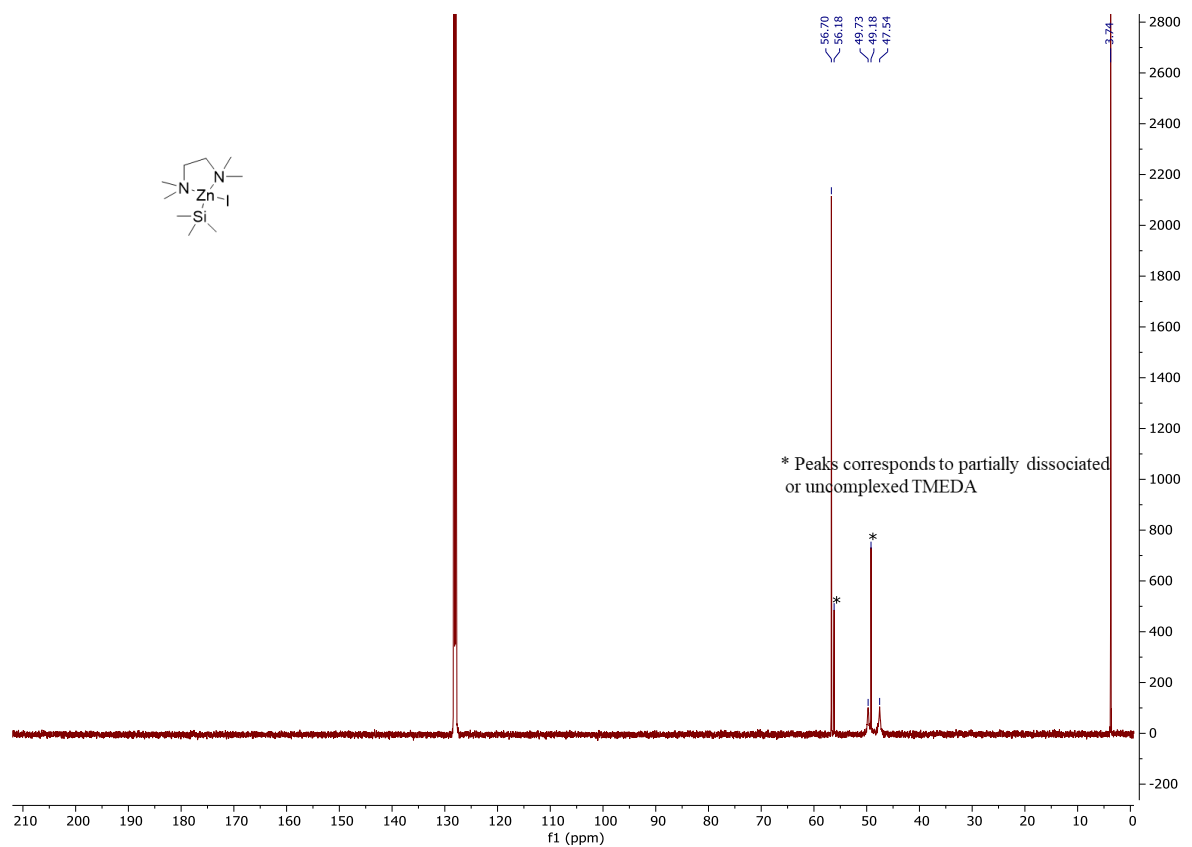
$^1\text{H}/^1\text{H}$ COSY of 2a



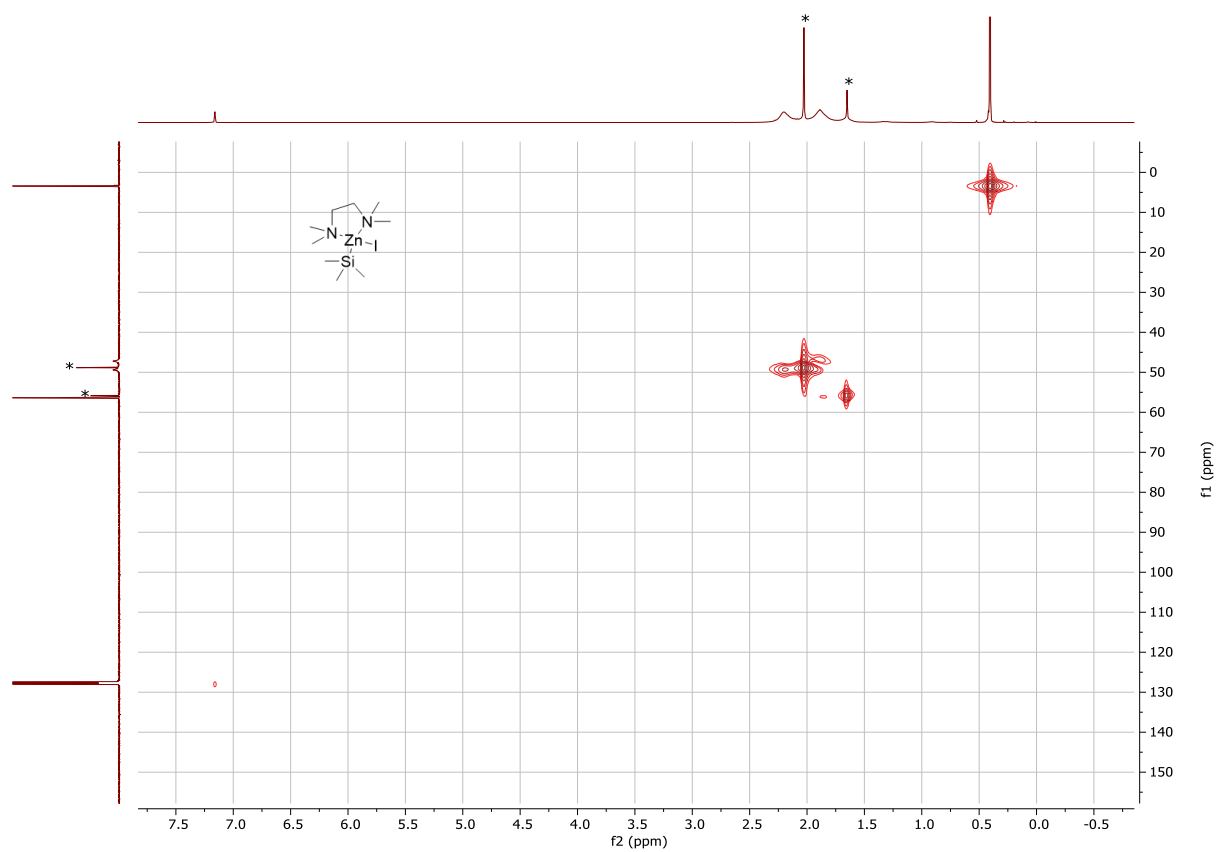
^1H NMR (500 MHz, C_6D_6) of **2b**



^{13}C NMR (126 MHz, C_6D_6) of **2b**



$^1\text{H}/^{13}\text{C}$ HMQC of 2b



$^1\text{H}/^1\text{H}$ COSY of 2b

