Supporting Information

Direct Trifluoromethylsilylation and Cyanosilylation of Aldehydes *via* Electrochemically Induced Intramolecular Pathway

Hui Yang, [†] Yongli Shen, [†] Zihui Xiao, Caiyan Liu, Kedong Yuan* and Yi Ding

Tianjin Key Laboratory of Advanced Functional Porous Materials, Institute for New Energy Materials & Low-Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, P. R. China.

[†] *These two authors* contribute equally to this work.

Email: kedong.yuan@tjut.edu.cn

General Information

Unless otherwise noted, all electrolysis reactions for products preparation were handled under air, and performed in an undivided electrolysis cell. Platinum plates (1 x 1 cm), copper plates (1 x 1 cm) and other electrodes (1 x 1 cm) were used for reaction optimization and substrate scope studies. HPLC grade solvents, *N,N'*-dimethylformamide (DMF), dichloromethane (DCM), acetonitrile and tetrahydrofuran (THF) were purchased from commercial sources and used without further purification. The new trifluoromethylsilylation and cyanosilylation products were fully characterized by using ^{1}H, ^{19}F, ^{13}C NMR and HRMS. ^{1}H NMR spectra were recorded on a Bruker GPX 400 MHz spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.26 ppm for ^{1}H NMR; 77.0 ppm for ^{13}C NMR), Coupling constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. Known trifluoromethylsilylation and cyanosilylation products were analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data. Mass spectra (HRMS) were conducted at Agilent Technologies 5973N (EI).

Graphical guide for reaction setup and reaction chronopotentiometry plot

Picture S1. Representative reaction set-up and purified products.

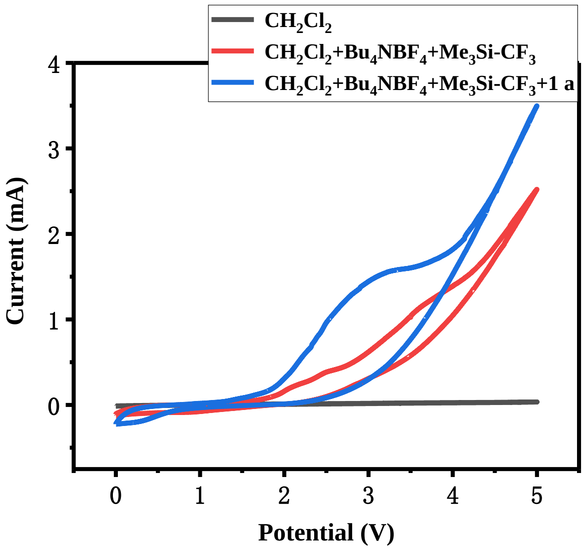


Figure S1. Cyclic voltammograms of **1a** and Me$_3$Si-CF$_3$
(**Conditions**: Pt working electrode, Cu counter, and Ag/AgCl reference electrodes, in 0.04 M of Bu$_4$NBF$_4$/CH$_2$Cl$_2$, scan rate: 0.05 V/s.)

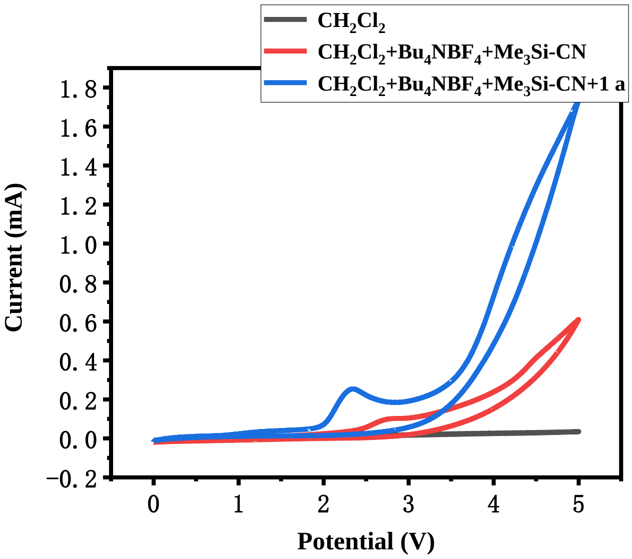


Figure S2. Cyclic voltammograms of **1a** and Me$_3$Si-CN
(**Conditions**: Pt working electrode, Cu counter, and Ag/AgCl reference electrodes, in 0.04 M of Bu$_4$NBF$_4$/CH$_2$Cl$_2$, scan rate: 0.05 V/s.)

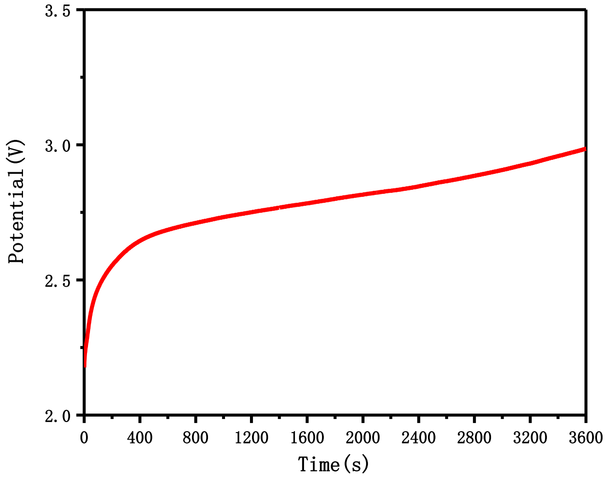


Figure S3. Chronopotentiometry plot at a constant current of 2 mA for electrolysis of **1a** and Me_3SiCF_3 in Bu_4NBF_4/CH_2Cl_2 electrolyte (vs. Ag/AgCl).

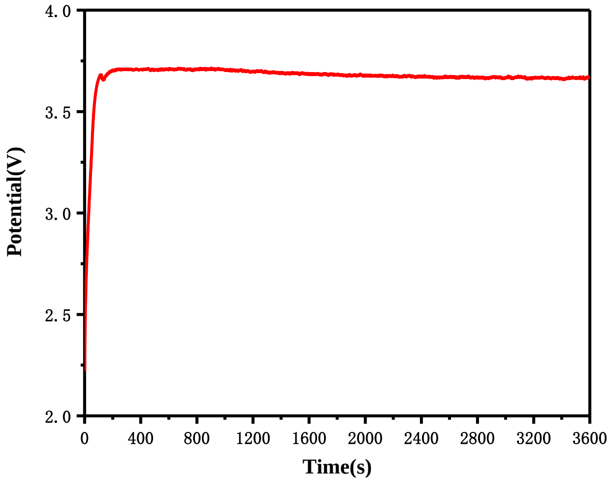
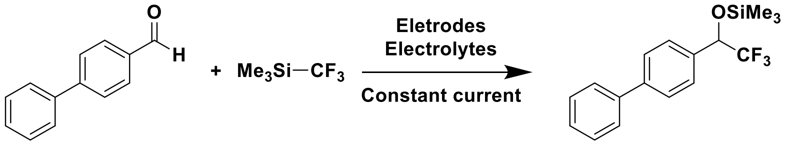


Figure S4. Chronopotentiometry plot at a constant current of 2 mA for electrolysis of benzaldehyde and Me_3SiCN in Bu_4NBF_4/CH_2Cl_2 electrolyte (vs. Ag/AgCl).

Reaction optimization for trifluoromethylsilation of 4-phenylbenzaldehyde

Table S1. Optimization of trifluoromethylsilylation of 4-phenylbenzaldehyde[a]



1a **3a**

Entry	Anode	Cathode	Electrolyte	Current (mA)	Solvent	Yield (%)
1	graphite	graphite	Bu_4NBF_4	2	CH_3CN	72
2	Pt	graphite	Bu_4NBF_4	2	CH_3CN	78
3	Pt	Ni	Bu_4NBF_4	2	CH_3CN	80
4[c]	Pt	Cu	Bu_4NBF_4	2	CH_3CN	86(71)
5	Pt	Au	Bu_4NBF_4	0	CH_3CN	84
6	Pt	RVC	Bu_4NBF_4	2	CH_3CN	63
7	RVC	Cu	Bu_4NBF_4	2	CH_3CN	68
8	Au	Cu	Bu_4NBF_4	2	CH_3CN	78
9	Ag	Cu	Bu_4NBF_4	2	CH_3CN	81
10	Nickel foam	Cu	Bu_4NBF_4	2	CH_3CN	80
11	Glass carbon	Cu	Bu_4NBF_4	2	CH_3CN	52
12	Pt	Cu	Bu_4NClO_4	2	CH_3CN	80
13	Pt	Cu	Bu_4NBr	2	CH_3CN	37
14	Pt	Cu	Bu_4NPF_6	2	CH_3CN	61
15	Pt	Cu	Bu_4NBF_4	2	CH_2Cl_2	100(93)
16	Pt	Cu	Bu_4NBF_4	2	DMF	0
17	Pt	Cu	Bu_4NBF_4	2	THF	0
18	Pt	Cu	Bu_4NBF_4	0	CH_2Cl_2	0
19	Pt	Cu	Bu_4NClO_4	2	CH_2Cl_2	99
20	Pt	Cu	Bu_4NClO_4	2	CH_2Cl_2	99
21[d]	Pt	Cu	Bu_4NBr	2	CH_2Cl_2	43
22	Pt	Cu	Bu_4NBF_4	1	CH_2Cl_2	95
23	Pt	Cu	Bu_4NBF_4	5	CH_2Cl_2	57

[a] Reaction conditions: **1a** (1.0 mmol); surpporting eletrolyte (0.2 mmol, 0.04 M); $TMSCF_3$ (1.5 mmol) in 5.0 mL solvent; Anode, 1 X1 cm plate, Cathode; 1 X1 cm plate; reaction in an undivided IKA ElectraSynth 2.0 cell, rt, 1.0 h. [b] Yields of **3a** were determined by GC using 50 μL dodecane as the internal standard; Isolated yields were given in parentheses. [c] **1a** was fully converted, while side product (cyanomethylation of **1a**) formed. [d] Reaction on 11 mmol (**1a**, 2.0g, 0.4 M solution in CH_2Cl_2).

Table S2. The representative conditions for trifluoromethylsilylation of aldehydes from Me_3SiCF_3

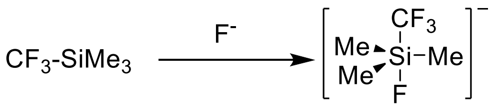
Entry	Catalysts	Temperature	Solvent	Time	Yields	Reference
1	tetrabutylammonium fluoride (TBAF)	0 °C -r.t.	THF	1 h	80-85%	Ref.15
2	AcOLi	0 °C	DMF	< 1 h	77-97%	Ref.16
3	$Cu(OAc)_2$/dppe	r.t.	toluene	0.5-2 h	55-99%	Ref.12
4	$Ti(O^iPr)_4$	r.t.	DMF	0.5-6 h	67-99%	Ref.12
5	MS 4 Å	r.t.	DMSO	1 h	53-100%	Ref.17
6	$P(t\text{-}Bu)_3$	r.t.	DMF	1 h	62-99%	Ref.18
7	N-Heterocyclic carbene	0 °C-r.t.	THF or DMF	1 h	71-91%	Ref.19
8	Trimethylamine *N*-Oxide	r.t.	DMF	< 1 h	76-90%	Ref.20
9	Electrochemical (Cat-Free)	r.t.	CH_2Cl_2	1 h	68-95%	This work

Computational details

All geometric optimization and reaction mechanism calculations presented in this work are performed using the generalized gradient approximation (GGA)-Perdew, Burke and Ernzerhof (PBE)[1] as implemented in the all-electron DMol3 code[2,3]. Double numerical plus polarization (DNP) basis set was used throughout the calculation. The convergence criteria were set to be 2×10^{-5} Ha for energy, 0.004 $HaÅ^{-1}$ for force, and 0.005 Å for displacement convergence, respectively. A self-consistent field (SCF) density convergence with a threshold value of 1×10^{-6} Ha was specified. All electronic property analyses are deal with Multiwfn software[4]. Single point energy calculation also carried out for all stationary points involved in the potential energy surface using Gaussian09 software[5], with the aim of getting wave function files needed for the qualitative analysis the electronic characters.

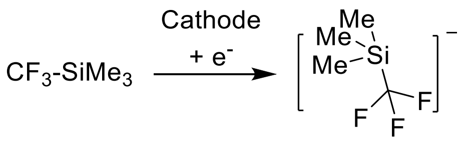
The Gibbs free energy changes (ΔG) of F anion to $[FMe_3SiCF_3]^-$ in THF (B3LYP/6-311G* and SMD solvent model) environment.

$$F^- + (CH_3)_3SiCF_3 \rightarrow [F(CH_3)_3SiCF_3]^- \qquad \Delta G = -0.33\ eV$$



The Gibbs free energy changes (ΔG) for cathode activation of Me_3SiCF_3 to $[Me_3SiCF_3]^-$ in CH_2Cl_2 environment

$$(CH_3)_3SiCF_3 + e^- \rightarrow [Me_3SiCF_3]^- \qquad \Delta G = -0.29\ eV$$



The calculation results show that both processes could proceed spontaneously. And we have optimized the two intermediates (Figure. 3 in the manuscript) involved in the article from a neutral form. As shown in Figure S5. a and c, the anionic intermediate structures are selected as initial guess to optimize its electrically neutral forms. The computational results show that the electrically neutral intermediates are unstable, and they will automatically transform into the reactants after geometric optimization (Figure S5. b and d). Therefore, it can be speculated the two intermediates involved in the article should exist in the form of anion.

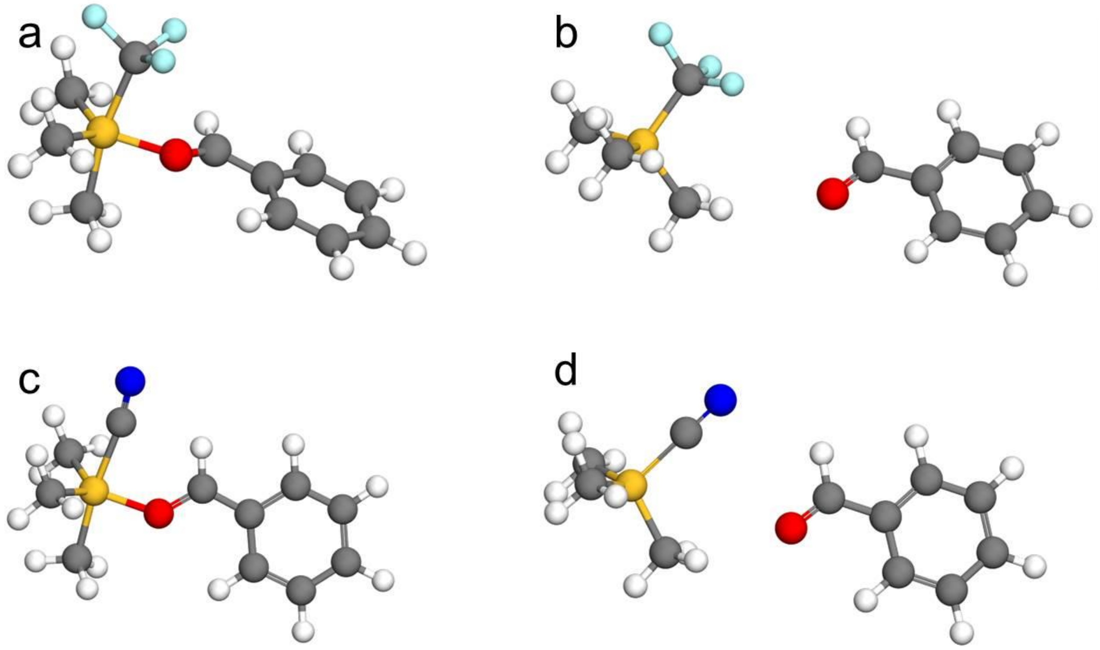


Figure S5. Optimized electrically neutral structures of the intermediate involved in this work. (a. Initial predicted structure of intermediate involve in the reaction between $(CH_3)_3Si\text{-}CF_3$ and PhCHO; b. optimized structure of electrically neutral form of a; c. Initial predicted structure of intermediate involved in the reaction between $(CH_3)_3Si\text{-}CN$ and PhCHO, d. optimized structure of electrically neutral form of c. Grey sphere: carbon, Yellow sphere: Si, Red sphere: O, White sphere: H, Light blue sphere: F and Blue sphere: N).

Calculation method:

The calculation of Gibbs free energy change is realized through the Gaussian09 software. B3LYP/6-311G* and SMD solvent model is used for the Geometric optimization and vibration analysis for all species (F^-, Me_3SiCF_3, $[FMe_3SiCF_3]^-$ and $[Me_3SiCF_3]^-$) to get the thermal correction to Gibbs Free Energy (G1), B2PLYPD3/def2TZVP is used to calculate higher precision electron energy under vacuum (G2), M052X/6-31G* is used to calculate the free energy of dissolution(G3). Gibbs free energy changes (ΔG) is calculated through

$$\Delta G = G2 + G1 + G3 + 1.89 kcal/mol$$

1.89kcal/mol is the free energy change of 1 atm (gas phase) → 1M concentration (solution) at 298.15K.

Reaction procedure A: trifluoromethylsilylation of aldehydes

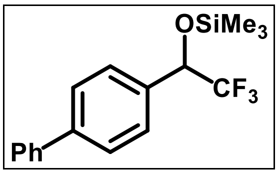
As a typical experiment, an undivided ElectroSyn 2.0 cell (10 mL) was equipped with platinum plates (anode, 1 x 1 cm) and copper plates (cathode,1 x 1 cm) as electrodes. To this electrolysis cell, 4-phenylbenzaldehyde (**1a**, 1.0 mmol, 182.2 mg), Bu_4NBF_4 (0.20 mmol, 65.9 mg), Me_3SiCF_3 (1.5 mmol, 213.3 mg) and 5 mL CH_2Cl_2 were added. The mixture was electrolyzed under 2 mA constant current at room temperature with magnetic stirring for 1 hour. Then, 50 µL dodecane was added to the reaction solution as the internal standard and a partial solution was filtered through a short silica gel column for GC and GC-MS analysis. The combined solution was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **3a** in 93% isolated yield.

Reaction procedure B: cyanosilylation of aldehydes

As a typical experiment, an oven dried beaker (10 mL) was equipped with platinum plates (anode, 1 x 1 cm) and copper plates (cathode,1 x 1 cm) as electrodes, which were connected to an electrochemical workstation regulated power supply. To this electrolysis cell, benzaldehyde (1.0 mmol, 106.1 mg), Bu_4NBF_4 (0.20 mmol, 65.9 mg), Me_3SiCN (2.0 mmol, 198.4 mg) and 5 mL CH_2Cl_2 were added. The mixture was electrolyzed under 2 mA constant current at room temperature with magnetic stirring for 1 hour. Then, A partial solution was filtered through a short silica gel column for GC and GC-MS analysis. The combined solution was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the desired product **4a** in 90% isolated yield.

Analytical Data

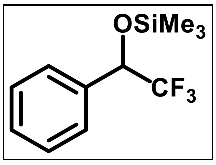
1-([1,1’-Biphenyl]-4-yl)-2,2,2-trifluoroethoxy)trimethylsilane (3a)[6]



3a was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless solid in 93% yield, 302 mg. **3a** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.67 (m, 9H), 4.99 (q, *J* = 6.5 Hz, 1H), 0.17 (s, 9H).

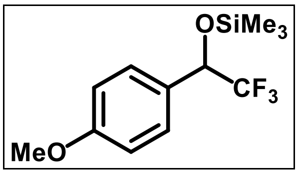
Trimethyl(2,2,2-trifluoro-1-(4-iodophenyl)ethoxy)silane (3b)[6]



3b was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 90% yield, 223 mg. **3b** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32−7.50 (m, 5H), 4.88 (q, *J* = 6.5 Hz, 1H), 0.04 (s, 9H).

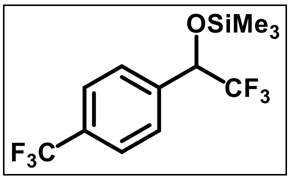
Trimethyl(2,2,2-trifluoro-1-(4-methoxyphenyl)ethoxysilane (3c)[7]



3c was prepared according to the general procedure A on 1.0 mmol scale for 4 h, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 80% yield, 223 mg. **3c** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 Hz, CDCl$_3$) δ 7.36 (d, *J*=8.6 Hz, 2H), 6.90 (d, *J*=8.6 Hz, 2H), 4.90 (q, *J*=6.6 Hz, 1H), 3.80 (s, 3H), 0.10 (s, 9H).

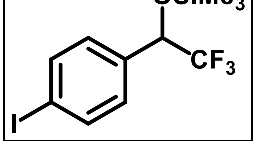
Trimethyl(2,2,2-trifluoro-1-(4-trifluoromethyl)phenyl)ethoxy)silane (3d)[10]



3d was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 81% yield, 256 mg. **3d** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 Hz, CDCl$_3$) δ 7.65 (d, *J*=8.3 Hz, 2H), 7.59 (d, *J*=8.3 Hz, 2H), 4.97 (q, *J*=6.5 Hz, 1H), 0.14 (s, 9H).

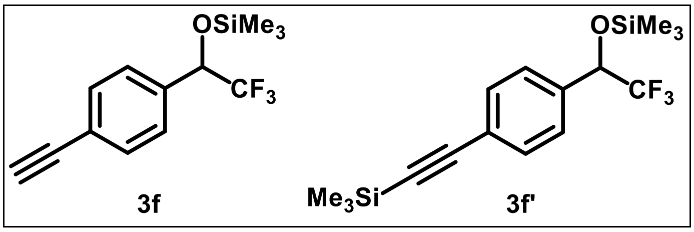
Trimethyl(2,2,2-trifluoro-1-(4-iodophenyl)ethoxy)silane (3e)



3e was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 96% yield, 359 mg.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70–7.54 (m, 2H), 7.18–7.02 (m, 2H), 4.79 (dt, *J* = 13.1, 6.5 Hz, 1H), 0.13 – -0.10 (m, 9H); ^{19}F NMR (376 MHz, CDCl$_3$) δ -78.37 (d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.5, 135.1, 129.3, 123.8 (q, *J* = 282.3 Hz), 95.2, 72.7 (q, *J* = 32.3 Hz), -0.4. HRMS calculated for $C_{11}H_{13}F_3IOSi^-$: [M-H]$^-$ 372.9732, found 372.9735.

(1-(4-ethynylphenyl)-2,2,2-trifluoroethoxy)trimethylsilane (3f)

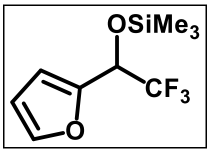


3f 3f'

3f was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 81% yield, 221 mg (obtained as an inseparable mixture of **3f** and partial of **3f'**).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70–7.54 (m, 2H), 7.18–7.02 (m, 2H), 4.79 (dt, *J* = 13.1, 6.5 Hz, 1H), 0.13 – -0.10 (m, 9H); ^{19}F NMR (376 MHz, CDCl$_3$) δ -78.37 (d, *J* =6.4 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 135.7, 131.9, 127.4, 123.8 (q, *J* =282.3 Hz), 123.0, 95.1, 83.0, 72.7 (q, *J* = 32.3 Hz), -0.3.

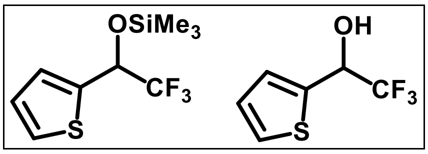
Trimethyl(2,2,2-trifluoro-1-(furan-2-yl)ethoxy)silane (3g)[12]



3g was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 83% yield, 198 mg. **3g** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (CDCl$_3$) δ 7.42-7.43 (m, 1 H), 6.37-6.47(m, 2 H), 4.98 (q, *J* =6.4 Hz, 1 H), 0.13 (s, 9 H).

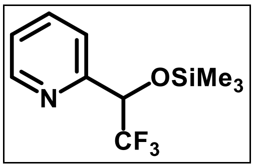
Trimethyl(2,2,2-trifluoro-1-(thiophen-2-yl)ethoxy)silane (3h)[12]



3h was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 91% yield, 198 mg (contains 12% desilylated alcohol product, 22mg). **3h** and desilylated alcohol product were analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR ($CDCl_3$) δ 7.42-7.43 (m, 1 H), 6.37-6.47(m, 2 H), 4.98 (q, *J* =6.4 Hz, 1 H), 0.13 (s, 9 H).

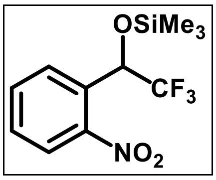
2-(2,2,2-trifluoro-1-((trimethylsilyl)oxy)ethyl)pyridine (3i)[5]



3i was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 87% yield, 217 mg. **3i** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.56 (dq, *J* = 1.0 Hz, *J* = 5.0 Hz, 1 H), 7.75 (td, *J* = 1.5, 7.5 Hz, 1 H), 7.63 (d, *J* = 7.5 Hz, 1 H), 7.28 (ddd, *J* = 1.5, 5.0, 7.5 Hz, 1 H), 5.08 (q, *J* = 6.5 Hz, 1 H), 0.11 (s, 9 H)

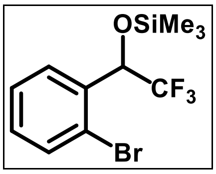
Trimethyl(2,2,2-trifluoro-1-(2-nitrophenyl)ethoxy)silane (3j)[11]



3j was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a yellow oil in 95% yield, 279 mg. **3j** was analyzed by GC-MS, HRMS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* =8.1 Hz, 1H), 7.92 (d, *J* =8.1 Hz, 1H), 7.66 (t, *J* =7.6 Hz, 1H), 7.50 (dd, *J* = 11.1, 4.5 Hz, 1H), 6.16 (q, *J* =5.8 Hz, 1H), 0.16 (s, 9H). HRMS calculated for $C_{11}H_{13}F_3NOSi^-$: $[M-H]^-$ 292.0617, found 292.0611.

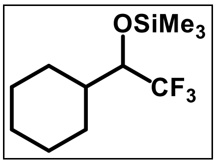
(1-(2-bromophenyl)-2,2,2-trifluoroethoxy)trimethylsilane (3k)



3k was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless solid in 93% yield, 304 mg.

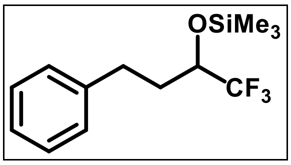
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.24 (td, *J* = 7.7, 1.1 Hz, 1H), 7.13–7.07 (m, 1H), 5.40 (q, *J* = 6.2 Hz, 1H), 0.00–-0.02 (m, 9H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.99 (d, *J* = 6.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 132.6, 130.6, 130.2, 127.6, 123.4, 124.2 (q, *J* = 282.8 Hz), 71.6 (q, *J* = 32.7 Hz), -0.38. HRMS calculated for $C_{11}H_{15}F_3BrOSi^+$: $[M+H]^+$ 327.0028, found 327.0091.

Trimethyl- (1-Cyclohexyl-2,2,2-trifluoromethyl-methoxy)-silane (3l)[7]



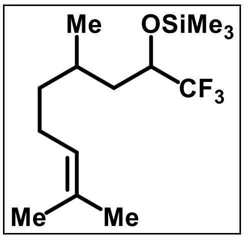
3l was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 68% yield, 173 mg. **3l** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.
^{1}H NMR (400 Hz, $CDCl_3$) δ 0.15 (s, 9H), 1.00-2.10 (m, 11H), 3.60-3.82 (m, 1H)

Trimethyl-(3-phenyl-1-trifluoromethyl-propoxy)-silane (3m)[7]



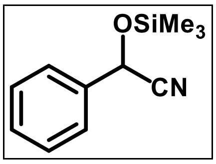
3m was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 92% yield, 254 mg. **3m** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.
^{1}H NMR (400 Hz, $CDCl_3$) δ 7.10-7.45 (m, 5H), 3.80-3.98 (m, 1H), 2.50-2.82 (m, 2H), 1.80-2.15 (m, 2H), 0.22 (s, 9H).

Trimethyl((1,1,1-trifluoro-4,8-dimethylnon-7-en-2-yl)oxy)silane (3n)



3n was prepared according to the general procedure A on 1.0 mmol scale for 4 h, and isolated by column chromatography using petroleum ether as a colorless oil in 76% yield, 225 mg (mixed diastereoisomers).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14–5.01 (m, 1H), 4.04–3.90 (m, 1H), 2.11–1.87 (m, 2H), 1.73–1.57 (m, 7H), 1.51 (m, 1H), 1.46–1.20 (m, 3H), 1.17–1.03 (m, 1H), 0.99 – 0.84 (m, 3H), 0.18 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.92– -79.35 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5, 125.4 (q, *J* =282.4 Hz), 124.4, 69.3 (q, *J* =30.6 Hz), 38.0, 37.4, 35.7, 25.7, 25.2(d, *J* =27.2 Hz), 18.4, 17.5, -0.1. HRMS calculated for $C_{14}H_{28}F_3OSi^+$: $[M+H]^+$ 297.1862, found 297.1834.

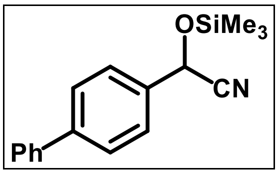
2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (4a)[8]



4a was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 90% yield, 185 mg. **4a** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.39 (m, 5H), 5.50 (s, 1H), 0.23 (s, 9H).

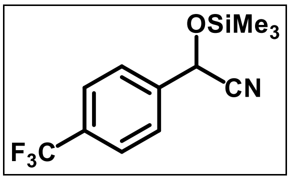
2-([1,1'-biphenyl]-4-yl)-2-((trimethylsilyl)oxy)acetonitrile (4b)[8]



4b was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 73% yield, 205mg. **4b** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.60−7.51 (m, 7H), 7.45−7.41 (m, 2H), 7.36−7.33 (m, 1H), 5.53 (s, 1H), 0.25 (s, 9H).

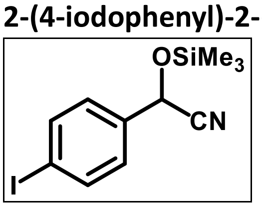
2-(4-trifluoromethylphenyl)-2-trimethylsilyloxyacetonitrile (4c)[9]



4c was prepared according to the general procedure B on 1.0 mmol scale for 6 h, and isolated by column chromatography using petroleum ether/ethyl acetate as a pale-yellow oil in 65% yield, 177 mg. **4c** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* =8.2 Hz, 2H), 7.61 (d, *J* =8.2 Hz, 2H), 5.55 (s, 1H), 0.27 (s, 9H).

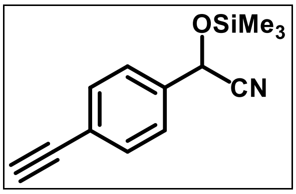
2-(4-iodophenyl)-2-((trimethylsilyl)oxy)acetonitrile (4d)



4d was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 76% yield, 174 mg (obtained as an inseparable mixture of **4d** and desilylated alcohol product after purification).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.43 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 130.8, 128.1, 118.7, 96.2, 63.1, -0.3. HRMS calculated for $C_{11}H_{15}NOISi^+$: $[M+H]^+$ 331.9968, found 332.0086.

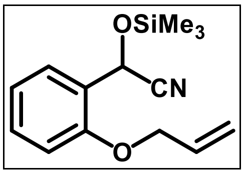
2-(4-ethynylphenyl)-2-((trimethylsilyl)oxy)acetonitrile (4e)



4e was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil, 96% yield, 220 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* =8.3 Hz, 2H), 7.43 (d, *J* =8.3 Hz, 2H), 5.49 (s, 1H), 3.13 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 132.7, 126.2, 123.3, 118.8, 82.8, 78.3, 63.2, -0.3. HRMS calculated for $C_{13}H_{16}NOSi^+$: $[M+H]^+$ 230.1001, found 230.1044.

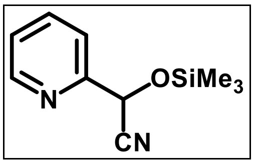
2-(2-(allyloxy)phenyl)-2-((trimethylsilyl)oxy)acetonitrile (4f)



4f was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 92% yield, 240 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.33 (td, *J* =11.5, 4.2 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.15–5.99 (m, 1H), 5.83 (s, 1H), 5.43 (d, *J* =17.3 Hz, 1H), 5.32 (d, *J* =10.5 Hz, 1H), 4.67–4.57 (m, 2H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 132.7, 130.3, 127.5, 124.8, 121.1, 119.3, 118.0, 111.7. HRMS calculated for $C_{14}H_{20}NO_2Si^+$: $[M+H]^+$ 262.1263, found 262.1259.

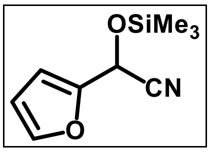
2-(pyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (4g)[13]



4g was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 92% yield, 190 mg. **4g** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (d, *J* =6.1 Hz, 1 H), 7.79 (t, *J* =8.0 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.30−7.28 (m, 1 H), 5.58 (s, 1 H), 0.26 (s, 9 H).

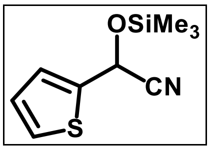
2-(furan-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (4h)[13]



4h was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether as a colorless oil in 92% yield, 179 mg. **4h** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46-7.44 (m, 1 H), 6.54 (d, *J* =3 Hz, 1 H), 6.40−6.39 (m, 1 H), 5.54 (s, 1 H), 0.20 (s, 9 H).

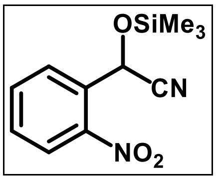
2-(thiophen-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (4i)[13]



4i was prepared according to the general procedure A on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 95% yield, 201 mg. **4i** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (dd, *J* =7.0 Hz, 2.1 Hz, 1 H), 7.18 (tt, *J* = 5.2, 1.1 Hz, 1 H), 7.01−6.99 (m, 1 H), 5.72 (s, 1 H), 0.24 (s, 9 H).

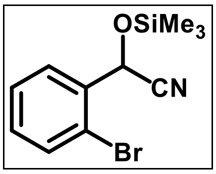
2-(2-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile (4j)[14]



4j was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a yellow oil in 86% yield, 217 mg. **4j** was analyzed by GC-MS, HRMS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, J = 8.20 Hz, 1H), 7.99 (d, J = 8.20 Hz, 1H), 7.79 (t, J = 7.80 Hz, 1H), 7.64 (t, J = 7.80 Hz, 1H), 6.20 (s, 1H), 0.27 (s, 9H). HRMS calculated for $C_{11}H_{14}N_2O_3Si^+$: $[M+H]^+$ 251.0852, found 251.0880.

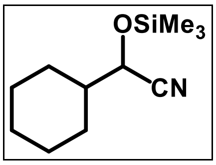
2-(2-bromophenyl)-2-((trimethylsilyl)oxy)acetonitrile (4k)[9]



4k was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 89% yield, 253 mg. **4k** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19-7.97(m, 4H), 5.81(s, 1H), 0.32 (s, 9H)

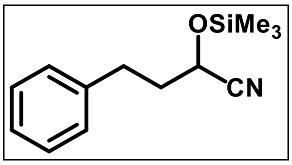
2-cyclohexyl-2-((trimethylsilyl)oxy)acetonitrile (4l)[8]



4l was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 63% yield, 139 mg. **4l** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.16 (d, *J* =6.4 Hz, 1H), 1.89−1.78 (m, 4H), 1.72−1.63 (m, 2H), 1.27−1.04 (m, 5H), 0.20 (s, 9H).

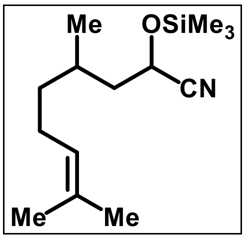
4-Phenyl-2-(trimethylsilyloxy)butanenitrile (4m)[8]



4m was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 88% yield, 205 mg. **4m** was analyzed by GC-MS, ^{1}H NMR and verified by comparison with literature data.

^{1}H NMR (400MHz, CDCl$_3$) δ 7.33–7.29 (m, 2H), 7.24–7.18 (m, 3H), 4.37 (t, J = 6.5 Hz, 1H), 2.80 (t, J = 7.8 Hz, 2H), 2.15–2.09 (m, 2H), 0.20 (s, 9H).

4,8-dimethyl-2-((trimethylsilyl)oxy)non-7-enenitrile (4n)



4n was prepared according to the general procedure B on 1.0 mmol scale, and isolated by column chromatography using petroleum ether/ethyl acetate as a colorless oil in 85% yield, 215 mg (mixed diastereoisomers).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.07 (t, *J* =7.1 Hz, 1H), 4.43 (dd, *J* =12.3, 6.1 Hz, 1H), 2.05–1.91 (m, 2H), 1.87 (m, 1H), 1.72–1.49 (m, 8H), 1.40–1.29 (m, 1H), 1.26–1.12 (m, 1H), 0.93 (dd, *J* = 12.5, 6.5 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 131.5, 124.1, 120.4, 59.6, 43.1, 36.9, 28.2, 25.6, 25.1, 18.8, 17.6, -0.5. HRMS calculated for

$C_{14}H_{28}NOSi^+$: $[M+H]^+$ 254.1940, found 254.1967.

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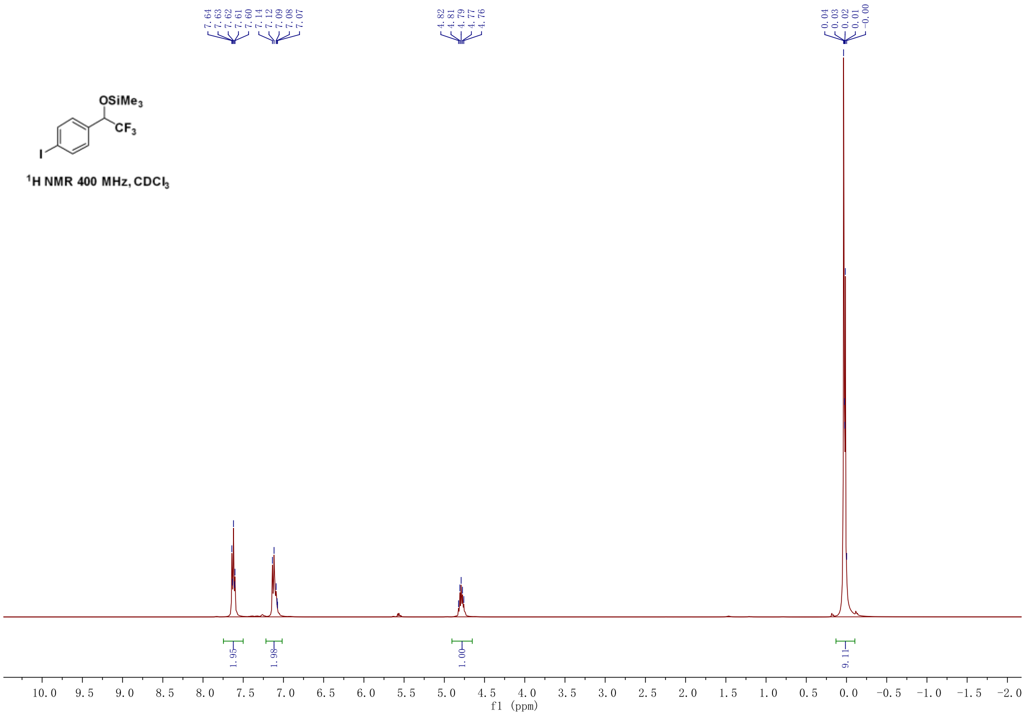
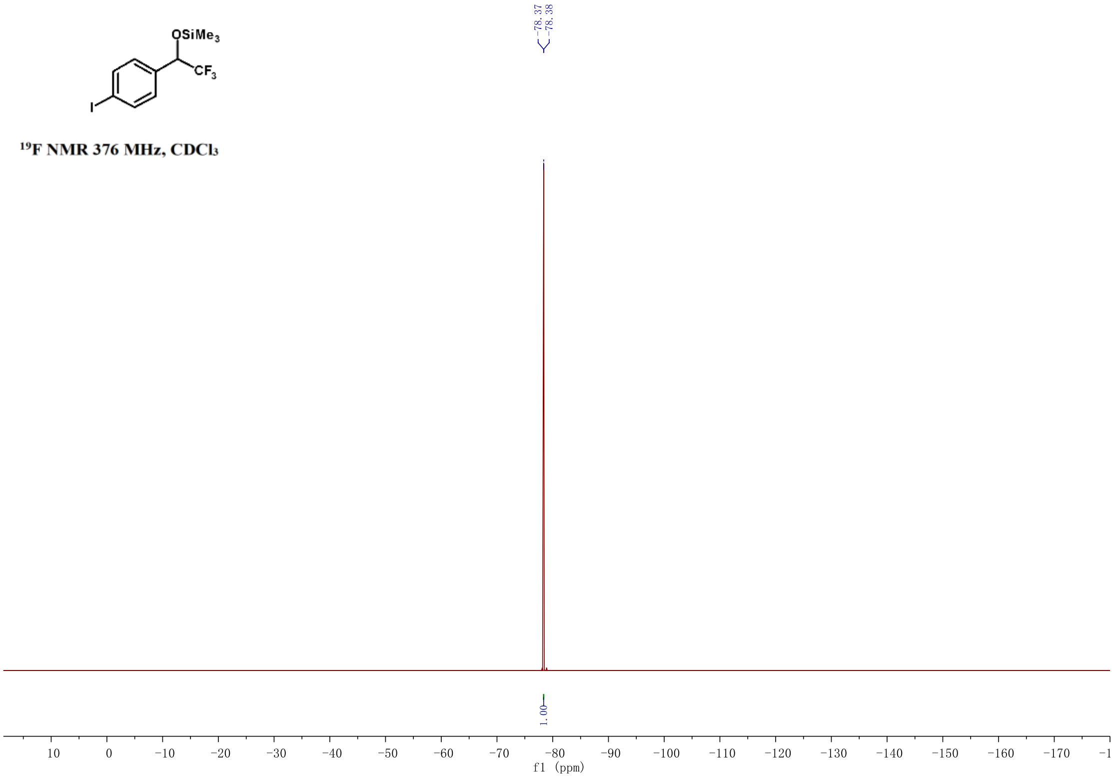
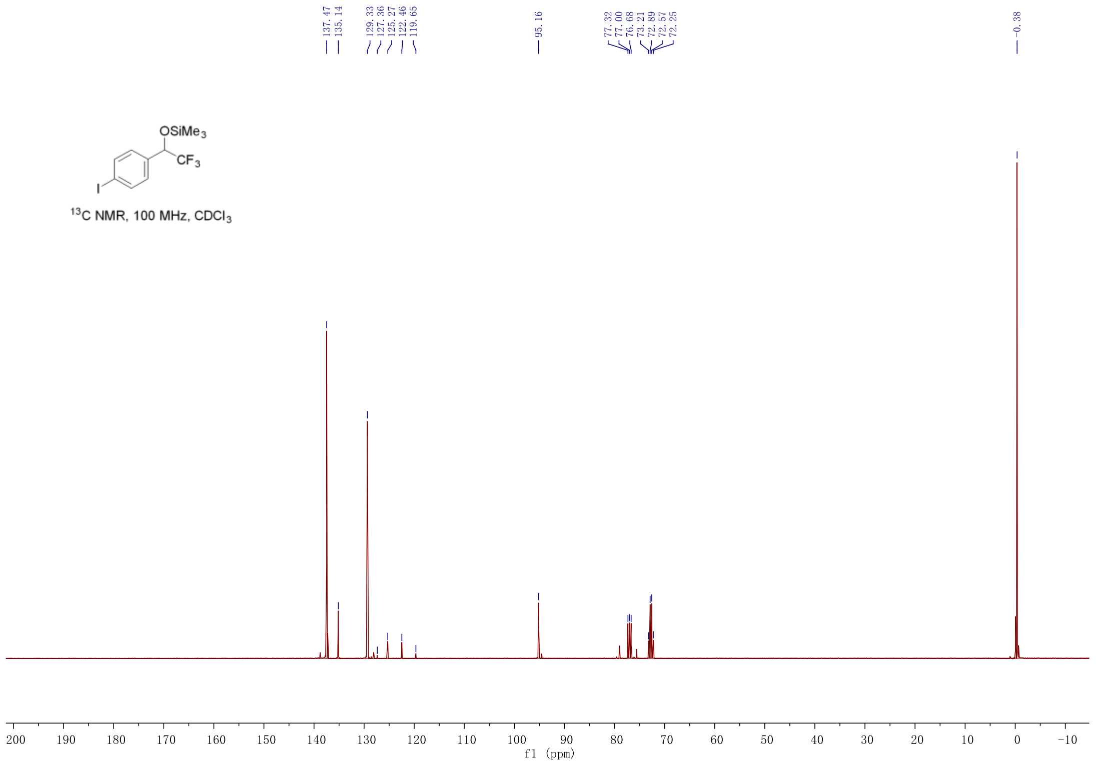
NMR Spectra

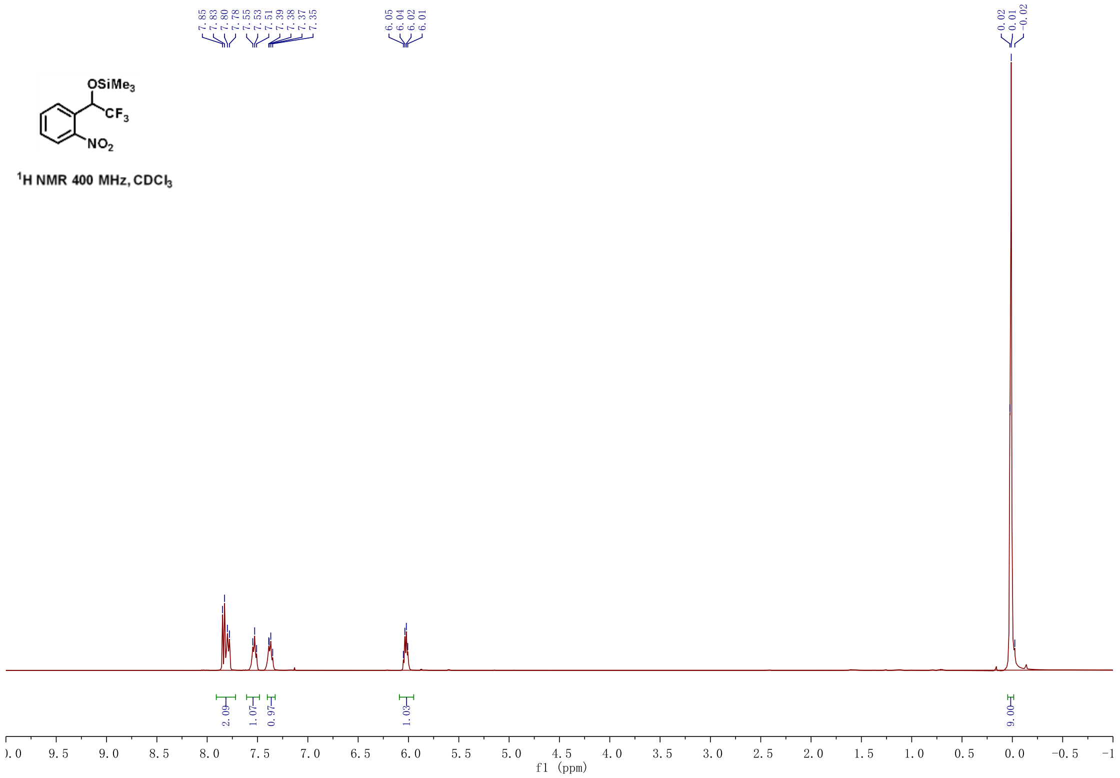
Trimethyl(2,2,2-trifluoro-1-(4-iodophenyl)ethoxy)silane (3e)

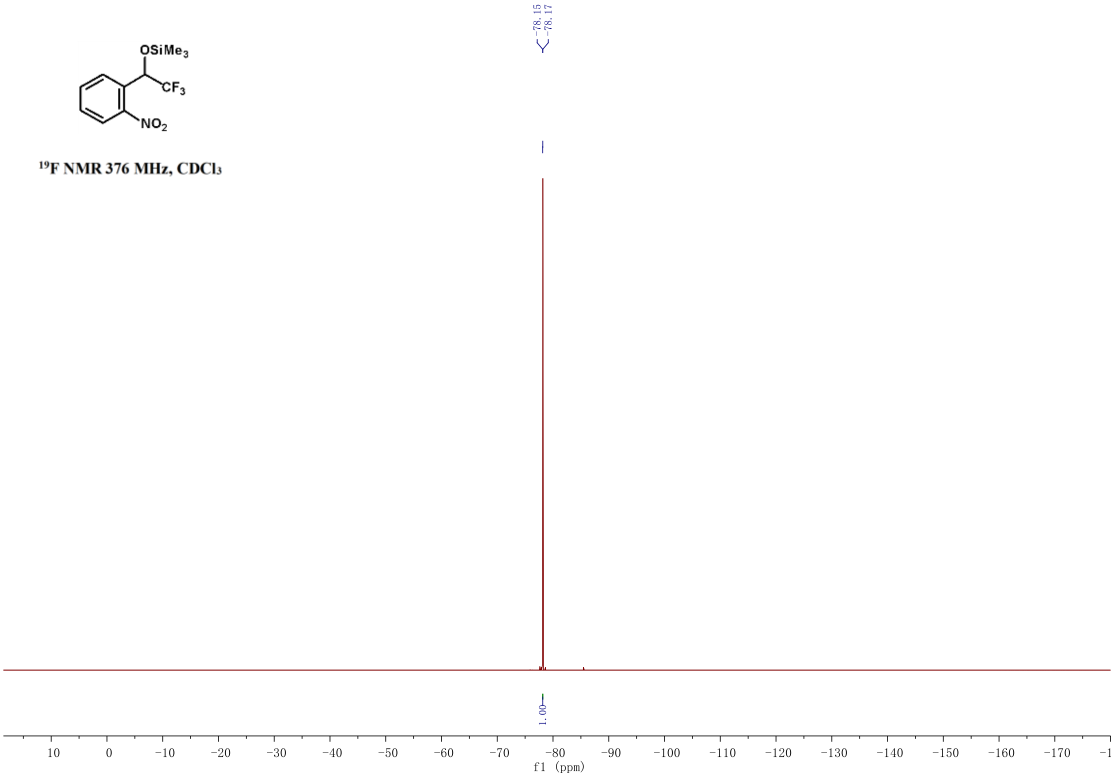


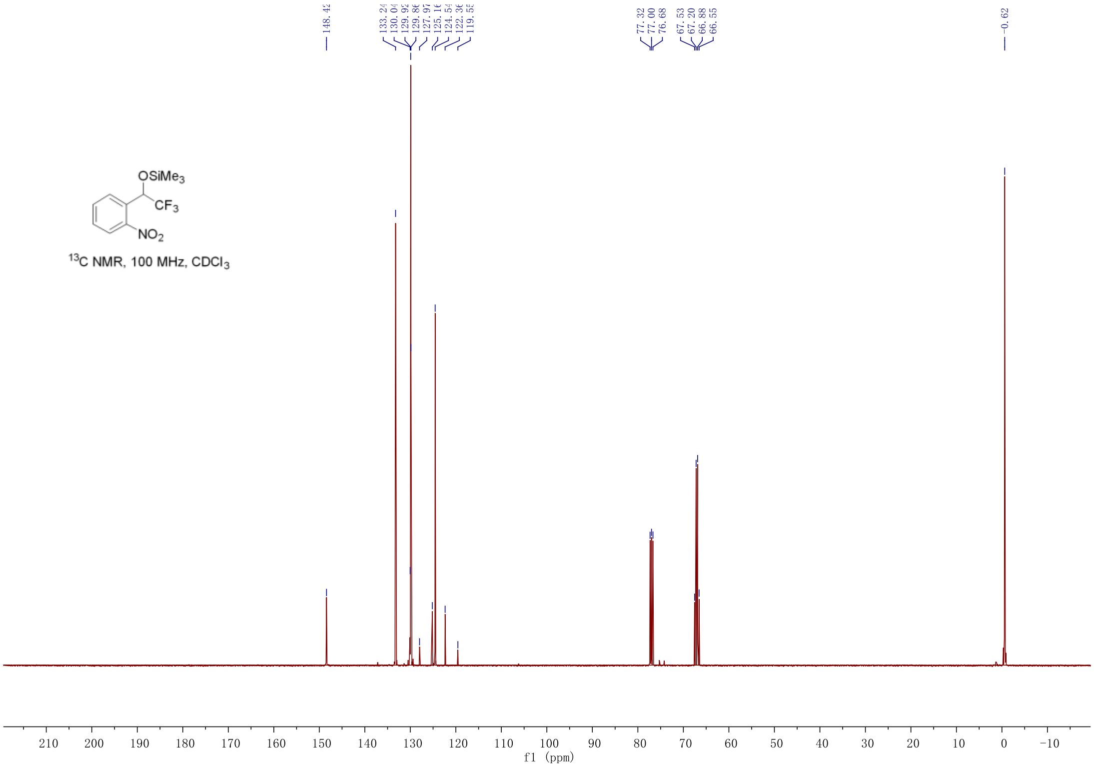




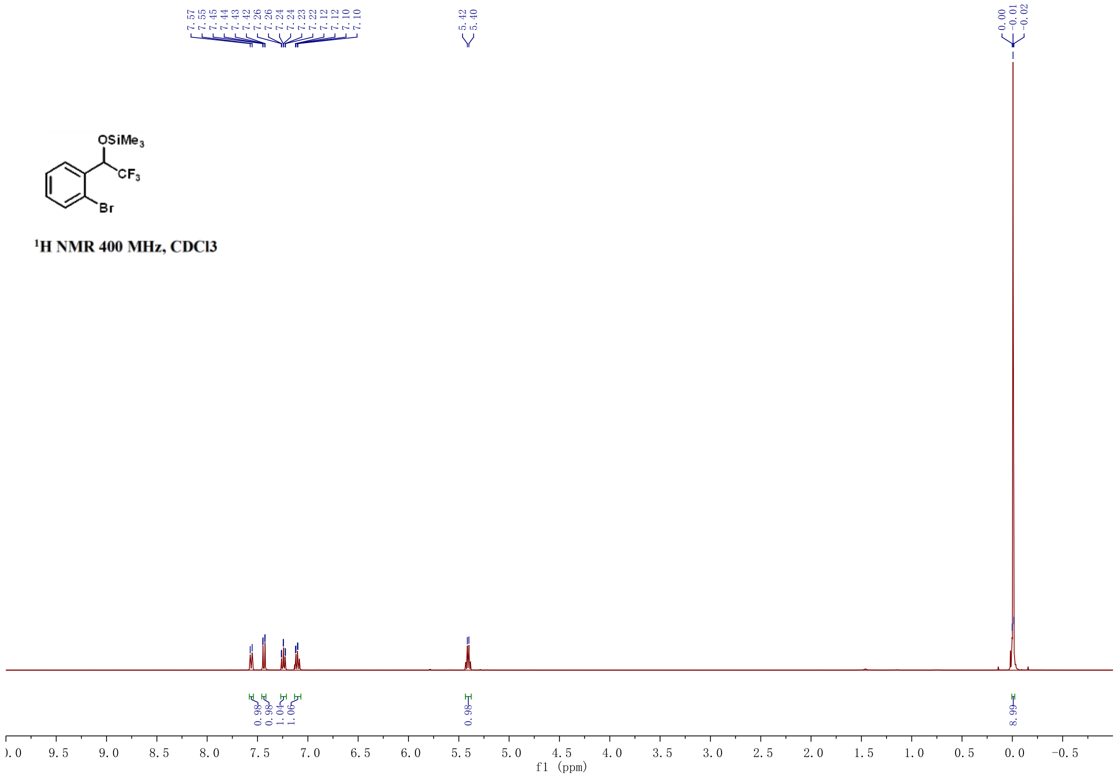
Trimethyl(2,2,2-trifluoro-1-(2-nitrophenyl)ethoxy)silane (3j)







(1-(2-bromophenyl)-2,2,2-trifluoroethoxy)trimethylsilane (3k)


7.57
7.55
7.45
7.44
7.43
7.42
7.26
7.26
7.24
7.24
7.23
7.22
7.12
7.12
7.10
7.10
5.42
5.40
0.00
-0.01
-0.02
OSiMe3
CF3
Br
¹H NMR 400 MHz, CDCl3
0.99
0.98
1.04
1.06
0.98
8.99
).0
9.5
9.0
8.5
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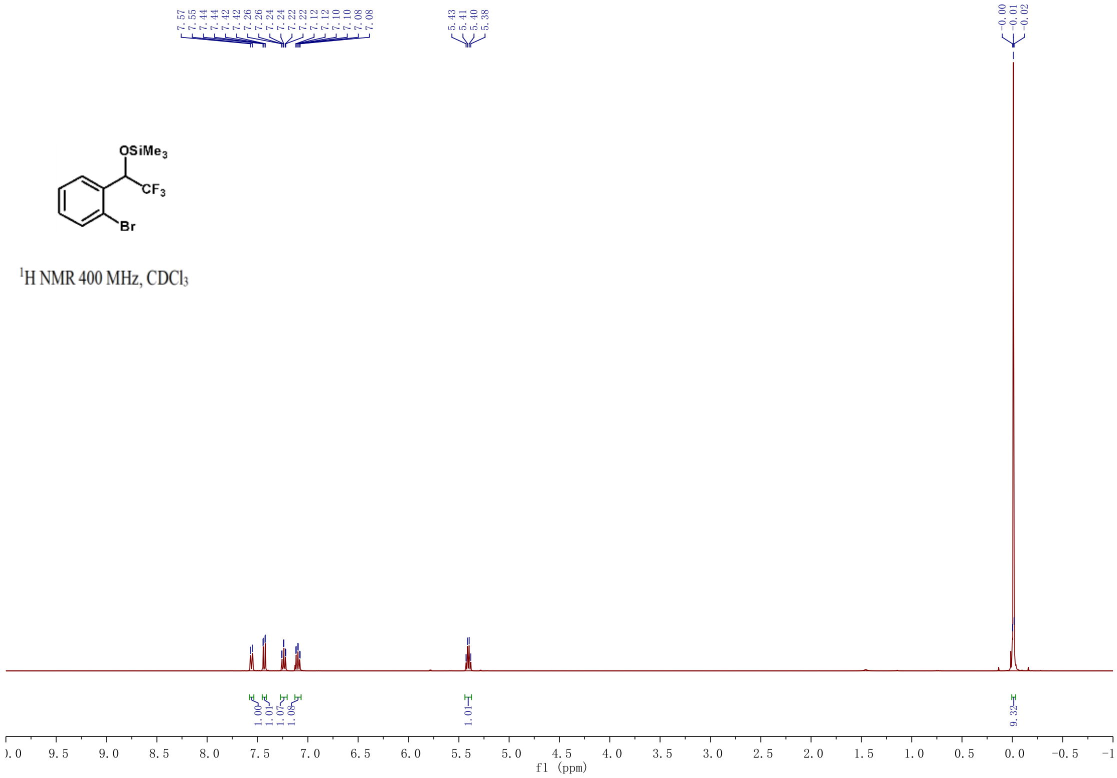
f1 (ppm)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7.08
7.08
5.43
5.41
5.40
5.38
-0.00
-0.01
-0.02
OSiMe3
CF3
Br
¹H NMR 400 MHz, CDCl3
1.00
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1.07
1.08
1.01
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1.5
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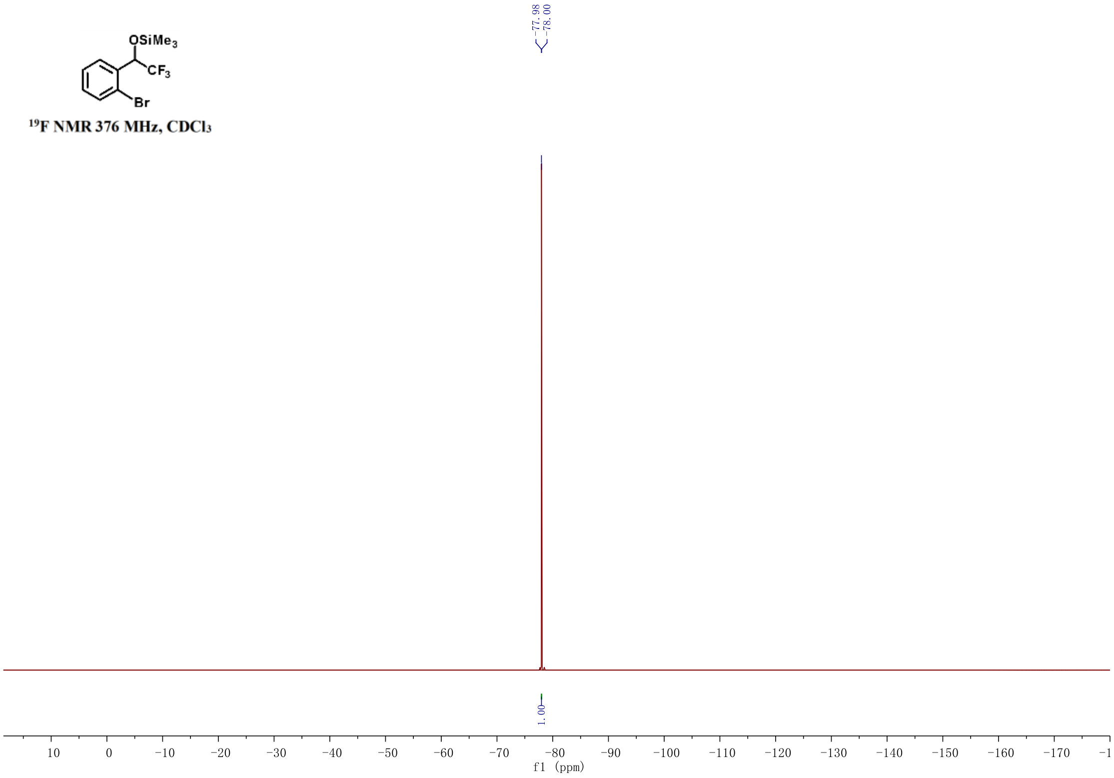
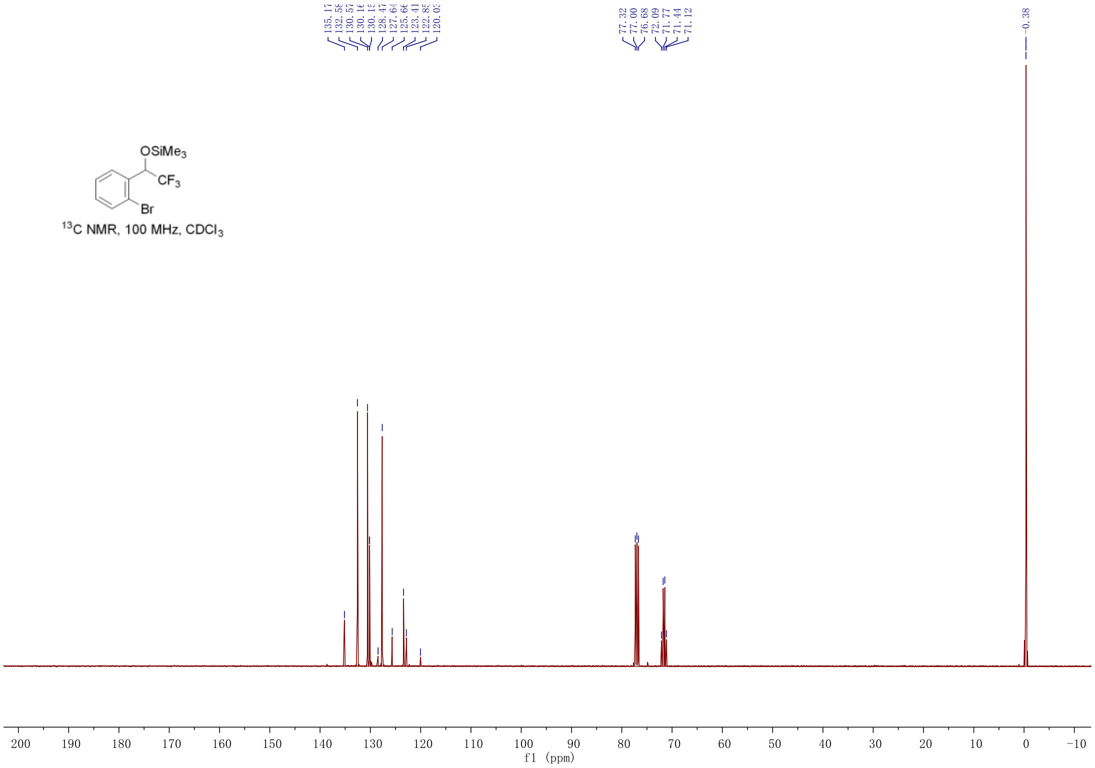
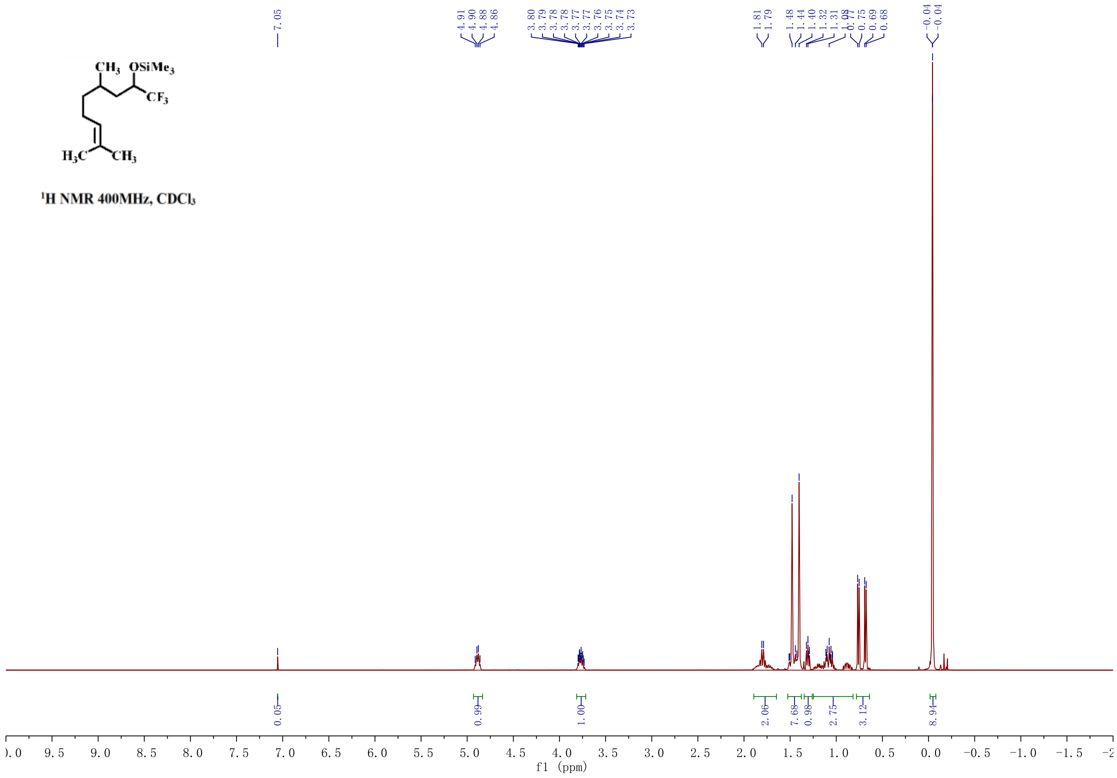
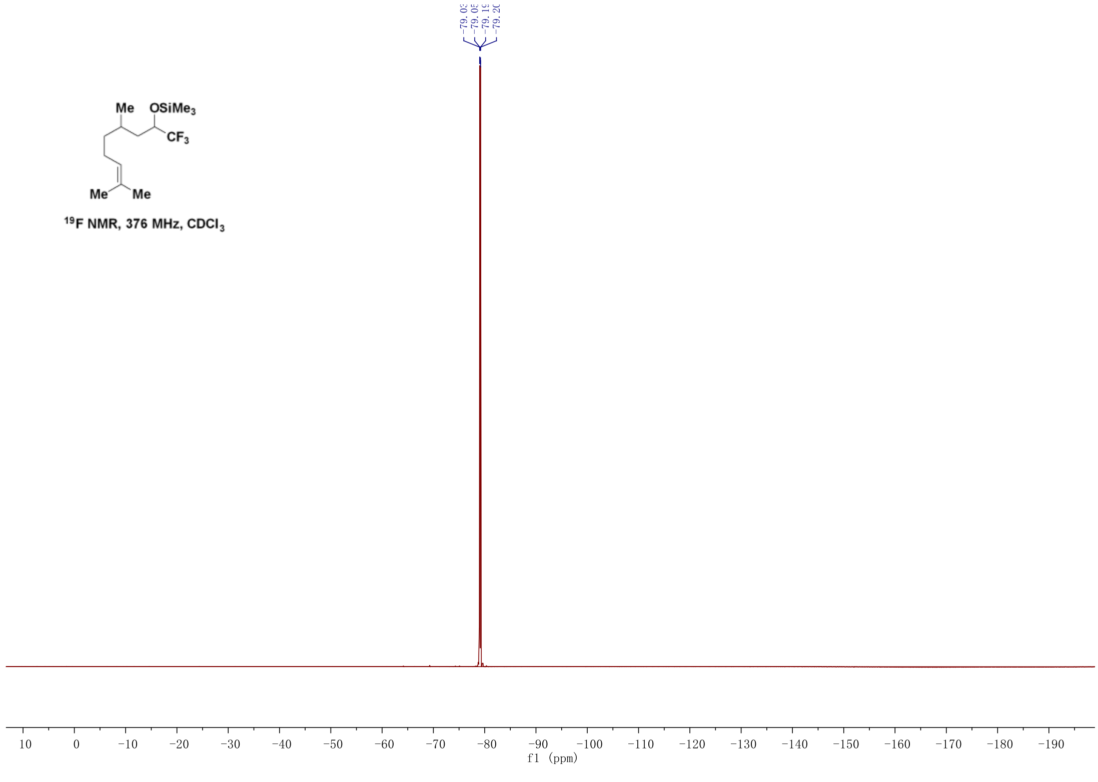
-0.5
-1
f1 (ppm)

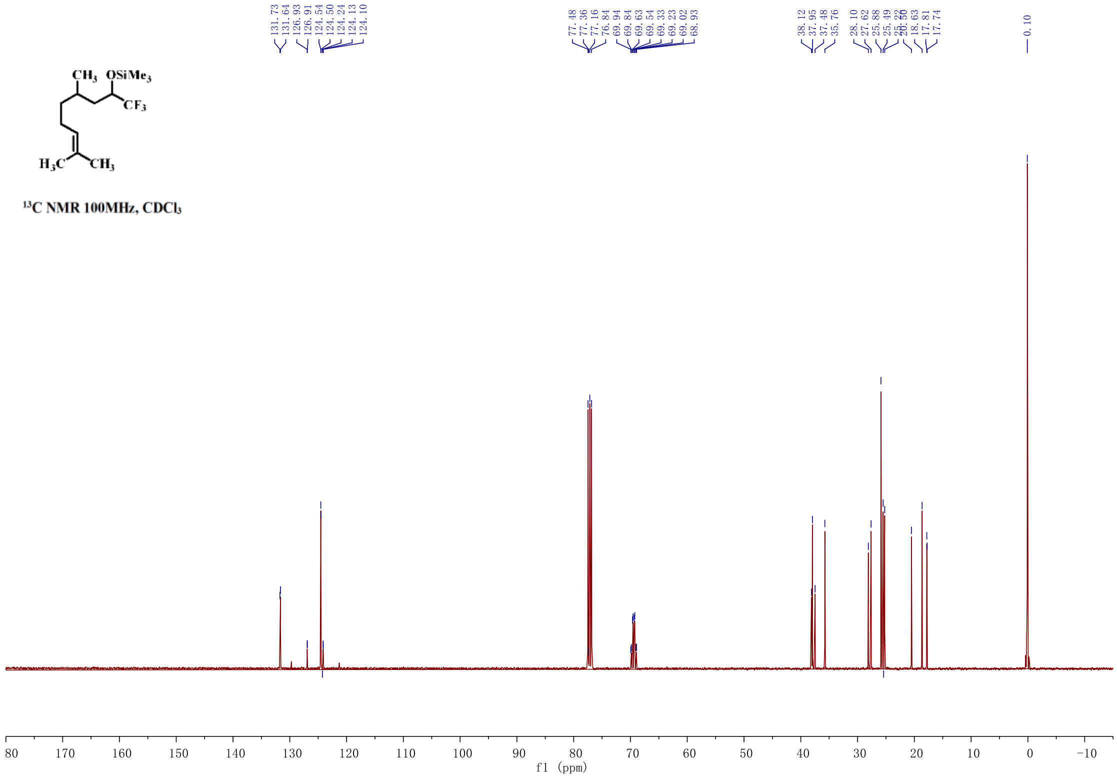




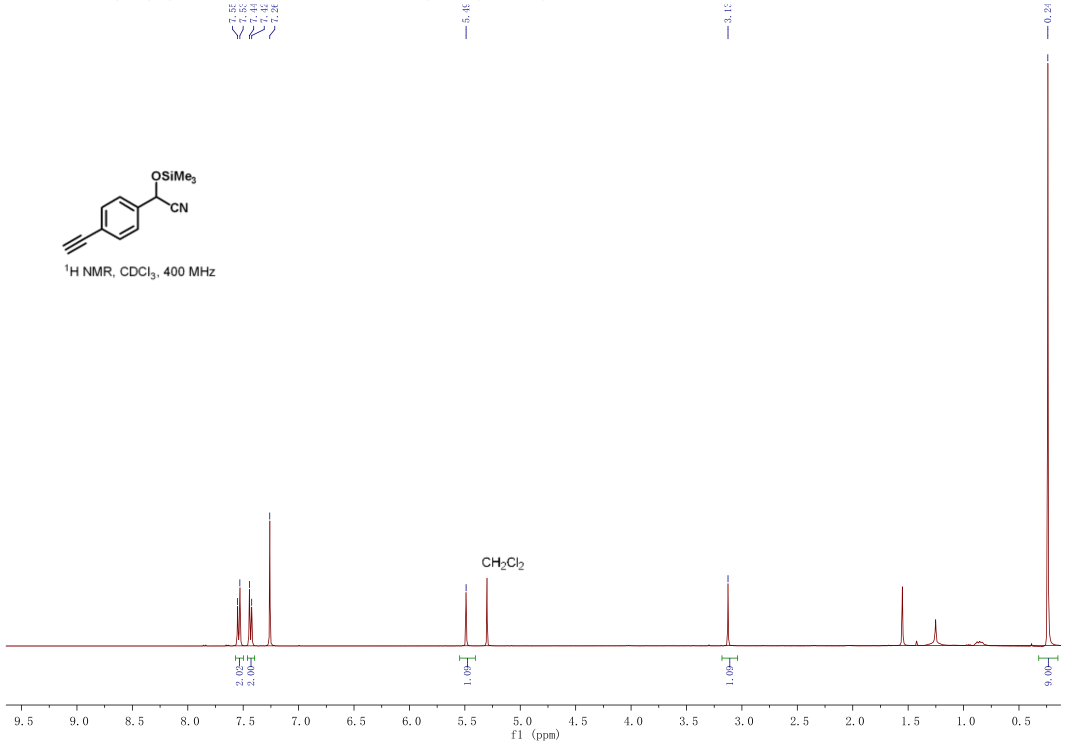
Trimethyl((1,1,1-trifluoro-4,8-dimethylnon-7-en-2-yl)oxy)silane (3g)

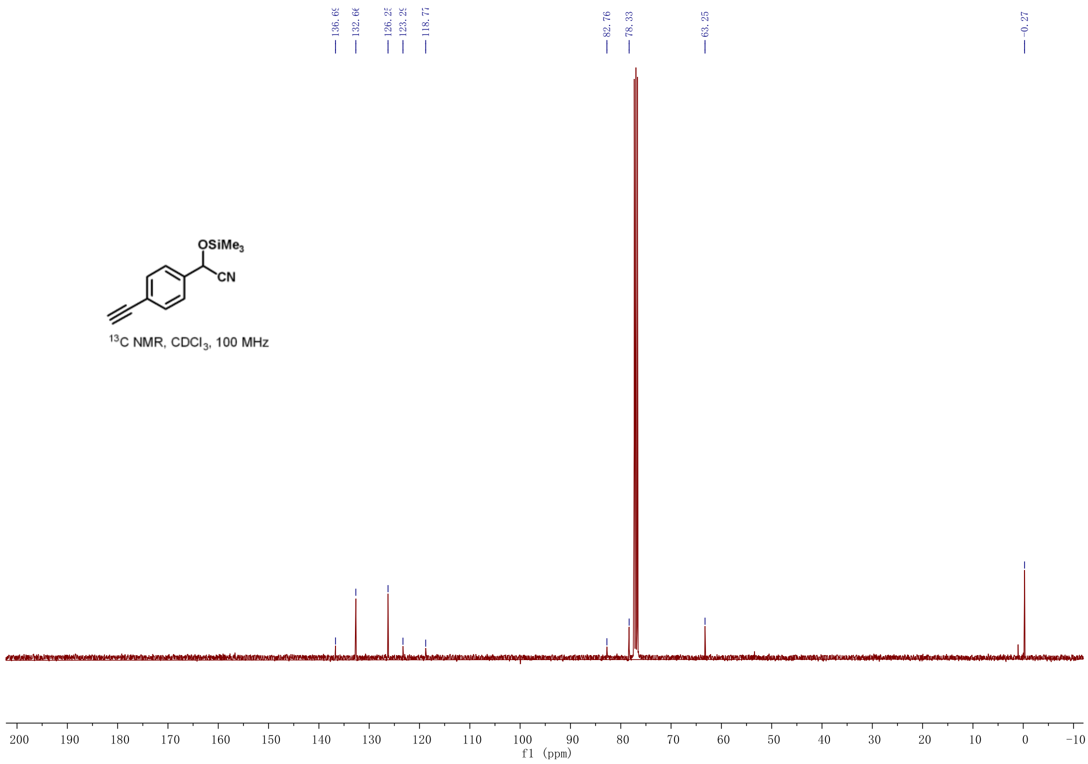

CH3 OSiMe3
CF3
H3C CH3
1H NMR 400MHz, CDCl3
7.05
4.91
4.90
4.88
4.86
3.80
3.79
3.78
3.78
3.77
3.77
3.76
3.75
3.74
3.73
1.81
1.79
1.48
1.44
1.40
1.32
1.31
1.08
0.77
0.75
0.69
0.68
-0.04
-0.04
0.05
0.99
1.00
2.06
7.68
0.98
2.75
3.12
8.94
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)


-79.03
-79.05
-79.19
-79.20
Me OSiMe3
CF3
Me Me
19F NMR, 376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

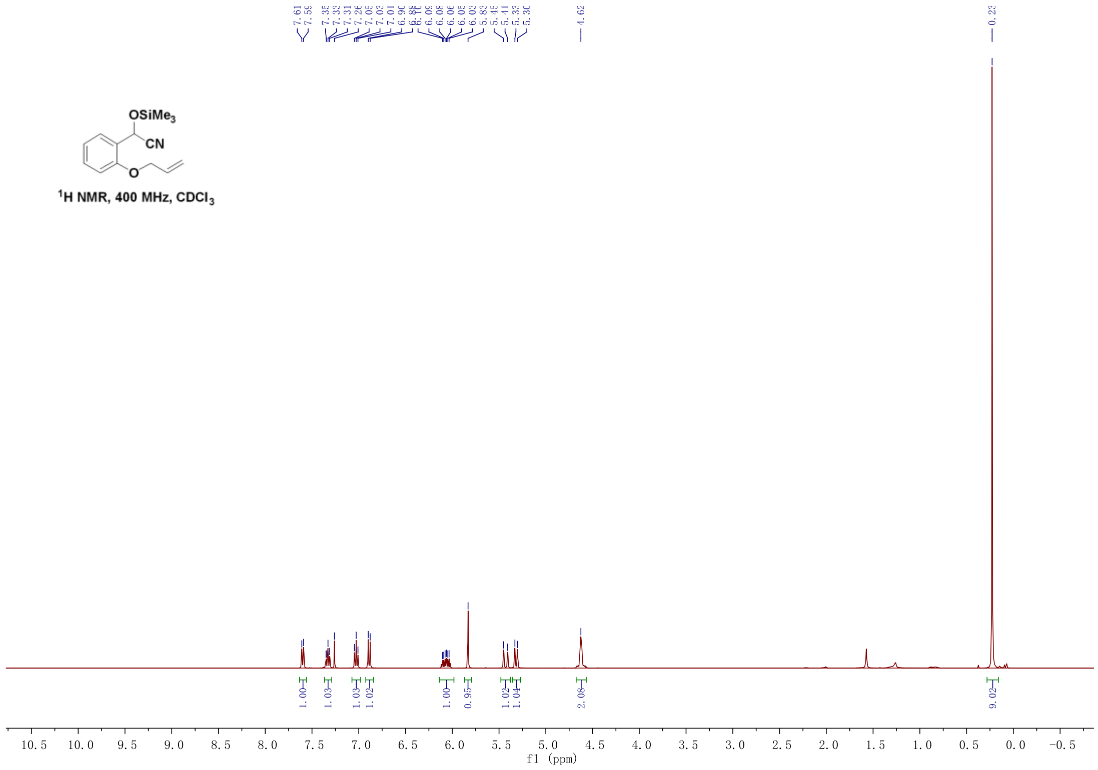


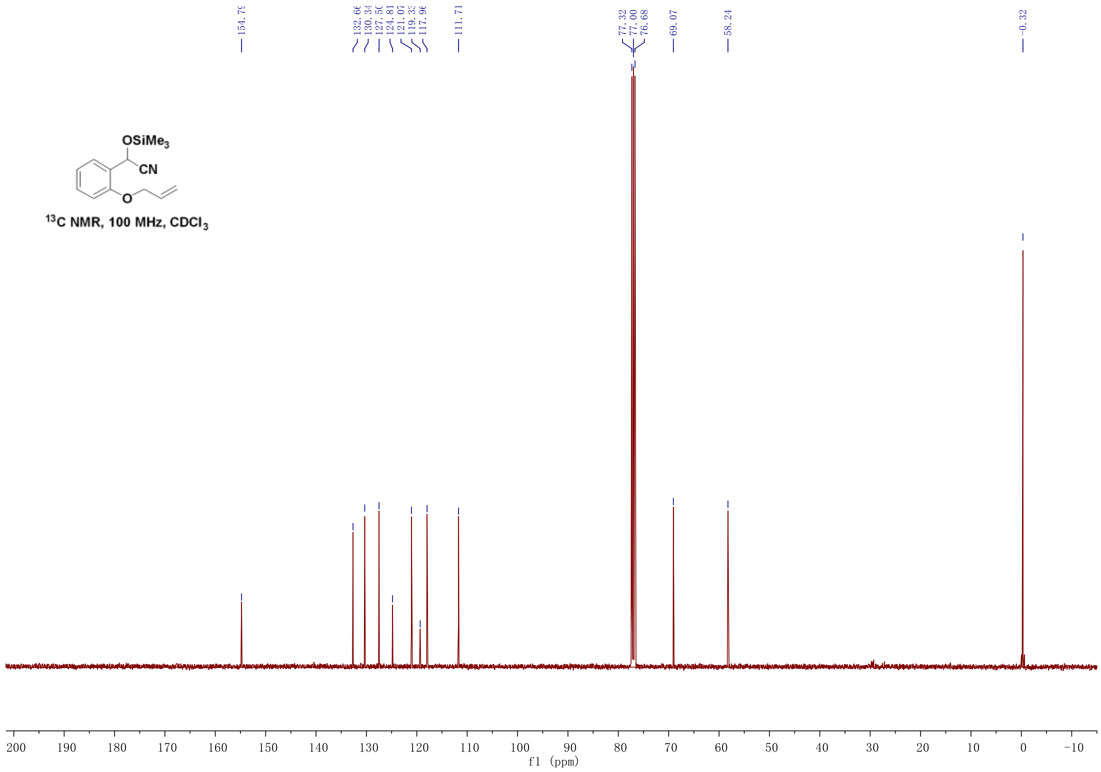
2-(4-ethynylphenyl)-2-((trimethylsilyl)oxy)acetonitrile (4e)



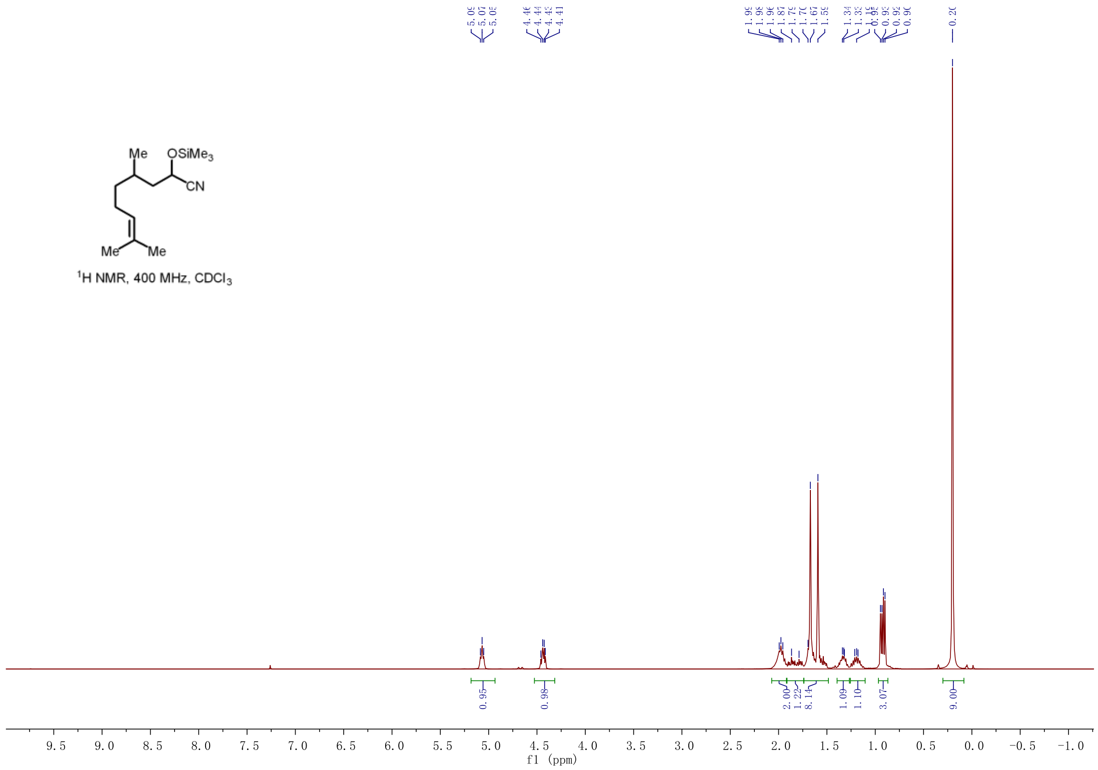


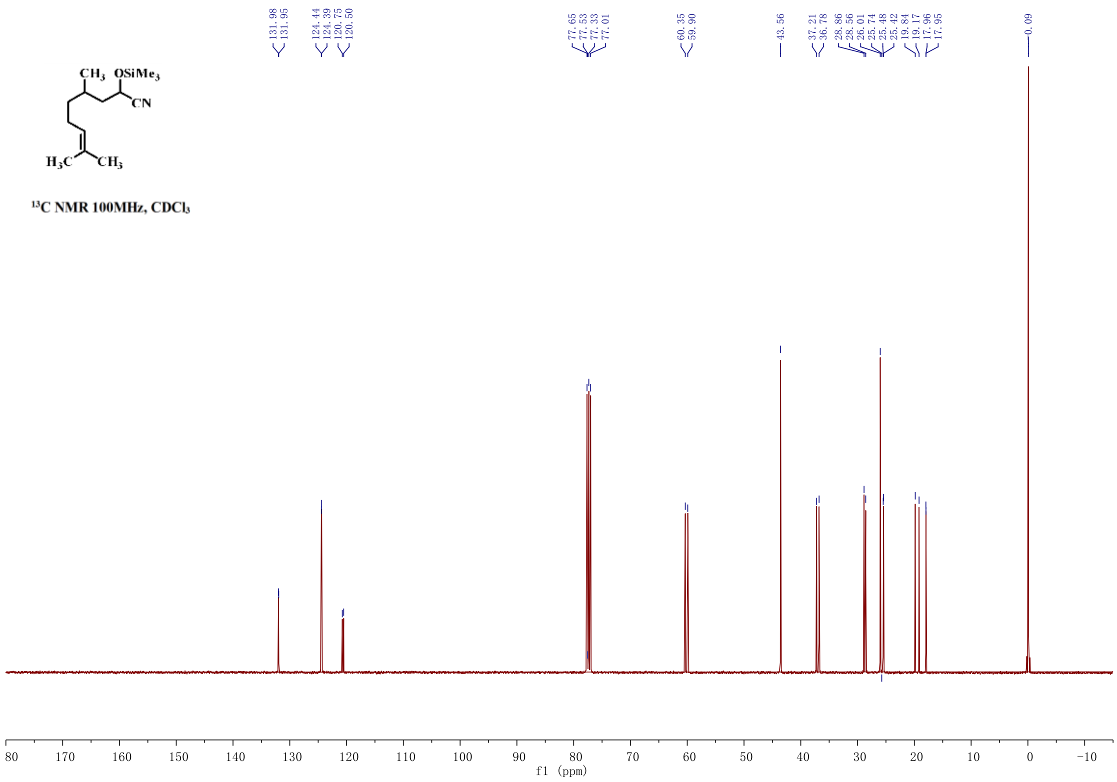
2-(2-(allyloxy)phenyl)-2-((trimethylsilyl)oxy)acetonitrile (4g)





4,8-dimethyl-2-((trimethylsilyl)oxy)non-7-enenitrile (4n)





^{13}C NMR 100MHz, $CDCl_3$