Supporting Information

*^t^*BuOK-Mediated Selective 1,2-Silylcarboxylation of Arylalkenes with Si-B/Si-Si/Si-Li Reagents and CO_2

Liuzhou Gao,[a,b]* Linghui Meng,[a] Yan Wen,[a] Jingyi Hu,[a] Yuxin Sun,[a] Shenglong Wang,[a] Guoqiang Wang,[b,]* and Yidong Wang,[a,]*

[a]School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, Jiangsu, P. R. China

[b]State Key Laboratory of Coordination Chemistry, Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, Jiangsu, P. R. China.

Correspondence to: gaoliuzhou@yzu.edu.cn; wangguoqiang710@nju.edu.cn; wangyd021@yzu.edu.cn.

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1. General Information

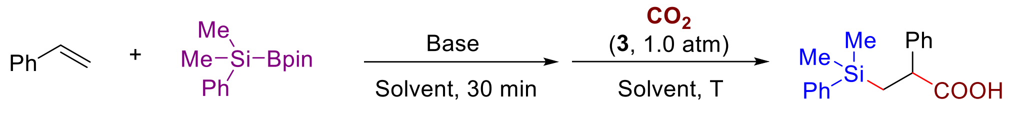
All reactions were carried out with standard Schlenk techniques under argon or in an argon-filled glove-box. The internal H_2O and O_2 levels were kept at less than 0.1 ppm. $PhMe_2SiBpin$ was purchased from TCI and Sigma-Aldrich. ^{t}BuOK was purchased from Sigma-Aldrich and stored in the glove box. Other chemicals purchased from Sigma-Aldrich, *J&K*, Acros, and Alfa Aesar Chemical Companies were used as received. Anhydrous solvents, such as ethyl acetate (EA), acetonitrile (MeCN), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) were purchased from *J&K* and used as received (water < 30 ppm, *J&K* Seal). All other solvents, such as THF, 1,4-dioxane and toluene (PhMe), used were vigorously dried, and stored in the glove box. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.06 ppm for ^{13}C{^{1}H NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using a neat thin-film technique. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an ESI or APCI ionization source and a TOF detector mass spectrometer.

2. Experimental Details for the Base-mediated 1,2-Silacarboxylation of Arylalkenes

2.1 Optimization Studies

General procedure A. In an argon-filled glovebox, styrene **1a** (0.2~0.24 mmol, 1.0~1.2 equiv.), $PhMe_2SiBpin$ **2a** (0.2~0.24 mmol, 1.0~1.2 equiv.), ^tBuOK (0.4~0.48 mmol, 2.0~2.4 equiv.), and solvent (1.0 mL) were added to an oven-dried Scklenk-tube. The reaction tube was sealed, and removed from the glovebox, and the reaction mixture was stirred at room temperature for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s (or the solution was cooled to -20 ^oC and then the dried CO_2 was added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 ^oC for about 2 min). After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was obtained. Further, benzyl ether (39.8 mg, 0.2 mmol, 1.0 equiv.) was added to the crude material, and then an aliquot (approximately 30 μL) of the reaction solution was then directly transferred to an NMR tube and $CDCl_3$ was added. The yield was determined by ^1H NMR analysis based on the integration of the targeted product and internal standard. The results are tabulated in Table S1.

Table S1. Optimization of Reaction Conditions.[a]

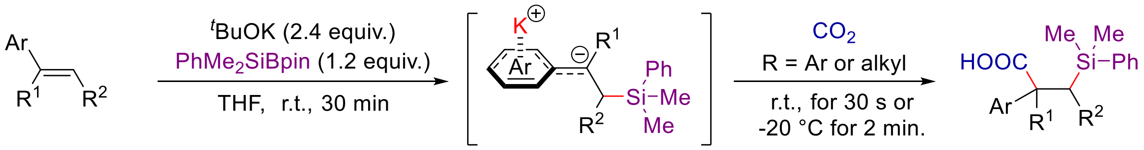


Entry	**1a/2** [equiv.]	Solvent	Base	T (°C)	Yield[b] **4a**
1	1:1	THF	w/o base	r.t.	N.D.
2	1:1	THF	^{t}BuOK (1.0 eq.)	r.t.	36%
3	1:1	THF	MeONa (2.0 eq.)	r.t.	trace
4	1:1	THF	MeOK (2.0 eq.)	r.t.	trace
5	1:1	THF	^{t}BuONa (2.0 eq.)	r.t.	12%
6	1:1	THF	^{t}BuOLi (2.0 eq.)	r.t.	N.D.
7	1:1	THF	KHMDS (2.0 eq.)	r.t.	trace
8	1:1	THF	CsF (2.0 eq.)	r.t.	N.D.
9	1:1	THF	CS_2CO_3 (2.0 eq.)	r.t.	trace
10	1:1.2	THF	^{t}BuOK (2.0 eq.)	r.t.	68%
11	1:1.2	THF	^{t}BuOK (2.4 eq.)	r.t.	76%
11	1:1.2	THF	^{t}BuOK (2.4 eq.)	r.t., -20 °C	80%(76%[c])
12	1:1.2	1,4-dioxane	^{t}BuOK (2.4 eq.)	r.t.	55%
13	1:1.2	PhMe	^{t}BuOK (2.4 eq.)	r.t.	trace
14	1:1.2	CH_3CN	^{t}BuOK (2.4 eq.)	r.t.	N.D.
15	1:1.2	DMF	^{t}BuOK (2.4 eq.)	r.t.	N.D.
16	1:1.2	DMAc	^{t}BuOK (2.4 eq.)	r.t.	N.D.
17	1:1.2	DMSO	^{t}BuOK (2.4 eq.)	r.t.	N.D.

[a]Reaction conditions: styrene **1a** (0.2~0.24 mmol, 1.0~1.2 equiv.), $PhMe_2SiBpin$ **2** (0.2~0.24 mmol, 1.0~1.2 equiv.), ^{t}BuOK (0.4~0.48 mmol, 2.0~2.4 equiv.), in dry solvent (1.5 mL), r.t. for 5 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature or -20 °C for about 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. [b]Yields were determined by ^1H NMR analysis with benzyl ether as an internal standard. [c]Isolated yield of analytically pure material after purification on preparative thin-layer chromatography.

2.2 General Procedure for the 1,2-Silacarboxylation of Arylalkenes

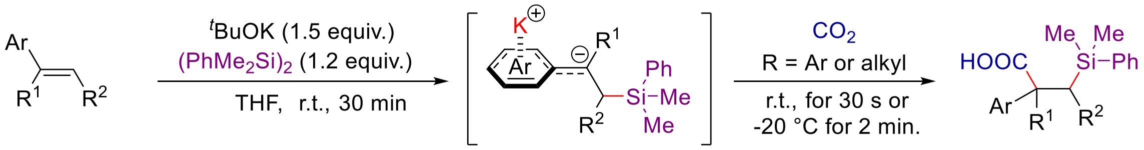
2.2.1 Synthetic Procedure for ^{t}BuOK-Mediated 1,2-Silacarboxylation of Arylalkenes with Si-B



General Procedure B: In an argon-filled glovebox, alkene (0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (0.2~0.24 mmol, 1.0~1.2 equiv.), ^{t}BuOK (0.4~0.48 mmol, 2.0~2.4 equiv.), and dry THF (1.5 mL) were added to an oven-dried Scklenk-tube. The reaction tube was sealed, and removed from the glovebox, and the reaction mixture was stirred at room temperature for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s (or stirred at -20 °C for 2 minutes). After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel or preparative TLC to afford the corresponding 1,2-silylcarboxylation products.

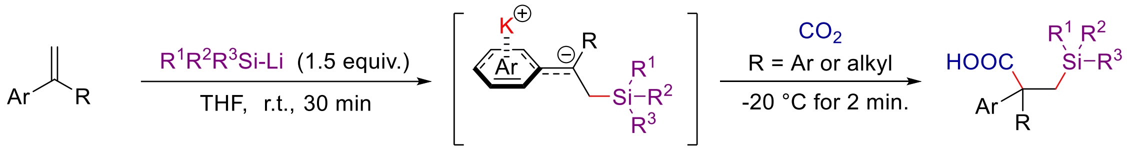
Figure S1. The photoes for the ^{t}BuOK-mediated selective 1,2-silacarboxylation of styrene

2.2.2 Synthetic Procedure for ^{t}BuOK-Mediated 1,2-Silacarboxylation of Arylalkenes with Si-Si



General Procedure C: In an argon-filled glovebox, alkene (0.2 mmol, 1.0 equiv.), $PhMe_2Si\text{-}SiMe_2Ph$ (0.24 mmol, 1.2 equiv.), ^{t}BuOK (0.3 mmol, 1.5 equiv.), and dry THF (1.5 mL) were added to an oven-dried Scklenk-tube. The reaction tube was sealed, and removed from the glovebox, and the reaction mixture was stirred at room temperature for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 °C for about 2 minutes. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel or preparative TLC to afford the corresponding 1,2-silylcarboxylation products.

2.2.1 Synthetic Procedure for *ᵗ*BuOK-Mediated 1,2-Silacarboxylation of Arylalkenes with Si-Li



General Procedure D: In an argon-filled glovebox, alkene (0.2 mmol, 1.0 equiv.), Si-Li reagent (0.3 mmol, 1.5 equiv.), and dry THF (1.5 mL) were added to an oven-dried Scklenk-tube. The reaction tube was sealed, and removed from the glovebox, and the reaction mixture was stirred at room temperature for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 °C for about 2 minutes. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel or preparative TLC to afford the corresponding 1,2-silylcarboxylation products.

2.2.2 Unsuccessful Examples

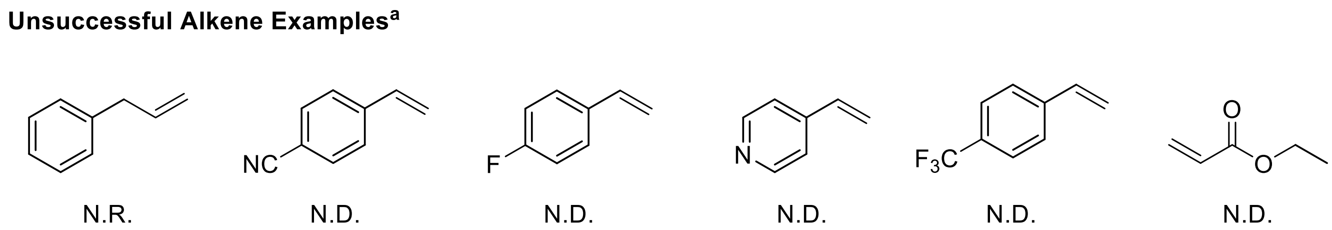
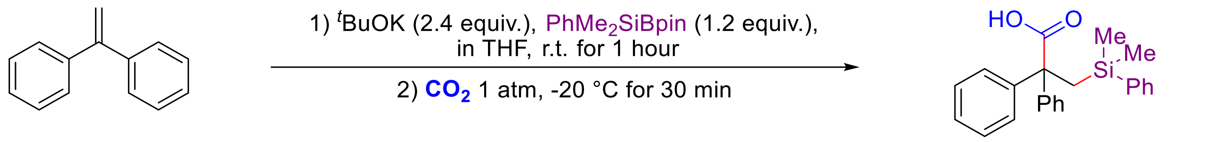


Figure S2. Unsuccessful examples in the selective 1,2-silylcarboxylation of arylalkenes. [a]Preformed under the standard conditions with $PhMe_2SiBpin$ **2a** as the model substrates. N.D.= Not detected.

As shown in Figure S2, our experiments suggested that alkyl alkene (e.g. allylbenzene), 4-cyanostyrene, 4-fluorostyrene, 4-vinylpyridine, 4-(trifluoromethyl)styrene, ethyl acrylate were not suitable substrates under the current reaction conditions. In fact, the presence of electron-withdrawing groups, such as 4-fluorine, 4-cyano, and 4-ester in the structure of styrene substrates will lead to incompatibility, resulting in either SN_{Ar} reactions or decomposition prior to conversion to carbon dioxide (the SN_{Ar} process see our recent work at ref. 17, *Chem. Sci.*, **2023**, *14*, 11881−11889.).

2.3 Gram-Scale Experiment



Synthetic Procedure: In an argon-filled glove box, an oven-dried 100 mL schlenk-tube was charged with 1,1-diphenylethylene (0.90 g, 5.0 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (1.57 g, 6.0 mmol, 1.2 equiv.), ^{t}BuOK (1.35 g, 10.0 mmol, 2.4 equiv.), in 25 mL THF. The reaction tube was sealed, and removed from the glovebox, and the reaction mixture was stirred at room temperature for 1 h. Then, the reaction mixture was taken into a -20 ^oC low-temperature bath, next, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for about 30 minutes. After the reaction finished, 1M HCl solution (~10.0 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (4×20 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 50:1→5:1, v/v) to afford the desired product **4p** as a colorless oil (1.45 g, 80%).

Product 4p, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H), 7.44 – 7.36 (m, 4H), 7.35 – 7.31 (m, 5H), 7.31 – 726 (m, 4H), 2.14 (s, 2H), 0.00 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.0, 144.6, 139.9, 133.7, 128.8, 128.7, 127.9, 127.6, 126.9, 58.3, 28.4, -2.1 ppm. **IR** (film): 3208, 3069, 3022, 2952, 1705, 1548, 1428, 1242, 1111, 737, 700 cm^{-1}. **HRMS** (ESI): calculated for $C_{23}H_{23}O_2Si^-$ [M-H]$^-$ 359.1473; found 359.1465.

2.4 Experimental Studies on the Reaction Mechanism

To further verify the involvement of the silanion intermediates **V** and the carbanion intermediates **VI** in the reaction, the NMR experiments were performed.

2.4.1 NMR analysis on the reaction of $PhMe_2SiBpin$, ^tBuOK and styrene.

Experimental procedure: In an argon-filled glove box, an oven-dried 10 mL schlenk-tube was charged $PhMe_2SiBpin$ (26.2 mg, 0.1 mmol, 1.0 equiv.), ^tBuOK (0.2 mmol, 2.0 equiv.), dry THF-d_8 (0.5 ML), stirred at room temperature for 30 min to afford the intermediate (**V**). Then the ^{11}B, ^{1}H, and ^{29}Si NMR analysis of the crude reaction mixture was carried out immediately, which is labeled as **b, e, g**. After which, adding 1.0 equiv. of styrene into another parallel experiment, and shaking for 5 min, the ^{11}B and ^{1}H NMR spectrum analysis of the reaction mixture was acquired again, which are labeled as **c**, **h**, and **d** (as shown in Figure S4-S5). In addition, the control NMR experiments were also conducted using $PhMe_2SiBpin$ (26.2 mg, 0.1 mmol, 1.0 equiv.) in dry THF-d_8 (0.5 ML), and the result of ^{11}B, ^{29}Si and ^{1}H NMR analysis was labeled as **a, d, f**.

Chemical equilibria analysis

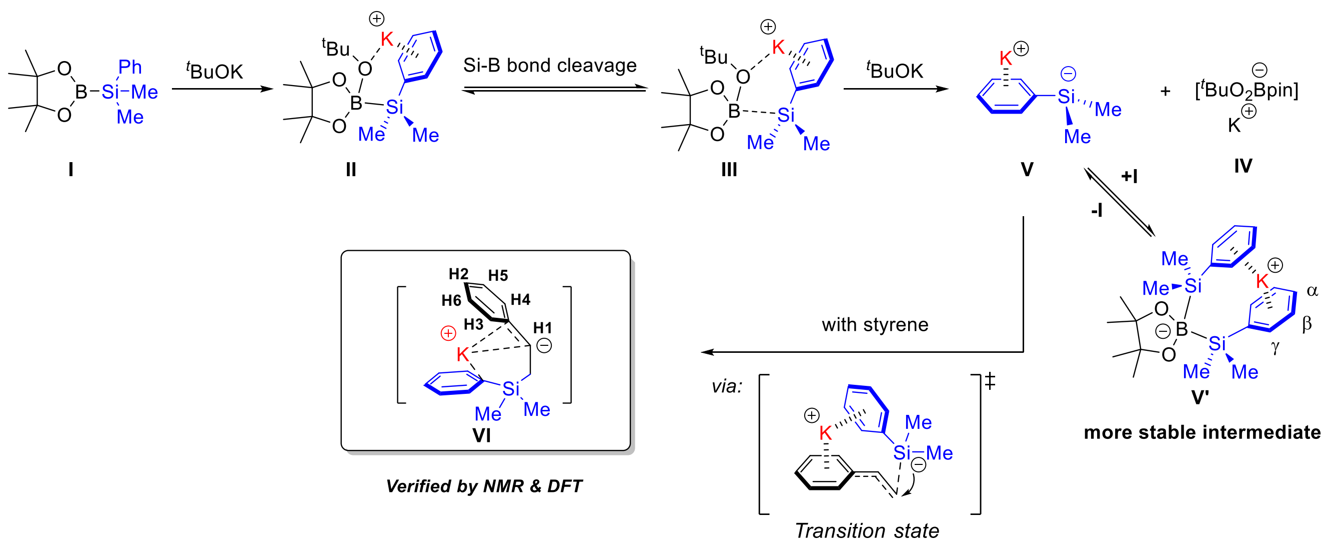


Figure S3. Chemical equilibria for the reaction of $PhMe_2SiBpin$, ^tBuOK and styrene.

The experimental results indicate that the mixed system primarily forms the $PhMe_2Si_2$-BpinK species (**V′**), which is consistent with the single-crystal structural data of **V′-1** (CCDC-893778) previously reported[1]. As shown in Figure S4, ^{11}B NMR analysis indicated that two tetracoordinated boron resonances at δ 5.2 and 4.3 can be attributed to two species of $[(PhMe_2Si)_2Bpin]^-K^+$ **V′** and $[(^tBuO)_2Bpin]^-K^+$ **IV′**, as corroborated by previous researches[2] and the DFT calculations. Additionally, the ^{1}H NMR spectrum indicated a notable change in the chemical shift of the phenyl group in $[(PhMe_2Si)_2Bpin]^-K^+$ **V′**, a finding that aligns with our DFT calculations. Furthermore, the ^{29}Si NMR spectrum showed only one peak at -26.3 ppm, which most likely corresponds to the

[(PhMe2Si)2Bpin]⁻K⁺ species **V′** according to previous reports[1] and our calculational NMR chemical shifts (Figure S4, red).

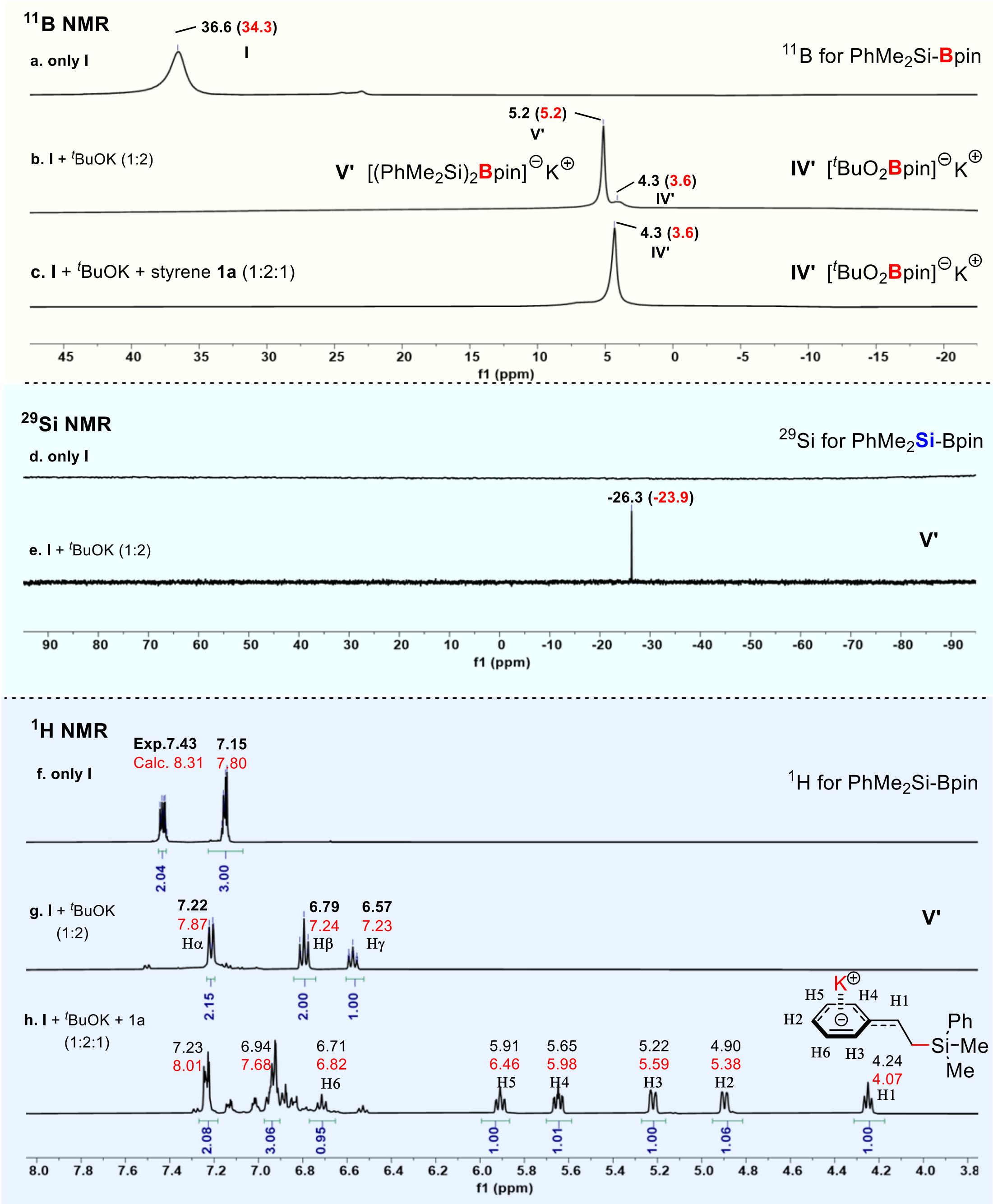


Figure S4. NMR analysis on the reaction of PhMe2SiBpin with/without ᵗBuOK and styrene. **a**, ¹¹B NMR spectrum of PhMe2SiBpin **I**; **b**, ¹¹B NMR spectrum for the reaction mixture of **I** and 2.0 equivalent of ᵗBuOK; **c**, ¹¹B NMR pectrum for the reaction mixture of PhMe2SiBpin, 2.0 equivalent of ᵗBuOK and styrene; **d**, ²⁹Si NMR spectrum of PhMe2SiBpin **I**; **e**, ²⁹Si NMR spectrum for the reaction mixture of **I** and 2.0 equivalent of ᵗBuOK; **f**, ¹H NMR spectrum of PhMe2SiBpin **I**; **g**, ¹H NMR spectrum for the reaction mixture of **I** and 2.0 equivalent of ᵗBuOK; **h**, ¹H NMR pectrum for the reaction mixture of PhMe2SiBpin, 2.0 equivalent of ᵗBuOK and styrene; Chemical shifts shown in red were computed with the Gauge-independent atomic orbital (GIAO) method[3] at B972/pcSseg-2 level of theory.

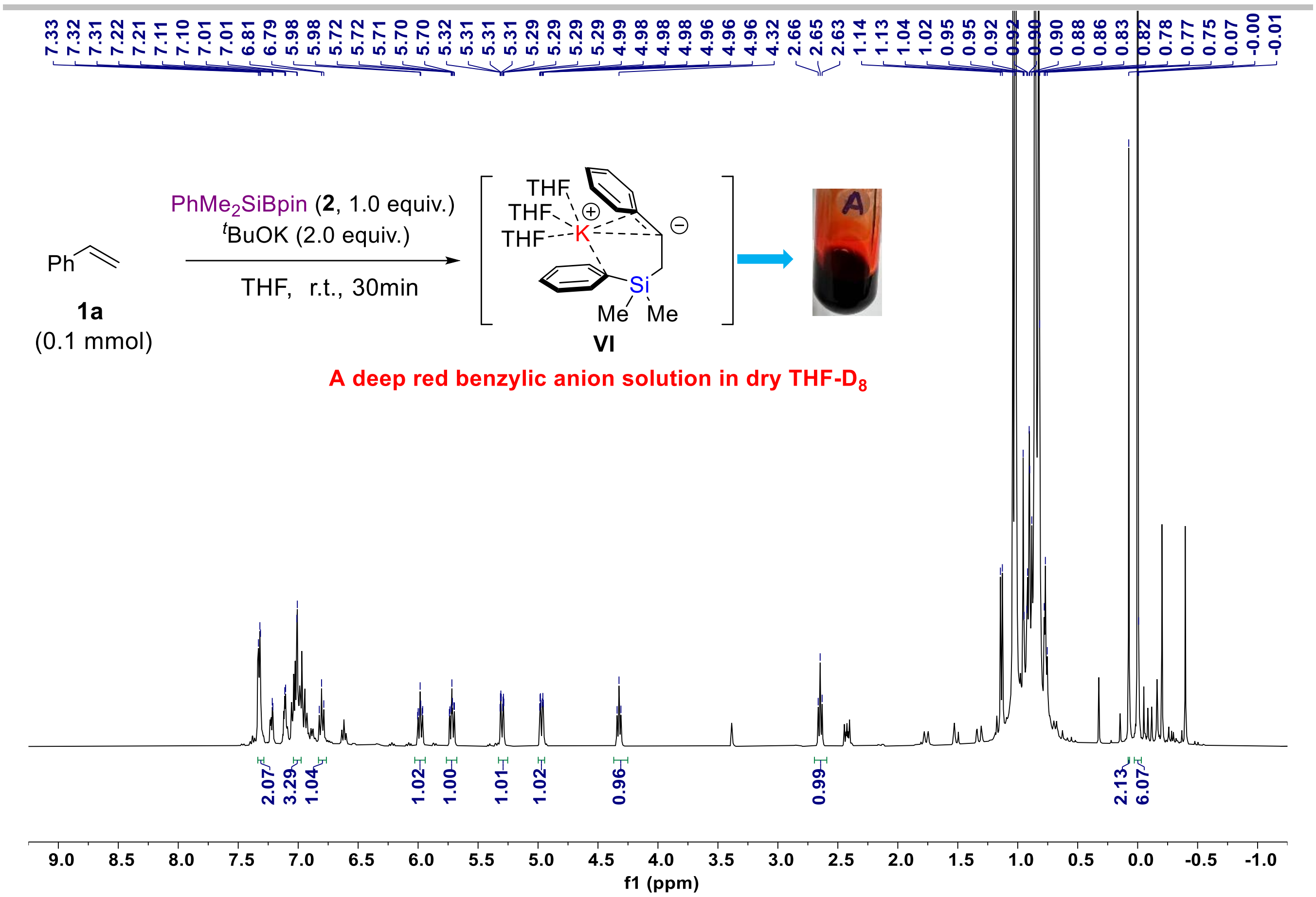


Figure S5. [1]H NMR pectrum for the reaction mixture of $PhMe_2SiBpin$, 2.0 equivalent of ^{t}BuOK and styrene.

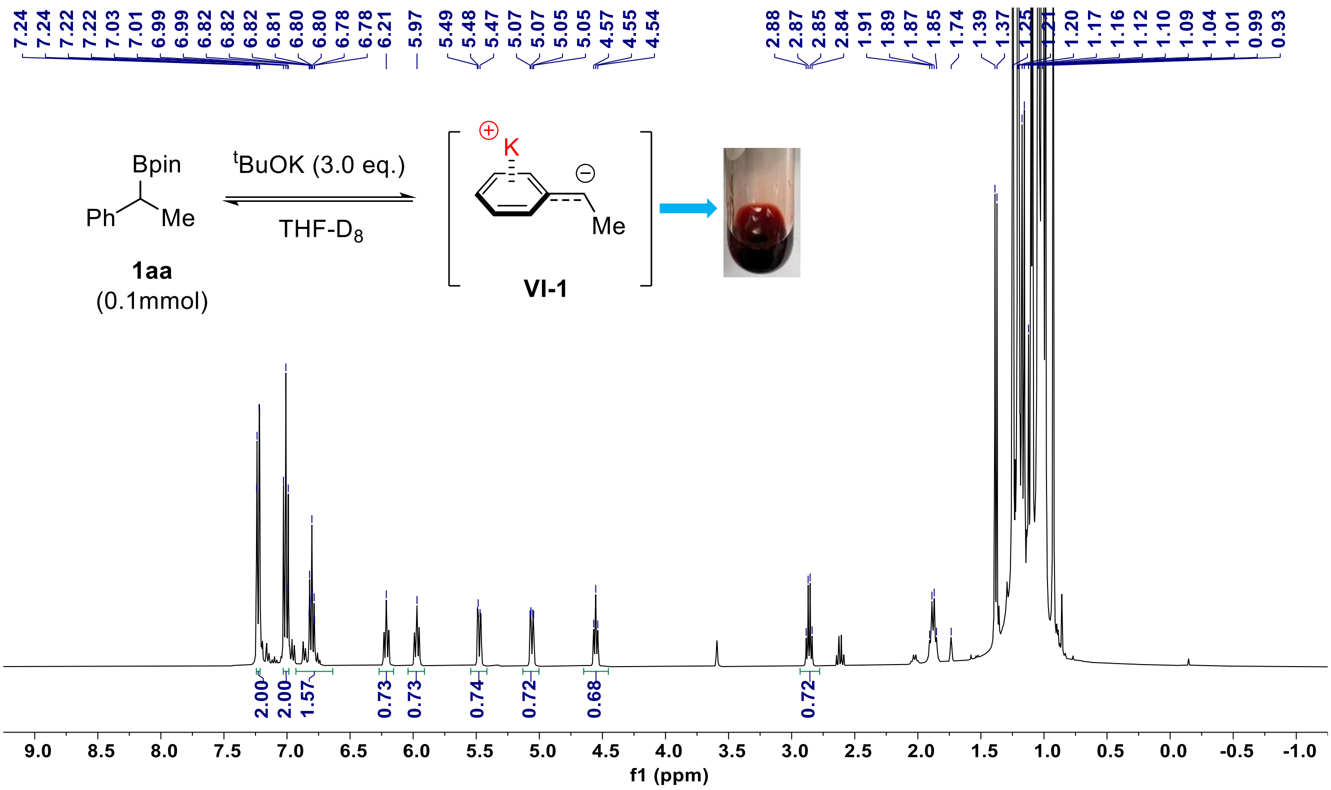


Figure S6. [1]H NMR pectrum for the reaction mixture of $PhCH(Bpin)CH_3$ **1aa**, 3.0 equivalent of ^{t}BuOK.

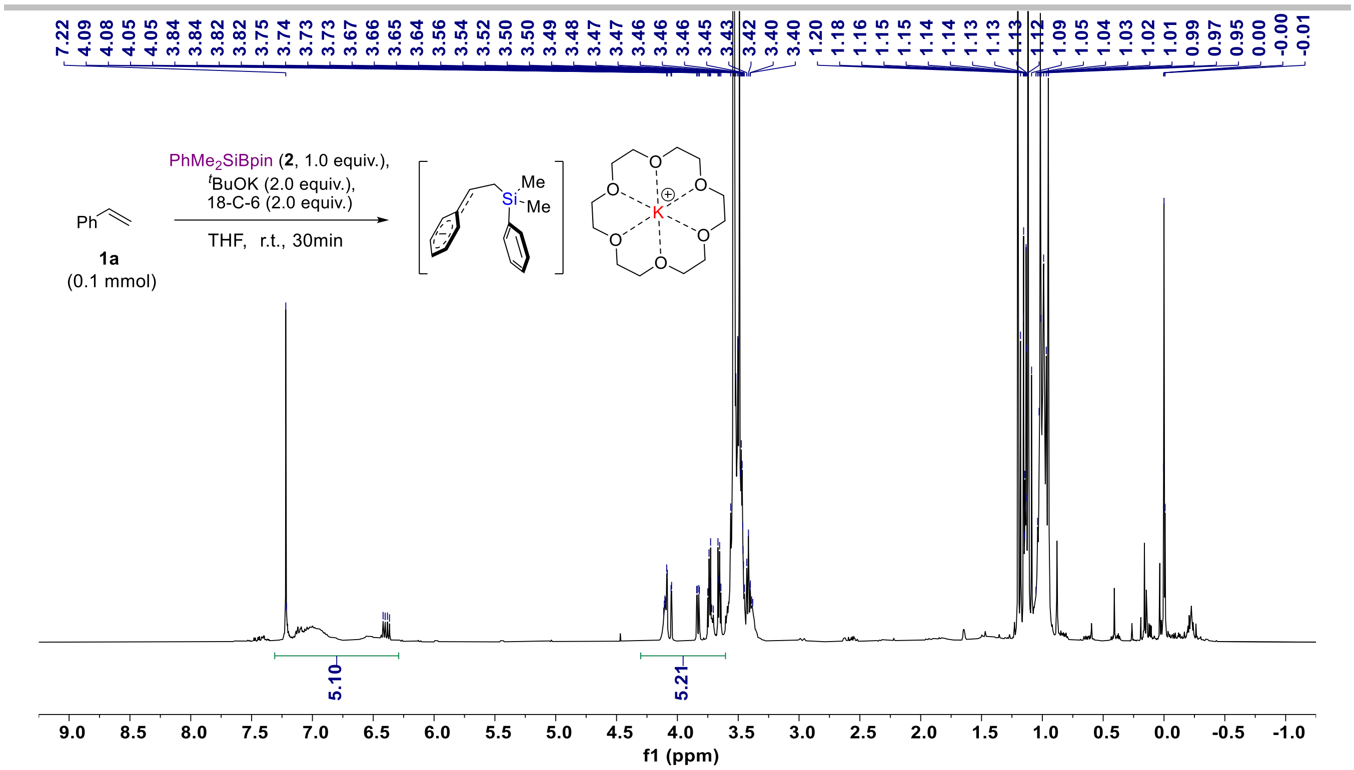
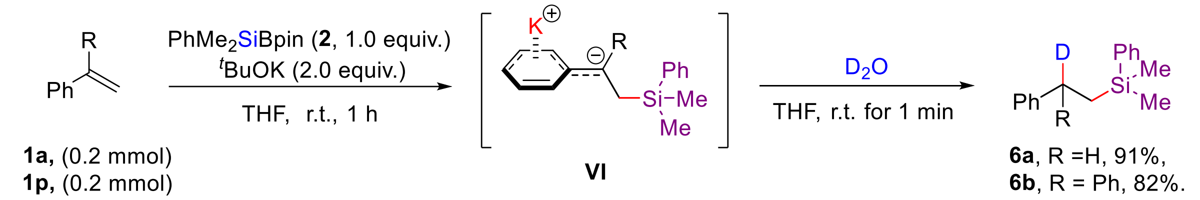


Figure S7. [1]H NMR pectrum for the reaction mixture of $PhMe_2SiBpin$, 2.0 equivalent of ^tBuOK and styrene with 2.0 equivalent 18-crown-6 as the additive, in THF-D_8.

2.4.2 Trapping the carbanion by deuterium oxide



Experimental procedure: In an argon-filled glove box, an oven-dried 10 mL schlenk tube was charged styrene **1a** (20.8 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (52.4 mg, 0.2 mmol, 1.0 equiv.), ^tBuOK (44.9 mg, 0.40 mmol, 2.0 equiv.), strried at room temperature for 10 min. Then the reaction mixture was quenched by deuterium oxide (D_2O, 50 μL) and diluted by ethyl acetate (2 mL). The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (3×3 mL). Then, the organic layers were combined, and dried over anhydrous sodium sulfate and filtered. After removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether) to afford the hydrosilylation product **3a** as colorless oil (44.0 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.56 (m, 2H), 7.44 – 7.39 (m, 3H), 7.35 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 2.72 – 2.62 (m, 1H), 1.17 (d, *J* = 9.1 Hz, 2H), 0.34 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 145.0, 139.1, 133.6, 129.0, 128.3, 127.8, 127.8, 125.6, 29.8 (t, 19.3 Hz), 17.7, -3.1 ppm.

Experimental procedure: In an argon-filled glove box, an oven-dried 10 mL schlenk tube was charged 1,1-diphenylethylene **1p** (36.0 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (52.4 mg, 0.2 mmol, 1.0 equiv.), ^{t}BuOK (44.9 mg, 0.40 mmol, 2.0 equiv.), strried at room temperature for 10 min. Then the reaction mixture was quenched by deuterium oxide (D_2O, 50 µL) and diluted by ethyl acetate (2 mL). The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (3×3 mL). Then, the organic layers were combined, and dried over anhydrous sodium sulfate and filtered. After removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether) to afford the hydrosilylation product **3b** as colorless oil (52.1 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 – 7.46 (m, 2H), 7.42 – 7.36 (m, 3H), 7.33 – 7.25 (m, 8H), 7.22 – 7.15 (m, 2H), 1.70 (s, 2H), 0.09 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 139.2, 133.6, 128.9, 128.4, 127.8, 127.6, 126.1, 46.8 (t, J = 19.4 Hz), 23.3, -2.7 ppm.

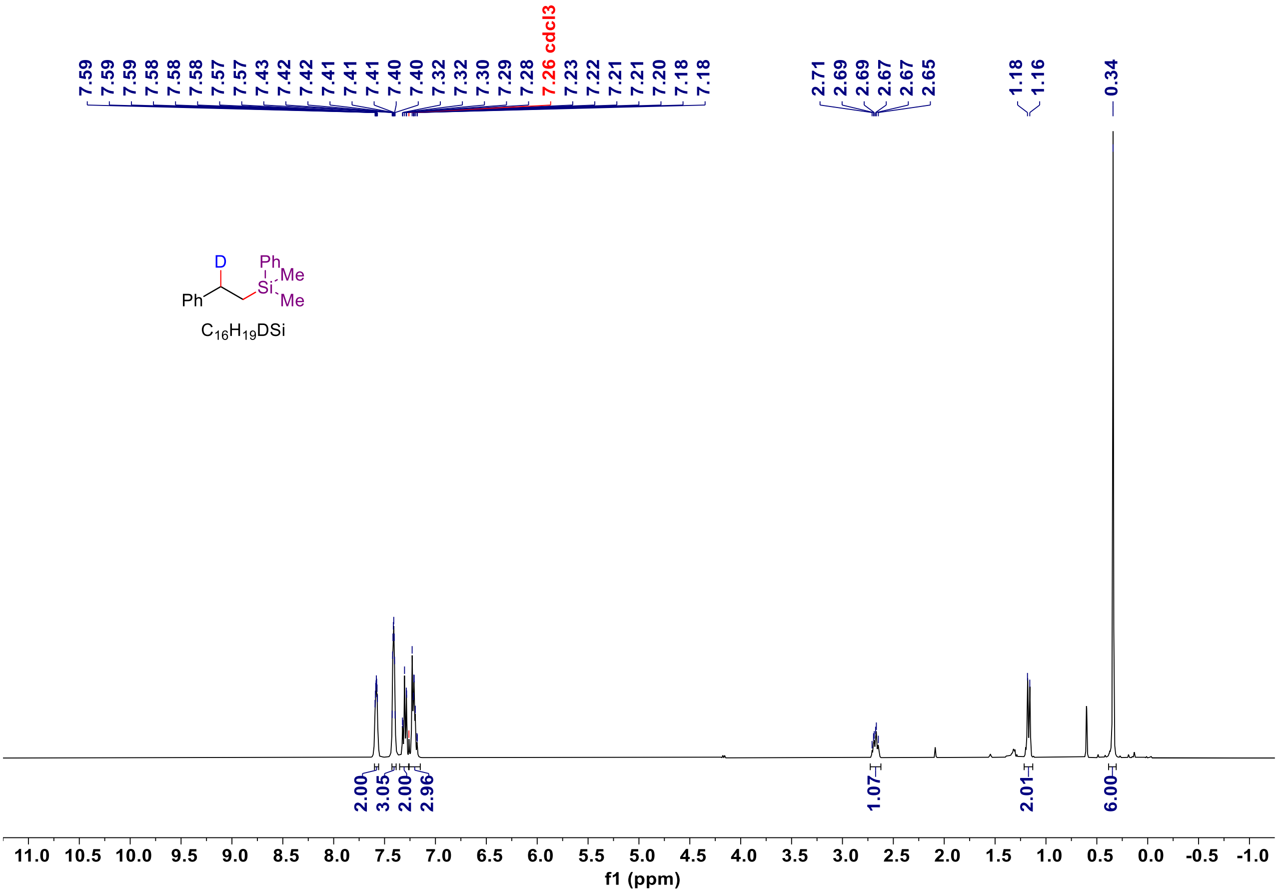


Figure S8. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **3a.**

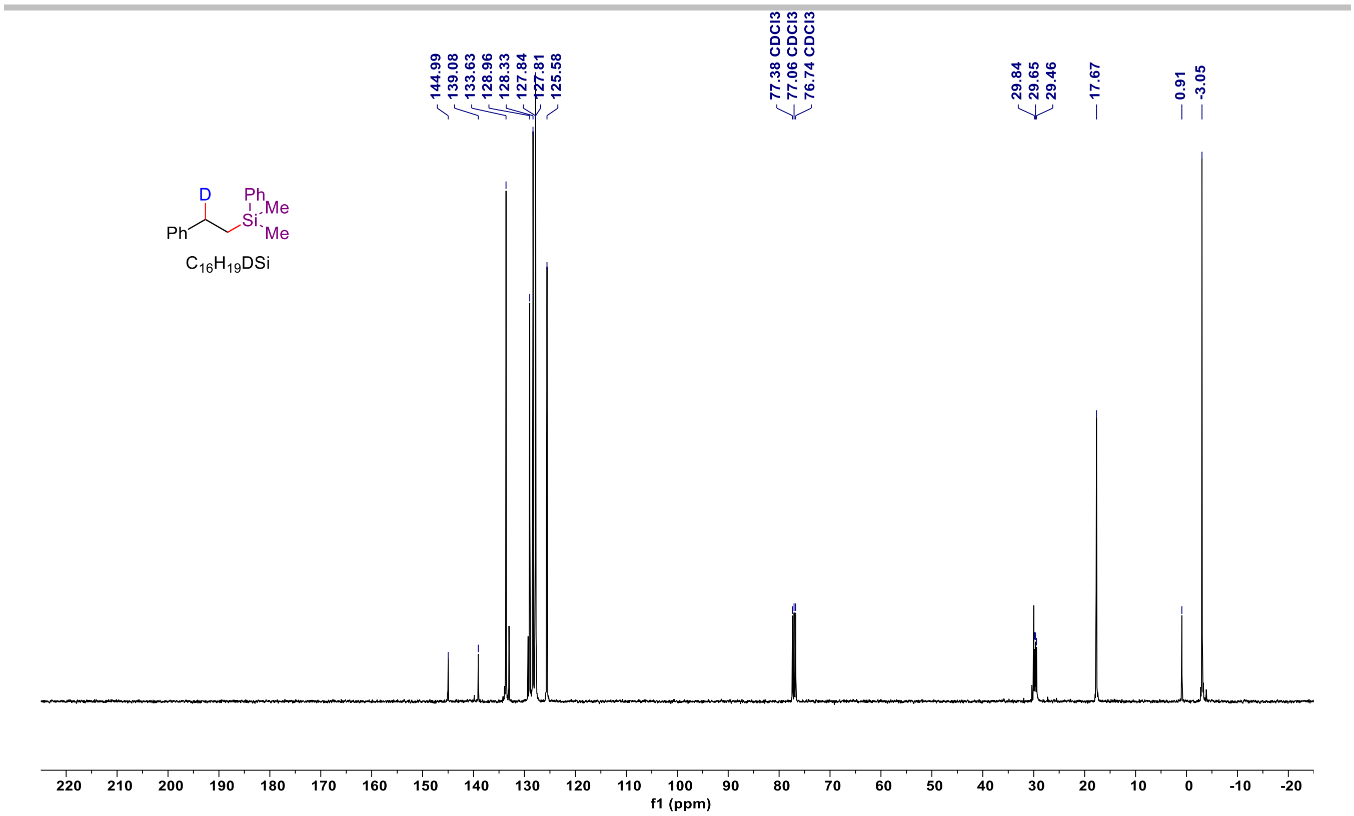


Figure S9. **^{13}C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **3a**.

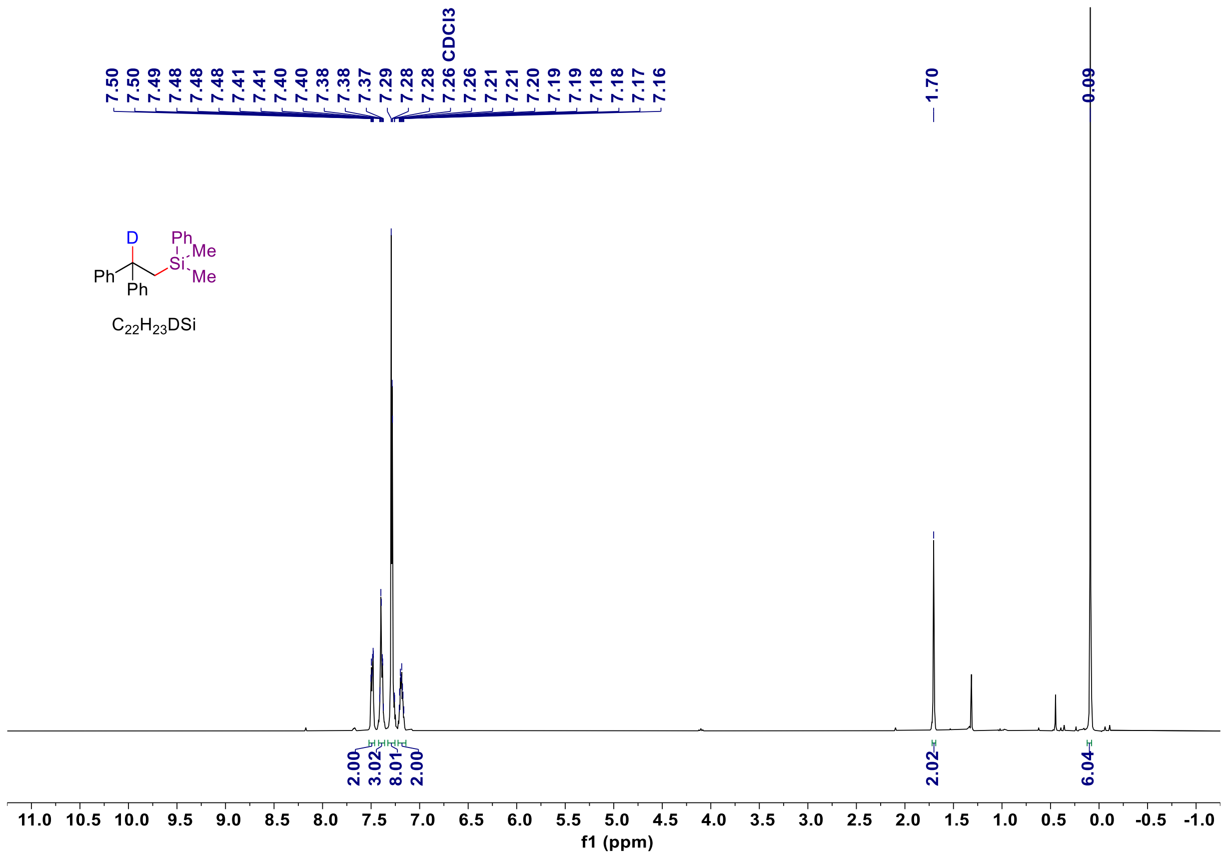


Figure S10. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **3b.**

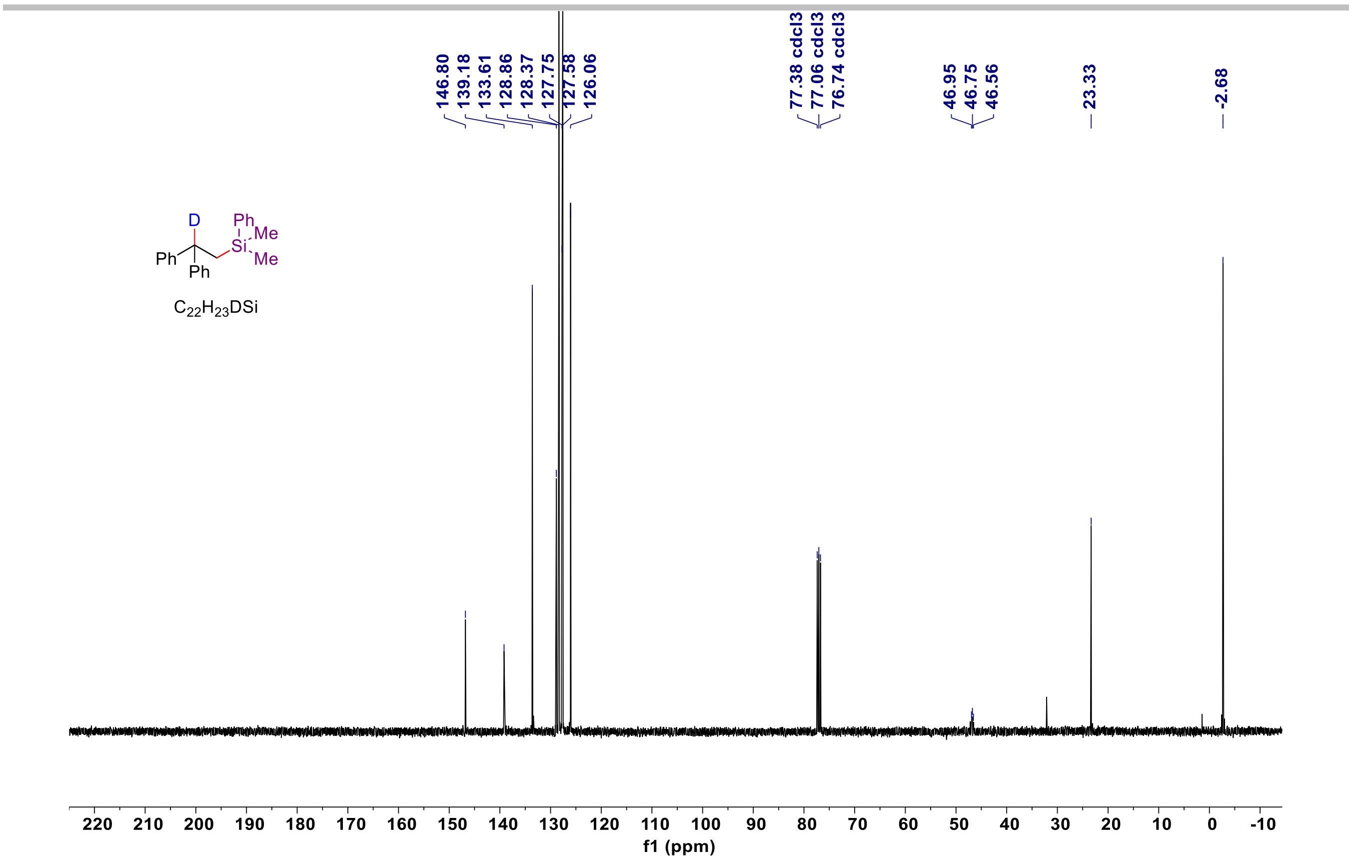
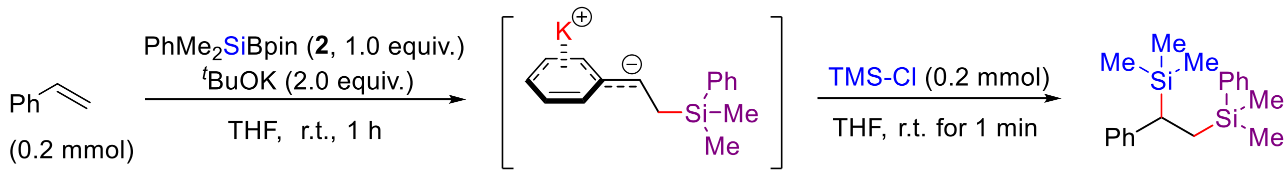


Figure S11. **^{13}C NMR** spectrum (100 MHz, $CDCl_3$) of compound **3b.**

2.4.3 Trapping the carbanion with cholrotrimethylsilane



Experimental procedure: In an argon-filled glove box, an oven-dried 10 mL Schlenk tube was charged with styrene **1a** (20.8 mg, 0.2 mmol, 1.0 equiv.), $PhMe_2SiBpin$ **2a** (52.4 mg, 0.2 mmol, 1.0 equiv.), ^{t}BuOK (44.9 mg, 0.40 mmol, 2.0 equiv.), stirred at room temperature for 30 min. Then the reaction mixture was quenched by chlorotrimethylsilane (TMSCl, 0.2 mmol, 1.0 equiv.) and diluted by ethyl acetate (2 mL). The organic phase was separated, and the aqueous layer was extracted with ethyl acetate (3×3 mL). Then, the organic layers were combined, and dried over anhydrous sodium sulfate and filtered. After removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether) to afford the hydrosilylation product **3c** as colorless oil (40.1 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.48 (m, 2H), 7.46 – 7.34 (m, 3H), 7.29 – 7.24 (m, 2H), 7.19 – 7.12 (m, 1H), 7.09 – 7.05 (m, 2H), 2.18 – 2.14 (m, 1H), 1.42 – 1.37 (m, 1H), 1.21 (dd, J = 15.2, 2.3 Hz, 1H), 0.16 (s, 3H), 0.07 (s, 3H), 0.00 (s, 9H) ppm. **^{13}C{^{1}H} NMR** (100 MHz,

$CDCl_3$): δ 144.8, 139.9, 133.6, 128.7, 127.9, 127.9, 127.7, 124.3, 31.5, 15.3, -1.9, -3.2, -3.3 ppm.
HRMS (ESI): calculated for $C_{19}H_{29}Si_2^+$ $[M+H]^+$ 313.1802; found 313.1798.

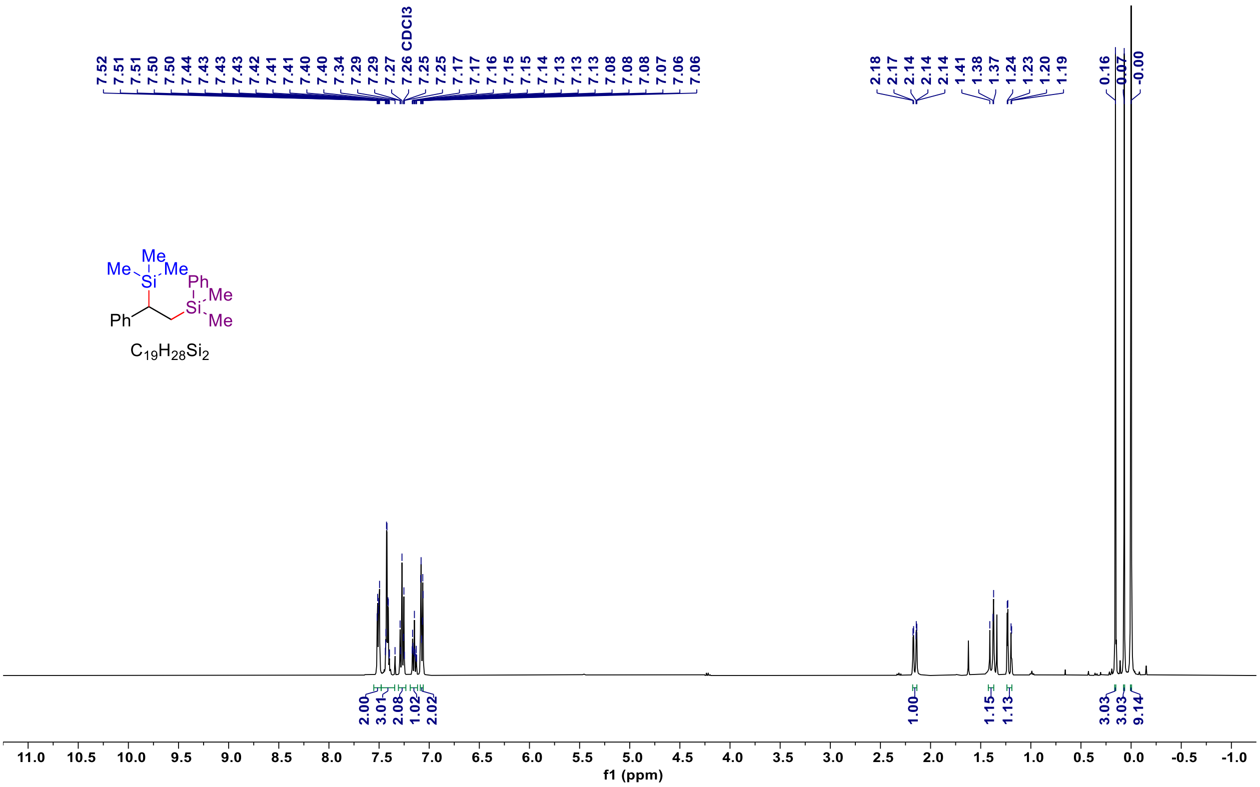


Figure S12. **^{1}H NMR** spectrum (400 MHz, $CDCl_3$) of compound **6c.**

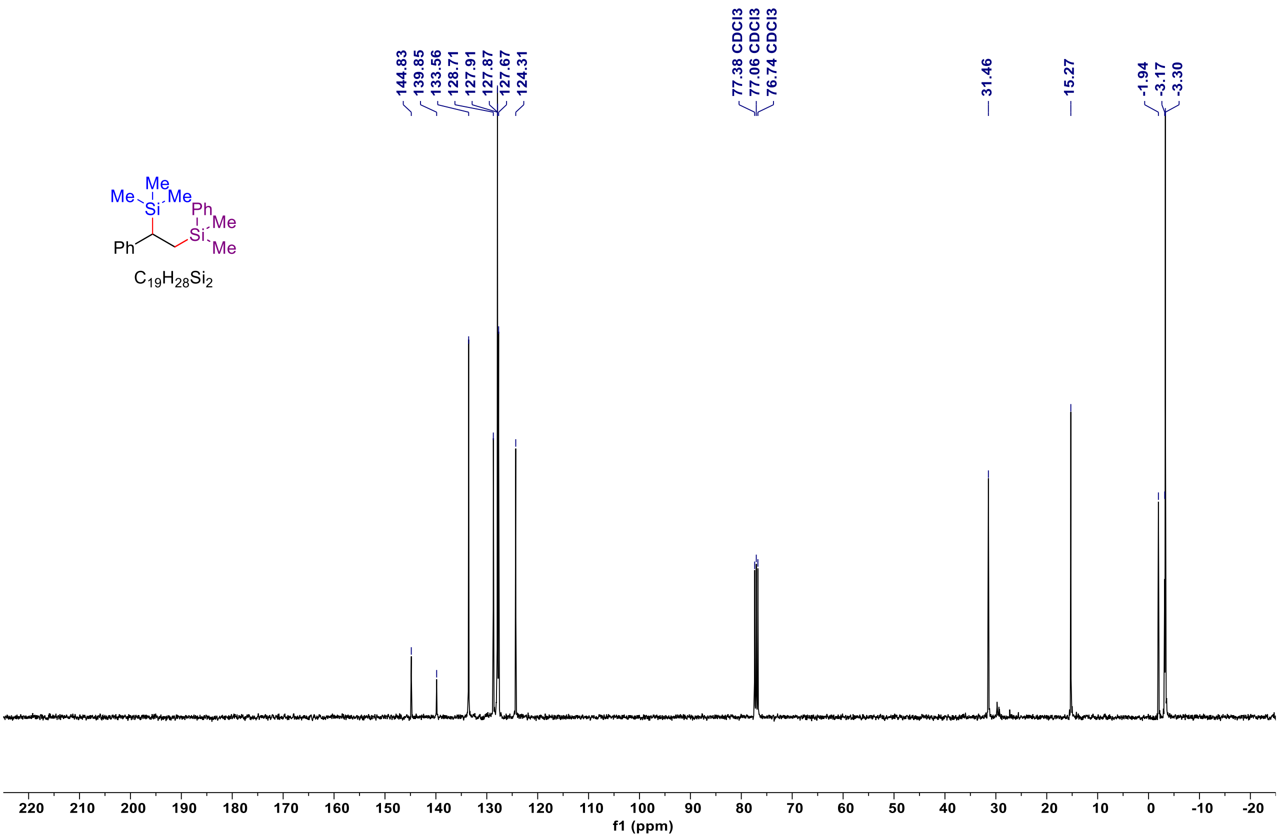
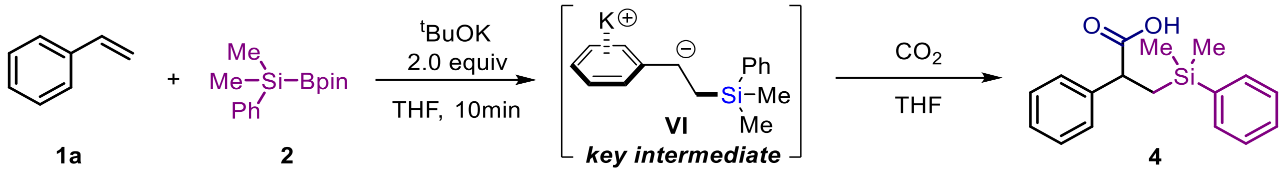


Figure S13. **$^{13}C\{^1H\}$ NMR** spectrum (100 MHz, $CDCl_3$) of compound **6c.**

These results confirm the involvement of the *β*-silyl carbanion intermediate **V**, which is also consistent with our DFT calculations.

2.4.4 Electron paramagnetic resonance (EPR) experiments



Entry	Sample (in PhMe)	EPR
(a)	$PhMe_2$Si-Bpin	inactive
(b)	$PhMe_2$Si-Bpin + ^{t}BuOK (2.0 eq.)	inactive
(c)	^{t}BuOK (2.0 eq.) + $PhMe_2$Si-Bpin + Styrene	inactive

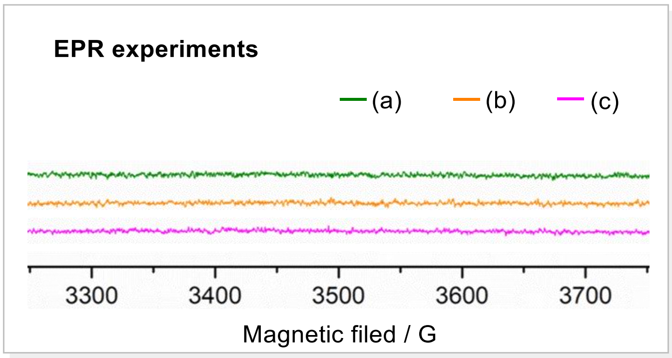
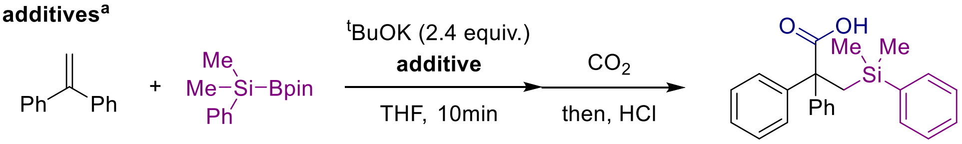


Figure S14. EPR experiments.

As shown in Figure S14, the EPR experiments were also conducted to detect the potential silyl or carbon radical. However, the reaction between $PhMe_2SiBpin$ and ^{t}BuOK (entry b) or styrene, $PhMe_2SiBpin$ and ^{t}BuOK (entry c) does not show any signal of free radicals. Our calculation results indicated that the silyl radical generation from complex **II** or **II** with ^{t}BuOK are thermodynamically unfavorable processes, and thes process are endergonic by 43.4 kcal/mol and 32.8 kcal/mol, respectively (see Figure S17 for details). These computational results are consistent with the fact that no radical species are detectable by EPR experiments under current reaction conditions. Thus, SET mechanisms for the silyl radical additon pathway can be excluded.

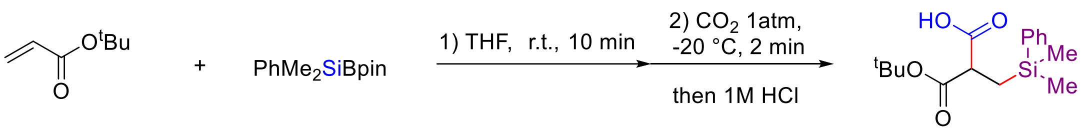
Effect of additives[a]



1p (0.2mmol) **2** (1.2 equiv.) **4p**

entry	additive	yield of 4p[b]
1	none	82%
2	10 mol% 1,10-phenanthroline	60%
3	10 mol% *N*-methylpyrrolidone	66%
4	1.0 equiv *N*-methylpyrrolidone	n.d.
5	1.0 equiv *N*-methylglycine	n.d.

Elimination of radical pathway: possible silyl conjugate addition of α,β-unsaturated carbonyl compound



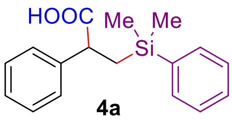
1a, (0.2 mmol) **2,** (1.0 equiv.) **3d,** n.d.

Figure S15. Control experiment.

To further investigate the reaction mechanism and exclude the possibility of a silyl radical pathway, we designed a series of control experiments. First, we introduced three typical SET promoters into the system: 1,10-phenanthroline, *N*-methylpyrrolidone (NMP), and *N*-methylglycine, which are known to significantly enhance radical reactions mediated by ^{t}BuOK. Notably, the addition of 10 mol% 1,10-phenanthroline and NMP reduced the reaction yields to 22% and 16%, respectively, while stoichiometric amounts of NMP or *N*-methylglycine completely suppressed the reaction. This observation further negates the possibility of a SET mechanism. Subsequently, tert-butyl acrylate was employed as a potential silyl radical acceptor, as its conjugate addition with silyl radicals has been well-documented in the literature[4]. However, the expected target product or silyl addition products were not detected, suggesting that the reaction may not proceed via a radical mechanism. Finally, electron spin resonance (ESR) spectroscopy conducted in the presence of styrene (see Figure S14) detected no radical signals. Collectively, these experimental evidences lead us to conclude that the ^{t}BuOK-mediated single-electron transfer model is not applicable to this system.

3. Spectroscopic Characterization Data

3.2.1 3-(dimethyl(phenyl)silyl)-2-phenylpropanoic acid (**4a**)



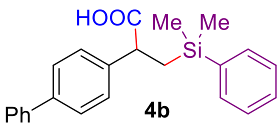
4a

$C_{17}H_{20}O_2Si$

M = 284.43 g/mol

Prepared according to general procedure B from styrene (20.8 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4a** as a colorless oil (43.4 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 7.29 – 7.24 (m, 5H), 3.61 (t, *J* = 7.8 Hz, 1H), 1.64 (dd, *J* = 14.8, 7.4 Hz, 1H), 1.38 (dd, *J* = 14.8, 8.3 Hz, 1H), 0.14 (s, 3H), 0.14 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.8, 140.1, 138.1, 133.6, 129.1, 128.6, 128.1, 127.8, 127.5, 47.2, 20.3, -2.7, -3.1 ppm. **IR** (film): 3252, 3068, 3028, 2954, 1703, 1550, 1426, 1248, 1113, 865, 836, 729, 698 cm^{-1}. **HRMS** (ESI): calculated for $C_{17}H_{19}O_2Si^-$ $[M-H]^-$ 283.1160; found 283.1156.

3.2.2 2-([1,1'-biphenyl]-4-yl)-3-(dimethyl(phenyl)silyl)propanoic acid (**4b**)



4b

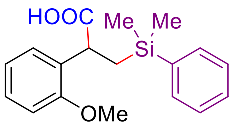
$C_{23}H_{24}O_2Si$

M = 360.53 g/mol

Prepared according to general procedure B from 4-vinyl-1,1'-biphenyl (36.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4b** as gum (49.0 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45

– 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 5H), 7.20 – 7.09 (m, 9H), 3.48 (t, *J* = 7.8 Hz, 1H), 1.50 (dd, *J* = 14.8, 7.4 Hz, 1H), 1.24 (dd, *J* = 14.8, 8.4 Hz, 1H), 0.04 (s, 3H), 0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.0, 140.7, 140.4, 139.1, 138.0, 133.6, 129.1, 128.8, 128.4, 127.8, 127.6, 127.3, 127.1, 46.7, 20.3, -2.8, -3.0 ppm. **HRMS** (ESI): calculated for $C_{23}H_{23}O_2Si^-$ $[M-H]^-$ 359.1473; found 359.1469.

3.2.3 3-(dimethyl(phenyl)silyl)-2-(2-methoxyphenyl)propanoic acid (**4c**)



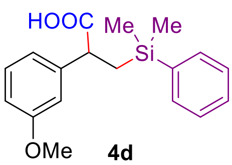
4c

$C_{18}H_{22}O_3Si$

M = 314.46 g/mol

Prepared according to general procedure B from 2-methoxy-styrene (26.8 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4c** as gum (39.2 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 7.24 – 7.17 (m, 2H), 6.89 (td, *J* = 7.5, 1.1 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.12 (dd, *J* = 8.9, 6.6 Hz, 1H), 3.76 (s, 3H), 1.62 (dd, *J* = 14.8, 6.6 Hz, 1H), 1.40 (dd, *J* = 14.9, 9.0 Hz, 1H), 0.15 (s, 3H), 0.13 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.9, 156.6, 138.7, 133.6, 128.9, 128.7, 128.4, 127.7, 120.7, 110.8, 55.4, 39.9, 19.0, -2.8, -3.0 ppm. **HRMS** (ESI): calculated for $C_{18}H_{21}O_3Si^-$ $[M-H]^-$ 313.1265; found 313.1268.

3.2.4 3-(dimethyl(phenyl)silyl)-2-(3-methoxyphenyl)propanoic acid (**4d**)



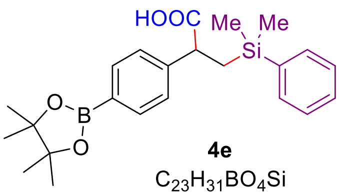
4d

$C_{18}H_{22}O_3Si$

M = 314.46 g/mol

Prepared according to general procedure B from 3-methoxy-styrene (26.8 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4d** as gum (44.1 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 – 7.40 (m, 2H), 7.35 – 7.29 (m, 3H), 7.19 (td, *J* = 7.6, 1.0 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.81 – 6.74 (m, 2H), 3.76 (s, 3H), 3.57 (t, *J* = 7.8 Hz, 1H), 1.62 (dd, *J* = 14.8, 7.4 Hz, 1H), 1.36 (dd, *J* = 14.8, 8.3 Hz, 1H), 0.16 (s, 3H), 0.14 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.0, 159.7, 141.6, 138.1, 133.6, 129.6, 129.1, 127.8, 120.5, 113.7, 113.0, 55.2, 47.1, 20.3, -2.7, -3.0 ppm. **HRMS** (ESI): calculated for $C_{18}H_{21}O_3Si^-$ $[M-H]^-$ 313.1265; found 313.1268.

3.2.5 3-(dimethyl(phenyl)silyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoic acid (**4e**)



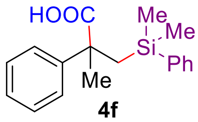
4e

$C_{23}H_{31}BO_4Si$

M = 410.39 g/mol

Prepared according to general procedure B from 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (46.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (52.8 mg, 0.20 mmol, 1.0 equiv.), ^{t}BuOK (44.9 mg, 0.40 mmol, 2.0 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4e** as gum (29.6 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 2H), 7.34 – 7.22 (m, 2H), 7.16 (dd, *J* = 4.9, 1.9 Hz, 2H), 7.15 – 7.08 (m, 3H), 3.46 (t, *J* = 7.8 Hz, 1H), 1.50 (dd, *J* = 14.8, 7.4 Hz, 1H), 1.23 (d, *J* = 8.3 Hz, 1H), 1.19 (s, 12H), -0.01 (s, 3H), -0.03 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 179.1, 143.4, 138.1, 135.1, 133.6, 129.1, 127.8, 127.5, 83.8, 47.2, 29.8, 24.9, 20.2, -2.6, -3.0 ppm. **^{11}B{^{1}H} NMR** (128 MHz, $CDCl_3$): δ 30.98. **HRMS** (ESI): calculated for $C_{23}H_{30}BO_4Si^-$ $[M-H]^-$ 409.2012; found 409.2010.

3.2.6 3-(dimethyl(phenyl)silyl)-2-methyl-2-phenylpropanoic acid (**4f**)



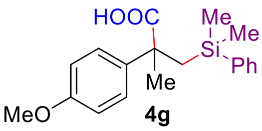
4f

$C_{18}H_{22}O_2Si$

M = 298.46 g/mol

Prepared according to general procedure B from α-methyl styrene (23.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4f** as colorless oil (44.1 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 2H), 7.21 (d, J = 7.2 Hz, 2H), 7.15 – 7.09 (m, 5H), 7.07 – 7.02 (m, 1H), 1.59 (d, J = 14.7 Hz, 1H), 1.47 (d, J = 14.6 Hz, 1H), 1.37 (s, 3H), 0.00 (s, 3H), -0.05 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 183.5, 144.6, 139.5, 133.6, 128.9, 128.4, 127.8, 126.9, 126.0, 48.6, 28.0, 25.4, -1.5, -1.6 ppm. **IR** (film): 3240, 3067, 3028, 2954, 1703, 1550, 1426, 1248, 1113, 865, 836, 729, 698 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{21}O_2Si^-$ [M-H]$^-$ 297.1316; found 297.1315.

3.2.7 3-(dimethyl(phenyl)silyl)-2-(4-methoxyphenyl)-2-methylpropanoic acid (**4g**)



4g

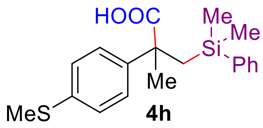
$C_{19}H_{24}O_3Si$

M = 328.48 g/mol

Prepared according to general procedure B from 4-methoxy-α-methyl styrene (29.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4g** as a colorless oil (28.5 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.36 – 7.27 (m, 5H), 6.82 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 1.73 (d, J = 14.7 Hz, 1H), 1.64 (d, J = 14.7 Hz, 1H), 1.53 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H) ppm. **^{13}C{^{1}H} NMR**

(100 MHz, $CDCl_3$): δ 182.0, 158.5, 139.6, 136.7, 133.6, 128.9, 127.7, 127.2, 113.7, 55.3, 47.7, 28.1, 25.4, -1.5, -1.6 ppm. **HRMS** (ESI): calculated for $C_{19}H_{23}O_3Si^-$ $[M-H]^-$ 327.1422; found 327.1418.

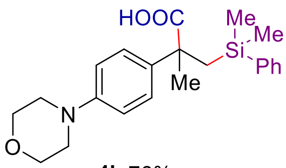
3.2.8 3-(dimethyl(phenyl)silyl)-2-methyl-2-(4-(methylthio)phenyl)propanoic acid (**4h**)



4h
$C_{19}H_{24}O_2SSi$
M = 344.54 g/mol

Prepared according to general procedure B from 4-methylthio-α-methyl styrene (32.8 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4h** as gum (35.2 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.36 (m, 2H), 7.35 – 7.27 (m, 5H), 7.18 (d, J = 8.6 Hz, 2H), 2.47 (s, 3H), 1.74 (d, J = 14.7 Hz, 1H), 1.63 (d, J = 14.7 Hz, 1H), 1.54 (s, 3H), 0.20 (s, 3H), 0.18 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 182.9, 141.4, 139.4, 137.0, 133.5, 128.9, 127.8, 126.6, 126.5, 48.1, 27.9, 25.2, 15.9, -1.5 ppm. **HRMS** (ESI): calculated for $C_{19}H_{23}O_2SSi^-$ $[M-H]^-$ 343.1194; found 343.1191.

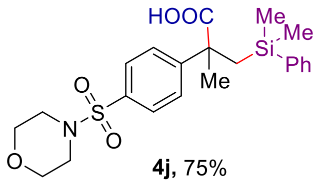
3.2.9 3-(dimethyl(phenyl)silyl)-2-methyl-2-(4-morpholinophenyl)propanoic acid (**4i**)



4i, 76%
$C_{22}H_{29}NO_3Si$
M = 383.56 g/mol

Prepared according to general procedure B from 4-(4-(prop-1-en-2-yl)phenyl)morpholine (40.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 °C and then the dried CO_2 is added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 °C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4i** as a colorless oil (58.5 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 – 7.39 (m, 2H), 7.36 – 7.26 (m, 5H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.90 – 3.82 (m, 4H), 3.18 – 3.08 (m, 4H), 1.74 (d, *J* = 14.7 Hz, 1H), 1.62 (d, *J* = 14.7 Hz, 1H), 1.53 (s, 3H), 0.19 (s, 3H), 0.18 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 182.7, 149.9, 139.7, 136.1, 133.5, 128.8, 127.7, 126.8, 115.4, 66.9, 49.3, 47.6, 27.8, 25.2, -1.51, -1.52 ppm. **HRMS** (ESI): calculated for $C_{22}H_{28}NO_3Si^-$ [M-H]$^-$ 382.1844; found 382.1840.

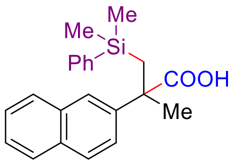
3.2.10 3-(dimethyl(phenyl)silyl)-2-methyl-2-(4-(morpholinosulfonyl)phenyl)propanoic acid (**4j**)



4j, 75%
$C_{22}H_{29}NO_5SSi$
M = 447.62 g/mol

Prepared according to general procedure B from 4-((4-(prop-1-en-2-yl)phenyl)sulfonyl)morpholine (53.4 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 ^{o}C and then the dried CO_2 is added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 ^{o}C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4j** as gum (67.1 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 – 7.62 (m, 2H), 7.59 – 7.50 (m, 2H), 7.46 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 5.30 (s, 1H), 3.80 – 3.70 (m, 4H), 3.05 – 2.94 (m, 4H), 1.77 (d, *J* = 14.7 Hz, 1H), 1.65 (d, *J* = 14.7 Hz, 1H), 1.57 (s, 3H), 0.19 (s, 3H), 0.16 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.4, 150.1, 138.7, 133.6, 133.5, 129.2, 127.9, 127.9, 127.0, 66.1, 48.9, 46.0, 28.2, 25.2, -1.5 ppm. **HRMS** (ESI): calculated for $C_{22}H_{28}NO_5SSi^-$ [M-H]$^-$ 446.1463; found 446.1456.

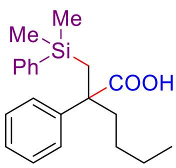
3.2.11 3-(dimethyl(phenyl)silyl)-2-methyl-2-(naphthalen-2-yl)propanoic acid (**4k**)



4k
$C_{22}H_{24}O_2Si$
M = 348.52 g/mol

Prepared according to general procedure B from 2-(prop-1-en-2-yl)naphthalene (33.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at –20 °C for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4k** as gum (47.4 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 – 7.76 (m, 4H), 7.58 – 7.51 (m, 1H), 7.51 – 7.41 (m, 4H), 7.34 – 7.27 (m, 3H), 1.89 (d, *J* = 14.7 Hz, 1H), 1.78 (d, *J* = 14.7 Hz, 1H), 1.68 (s, 3H), 0.22 (s, 3H), 0.19 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 183.3, 142.0, 139.4, 133.6, 133.2, 132.3, 128.9, 128.2, 128.0, 127.7, 127.4, 126.1, 125.9, 124.8, 124.4, 48.8, 27.8, 25.4, -1.50, -1.53 ppm. **HRMS** (ESI): calculated for $C_{22}H_{23}O_2Si^-$ [M-H]$^-$ 347.1473; found 347.1466.

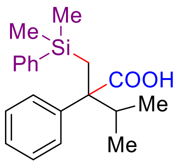
3.2.12 2-((dimethyl(phenyl)silyl)methyl)-2-phenylhexanoic acid (**4l**)



4l
$C_{21}H_{28}O_2Si$
M = 340.54 g/mol

Prepared according to general procedure B from hex-1-en-2-ylbenzene (32.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at – 20 °C for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4l** as a colorless oil (47.7 mg, 70% yield). **^{1}H NMR** (400 MHz, CDCl₃): δ 7.56 – 7.46 (m, 2H), 7.42 – 7.32 (m, 7H), 7.31 – 7.27 (m, 1H), 2.04 – 1.90 (m, 2H), 1.81 – 1.68 (m, 2H), 1.13 – 1.03 (m, 2H), 1.02 – 0.94 (m, 2H), 0.77 (t, J = 7.1 Hz, 3H), 0.22 (s, 3H), 0.12 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 183.0, 143.8, 139.6, 133.6, 128.9, 128.3, 127.7, 126.9, 126.4, 52.4, 37.1, 26.6, 23.5, 22.9, 14.0, -1.9, -2.1 ppm. **HRMS** (ESI): calculated for $C_{21}H_{27}O_2Si^-$ [M-H]$^-$ 339.1786; found 339.1782.

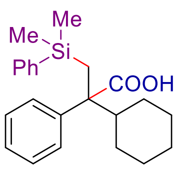
3.2.13 2-((dimethyl(phenyl)silyl)methyl)-3-methyl-2-phenylbutanoic acid (**4m**)



4m
$C_{20}H_{26}O_2Si$
M = 326.51 g/mol

Prepared according to general procedure B from (3-methylbut-1-en-2-yl)benzene (29.2 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at – 20 ºC for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4m** as a colorless oil (47.0 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 – 7.45 (m, 2H), 7.39 – 7.32 (m, 5H), 7.31 – 7.22 (m, 3H), 2.48 – 7.34 (m, 1H), 1.78 (d, J = 14.7 Hz, 1H), 1.55 (d, J = 14.8 Hz, 1H), 0.88 (d, J = 6.7 Hz, 3H), 0.83 (d, J = 6.7 Hz, 3H), 0.22 (s, 3H), 0.03 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 182.0, 140.8, 140.6, 133.5, 128.6, 128.2, 127.6, 127.5, 126.6, 57.7, 37.4, 24.1, 18.7, 18.4, -1.4, -1.9 ppm. **HRMS** (ESI): calculated for $C_{20}H_{25}O_2Si^-$ [M-H]$^-$ 325.1629; found 325.1624.

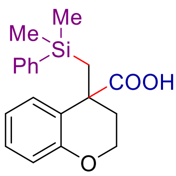
3.2.14 2-cyclohexyl-3-(dimethyl(phenyl)silyl)-2-phenylpropanoic acid (**4n**)



4n, 68%
$C_{23}H_{30}O_2Si$
M = 366.58 g/mol

Prepared according to general procedure B from (1-cyclohexylvinyl)benzene (37.2 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 ^{o}C and then the dried CO_2 is added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 ^{o}C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4n** as gum (50.1 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 2H), 7.36 – 7.22 (m, 8H), 2.01 – 1.91 (m, 1H), 1.88 – 1.76 (m, 2H), 1.74 – 1.54 (m, 5H), 1.20 – 0.94 (m, 3H), 0.92 – 0.75 (m, 2H), 0.22 (s, 3H), 0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 182.2, 141.0, 140.5, 133.6, 128.7, 128.3, 127.7, 127.5, 126.6, 57.6, 47.6, 29.0, 28.3, 27.0, 26.8, 26.4, 24.4, -1.5, -1.9 ppm. **HRMS** (ESI): calculated for $C_{23}H_{29}O_2Si^-$ [M-H]$^-$ 365.1942; found 365.1938.

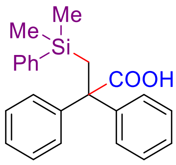
3.2.15 4-((dimethyl(phenyl)silyl)methyl)chromane-4-carboxylic acid (**4o**)



4o, 80%
$C_{19}H_{22}O_3Si$
M = 326.47 g/mol

Prepared according to general procedure B from 4-methylenechromane (29.2 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 ^{o}C and then the dried CO_2 is added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 ^{o}C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4o** as gum (52.4 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.2 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.29 – 7.21 (m, 3H), 7.14 (t, J = 7.7 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 4.24 – 4.01 (m, 2H), 2.44 – 2.32 (m, 1H), 1.95 – 1.88 (m, 1H), 1.87 – 1.77 (m, 1H), 1.62 – 1.50 (m, 1H), 0.23 (s, 3H), 0.21 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 182.1, 154.3, 138.8, 133.5, 129.7, 129.1, 128.6, 127.8, 124.5, 120.5, 117.3, 63.9, 43.9, 32.4, 29.0, -1.5, -1.6 ppm. **HRMS** (ESI): calculated for $C_{19}H_{21}O_3Si^-$ [M-H]$^-$ 325.1265; found 325.1258.

3.2.16 3-(dimethyl(phenyl)silyl)-2,2-diphenylpropanoic acid (**4p**)



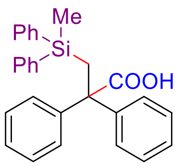
4p

$C_{23}H_{24}O_2Si$

M = 360.53 g/mol

Prepared according to general procedure B from 1,1-diphenylethylene (36.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4p** as a colorless oil (59.2 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.44 (m, 2H), 7.44 – 7.36 (m, 4H), 7.35 – 7.31 (m, 5H), 7.31 – 726 (m, 4H), 2.14 (s, 2H), 0.00 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.0, 144.6, 139.9, 133.7, 128.8, 128.7, 127.9, 127.6, 126.9, 58.3, 28.4, -2.1 ppm. **IR** (film): 3208, 3069, 3022, 2952, 1705, 1548, 1428, 1242, 1111, 737, 700 cm^{-1}. **HRMS** (ESI): calculated for $C_{23}H_{23}O_2Si^-$ $[M-H]^-$ 359.1473; found 359.1470.

3.2.17 3-(methyldiphenylsilyl)-2,2-diphenylpropanoic acid (**4pa**)



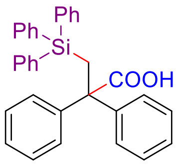
4pa

$C_{28}H_{26}O_2Si$

M = 422.60 g/mol

Prepared according to general procedure D from 1,1-diphenylethylene (36.0 mg, 0.20 mmol, 1.0 equiv.), $Ph_2MeSiLi$ (1.5 equiv.), stirred at room temperature for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 ^oC for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4pa** as gum (69.5 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.36 (m, 4H), 7.34 – 7.28 (m, 4H), 7.26 – 7.12 (m, 12H), 2.47 (s, 2H), 0.12 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.5, 144.3, 137.4, 134.7, 128.9, 128.8, 127.9, 127.5, 126.9, 58.1, 26.8, -3.8 ppm. **HRMS** (ESI): calculated for $C_{28}H_{25}O_2Si^-$ $[M-H]^-$ 421.1629; found 421.1625.

3.2.18 2,2-diphenyl-3-(triphenylsilyl)propanoic acid (**4pb**)



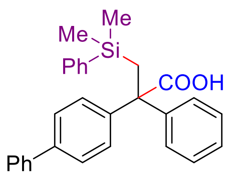
4pa

$C_{33}H_{28}O_2Si$

M = 484.67 g/mol

Prepared according to general procedure D from 1,1-diphenylethylene (36.0 mg, 0.20 mmol, 1.0 equiv.), Ph_3SiLi (1.5 equiv.), stirred at room temperature for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 ^oC for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4pb** as gum (68.0 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 12H), 7.25 – 7.21 (m, 7H), 7.21 – 7.14 (m, 6H), 2.82 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 179.4, 144.3, 136.1, 135.0, 129.1, 128.9, 127.9, 127.4, 126.9, 58.2, 25.9 ppm. **HRMS** (ESI): calculated for $C_{33}H_{27}O_2Si^-$ $[M-H]^-$ 483.1786; found 483.1781.

3.2.19 2-([1,1'-biphenyl]-4-yl)-3-(dimethyl(phenyl)silyl)-2-phenylpropanoic acid (**4q**)



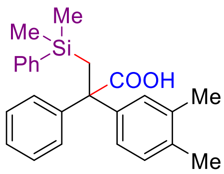
4q

$C_{29}H_{28}O_2Si$

M = 436.63 g/mol

Prepared according to general procedure B from 4-(1-phenylvinyl)-1,1'-biphenyl (51.2 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4q** as gum (70.9 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69 – 7.62 (m, 2H), 7.60 – 7.52 (m, 2H), 7.53 – 7.44 (m, 8H), 7.44 – 7.39 (m, 1H), 7.39 – 7.28 (m, 6H), 2.20 (s, 2H), 0.08 (s, 3H), 0.05 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.0, 144.4, 143.6, 140.6, 139.7, 139.6, 133.7, 129.2, 128.8, 128.7, 128.0, 127.5, 127.3, 127.1, 127.0, 126.5, 58.1, 28.4, -1.9, -2.0 ppm. **HRMS** (ESI): calculated for $C_{29}H_{27}O_2Si^-$ [M-H]$^-$ 435.1786; found 435.1780.

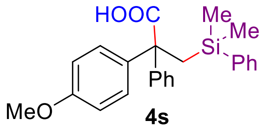
3.2.20 3-(dimethyl(phenyl)silyl)-2-(3,4-dimethylphenyl)-2-phenylpropanoic acid (**4r**)



4r
$C_{25}H_{28}O_2Si$
M = 388.58 g/mol

Prepared according to general procedure B from 1,2-dimethyl-4-(1-phenylvinyl)benzene (41.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4r** as gum (59.3 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.40 (d, J = 7.0 Hz, 2H), 7.34 – 7.24 (m, 6H), 7.12 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 7.8 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H), 2.18 – 2.06 (m, 2H), 0.05 (s, 3H), -0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.0, 144.6, 141.8, 140.0, 136.0, 135.2, 133.6, 129.9, 129.2, 128.8, 128.6, 127.9, 127.5, 126.8, 126.1, 57.9, 28.5, 19.9, 19.3, -1.9, -2.0 ppm. **HRMS** (ESI): calculated for $C_{25}H_{27}O_2Si^-$ [M-H]$^-$ 387.1786; found 387.1782.

3.2.21 3-(dimethyl(phenyl)silyl)-2-(4-methoxyphenyl)-2-phenylpropanoic acid (**4s**)



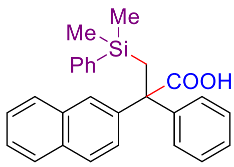
4s

$C_{24}H_{26}O_3Si$

M = 390.55 g/mol

Prepared according to general procedure B from 1-methoxy-4-(1-phenylvinyl)benzene (42.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4s** as gum (60.2 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 – 7.44 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.20 (m, 8H), 6.85 (dd, *J* = 9.0, 2.4 Hz, 2H), 3.84 (s, 3H), 2.19 – 2.05 (m, 2H), 0.03 (s, 3H), 0.00 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.0, 158.4, 144.7, 139.9, 136.5, 133.7, 129.9, 128.7, 127.9, 127.7, 127.5, 126.9, 113.2, 57.6, 55.2, 28.5, -1.9, -2.0 ppm. **HRMS** (ESI): calculated for $C_{24}H_{25}O_3Si^-$ [M-H]$^-$ 389.1578; found 389.1576.

3.2.22 3-(dimethyl(phenyl)silyl)-2-(naphthalen-2-yl)-2-phenylpropanoic acid (**4t**)



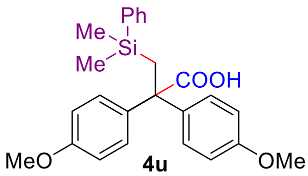
4t

$C_{27}H_{26}O_2Si$

M = 410.59 g/mol

Prepared according to general procedure B from 2-(1-phenylvinyl)naphthalene (46.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4t** as gum (64.2 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.86 – 7.74 (m, 2H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.43 – 7.36 (m, 4H), 7.34 – 7.27 (m, 4H), 7.26 – 7.16 (m, 3H), 2.27 – 2.16 (m, 2H), -0.01 (s, 3H), -0.05 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.3, 144.4, 141.6, 139.6, 133.7, 133.6, 132.8, 132.2, 128.8, 128.6, 128.3, 128.0, 127.5, 127.5, 127.5, 127.4, 127.0, 126.1, 126.1, 58.3, 28.3, -2.00, -2.02 ppm. **HRMS** (ESI): calculated for $C_{27}H_{25}O_2Si^-$ [M-H]$^-$ 409.1629; found 409.1623.

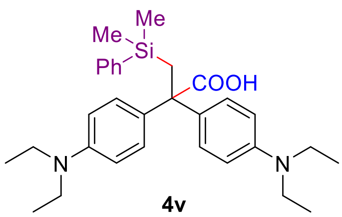
3.2.23 3-(dimethyl(phenyl)silyl)-2,2-bis(4-methoxyphenyl)propanoic acid (**4u**)



4u
$C_{25}H_{28}O_4Si$
M = 420.58 g/mol

Prepared according to general procedure B from 4,4'-(ethene-1,1-diyl)bis(methoxybenzene) (48.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4u** as gum (67.1 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 2H), 7.28 – 7.15 (m, 7H), 6.86 – 6.64 (m, 4H), 3.75 (s, 6H), 2.00 (s, 2H), -0.06 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.1, 158.3, 139.9, 136.8, 133.6, 129.8, 128.6, 127.5, 113.2, 56.9, 55.2, 28.6, -1.9 ppm. **HRMS** (ESI): calculated for $C_{25}H_{27}O_4Si^-$ [M-H]$^-$ 419.1684; found 419.1678.

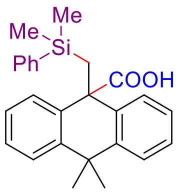
3.2.24 2,2-bis(4-(diethylamino)phenyl)-3-(dimethyl(phenyl)silyl)propanoic acid (**4v**)



4v
$C_{31}H_{42}N_2O_2Si$
M = 502.77 g/mol

Prepared according to general procedure B from 4,4'-(ethene-1,1-diyl)bis(*N,N*-diethylaniline) (64.5 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4v** as gum (88.6 mg, 88% yield). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.45 – 7.38 (2, 2H), 7.32 – 7.24 (m, 3H), 7.21 – 7.13 (m, 4H), 6.62 – 6.52 (m, 4H), 3.33 (q, *J* = 7.1 Hz, 8H), 2.01 (s, 2H), 1.15 (t, *J* = 7.1 Hz, 12H), 0.00 (s, 6H) ppm. ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.6, 146.4, 140.8, 133.7, 131.9, 129.6, 128.3, 127.4, 111.3, 56.5, 44.4, 28.6, 12.6, -1.8 ppm. **HRMS** (ESI): calculated for $C_{31}H_{41}N_2O_2Si^-$ [M-H]$^-$ 501.2943; found 501.2939.

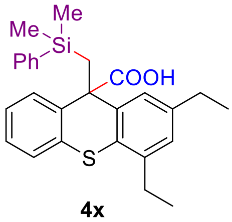
3.2.25 9-((dimethyl(phenyl)silyl)methyl)-10,10-dimethyl-9,10-dihydroanthracene-9-carboxylic acid (**4w**)



4w
$C_{26}H_{28}O_2Si$
M = 400.59 g/mol

Prepared according to general procedure B from 9,9-dimethyl-10-methylene-9,10-dihydroanthracene (44.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4w** as gum (66.8 mg, 83% yield). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.34 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 7.20 – 7.11 (m, 6H), 2.14 (s, 2H), 1.81 (s, 3H), 1.61 (s, 3H), -0.52 (s, 6H) ppm. ^{13}**C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.39, 142.33, 139.71, 134.31, 133.20, 128.52, 127.90, 127.52, 127.35, 127.28, 126.40, 51.02, 37.38, 36.96, 31.84, 30.27, 24.85, -2.91 ppm. **HRMS** (ESI): calculated for $C_{26}H_{27}O_2Si^-$ [M-H]$^-$ 399.1786; found 399.1782.

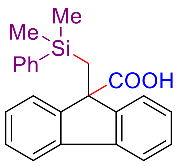
3.2.26 9-((dimethyl(phenyl)silyl)methyl)-2,4-diethyl-9H-thioxanthene-9-carboxylic acid (**4x**)



4x
$C_{27}H_{30}O_2SSi$
M = 446.68 g/mol

Prepared according to general procedure B from 2,4-diethyl-9-methylene-9*H*-thioxanthene (53.2 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4x** as gum (57.4 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 – 7.35 (m, 5H), 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.07 (s, 1H), 7.02 (s, 1H), 2.83 (q, *J* = 7.5 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.04 (s, 2H), 1.39 (t, *J* = 7.5 Hz, 3H), 1.33 (t, *J* = 7.6 Hz, 3H), 0.02 (s, 3H), 0.01 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.4, 141.8, 139.9, 139.3, 135.7, 134.9, 133.4, 130.6, 128.5, 127.8, 127.4, 127.3, 126.9, 126.5, 126.2, 126.0, 125.2, 56.0, 28.7, 28.6, 26.9, 15.7, 14.0, -2.4, -2.5 ppm. **HRMS** (ESI): calculated for $C_{27}H_{29}O_2SSi^-$ $[M-H]^-$ 445.1663; found 445.1660.

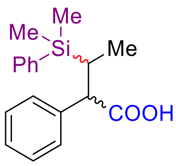
3.2.27 9-((dimethyl(phenyl)silyl)methyl)-9*H*-fluorene-9-carboxylic acid (**4y**)



4y
$C_{23}H_{22}O_2Si$
M = 358.51 g/mol

Prepared according to general procedure B from 9-methylene-9*H*-fluorene (35.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 ^{o}C and then the dried CO_2 was added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 ^{o}C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4y** as gum (48.7 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.35 (td, *J* = 7.5, 1.1 Hz, 2H), 7.21 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.19 – 7.17 (m, 1H), 7.16 – 7.14 (m, 1H), 7.12 – 7.06 (m, 2H), 2.11 (s, 2H), -0.50 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 179.9, 145.6, 140.8, 139.1, 133.1, 128.6, 128.4, 127.5, 127.6, 125.4, 120.0, 58.6, 25.0, -2.9 ppm. **HRMS** (ESI): calculated for $C_{23}H_{21}O_2Si^-$ [M-H]$^-$ 357.1316; found 357.1310.

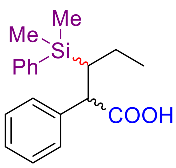
3.2.28 3-(dimethyl(phenyl)silyl)-2-phenylbutanoic acid (**4za**)



4za
$C_{18}H_{22}O_2Si$
M = 298.46 g/mol

Prepared according to general procedure B from *β*-methylstyrene (23.6 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred at – 20 ^{o}C for 2 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4za** as gum (33.4 mg, 56% yield, d.r.=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.38 (m, 2H), 7.37 – 7.31 (m, 5H), 7.30 – 7.27 (m, 3H), 3.45 (d, *J* = 11.8 Hz, 1H), 1.86 (dq, *J* = 11.7, 7.3 Hz, 1H), 1.11 (d, *J* = 7.3 Hz, 3H), 0.03 (s, 3H), -0.05 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.3, 138.0, 137.8, 133.9, 129.1, 128.9, 128.5, 127.8, 127.6, 55.4, 24.3, 14.7, -3.1, -4.7 ppm. **HRMS** (ESI): calculated for $C_{18}H_{21}O_2Si^-$ [M-H]$^-$ 297.1316; found 297.1315.

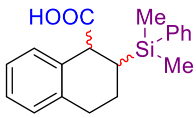
3.2.29 3-(dimethyl(phenyl)silyl)-2-phenylpentanoic acid (**4zb**)



4zb
$C_{19}H_{24}O_2Si$
M = 312.48 g/mol

Prepared according to general procedure B from *β*-ethylstyrene (26.4 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 ºC for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4zb** as a colorless oil (34.6 mg, 55% yield, d.r.=1:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 – 7.44 (m, 2H), 7.34 – 7.26 (m, 5H), 7.22 – 7.15 (m, 2H), 7.14 – 7.06 (m, 1H), 3.57 (d, *J* = 11.3 Hz, 1H), 1.74 (dt, *J* = 11.0, 5.4 Hz, 1H), 1.35 – 1.17 (m, 2H), 0.63 (t, *J* = 7.4 Hz, 3H), 0.33 (s, 3H), 0.31 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.7, 138.8, 137.6, 133.7, 129.4, 128.6, 128.3, 127.7, 127.6, 53.4, 31.3, 22.8, 13.2, -2.3, -3.2 ppm. **HRMS** (ESI): calculated for $C_{19}H_{23}O_2Si^-$ [M-H]$^-$ 311.1473; found 311.1469.

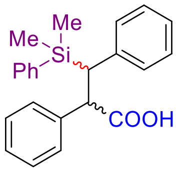
3.2.30 2-(dimethyl(phenyl)silyl)-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid (**4zc**)



4zc
$C_{19}H_{22}O_2Si$
M = 310.47 g/mol

Prepared according to general procedure B from 1,2-dihydronaphthalene (26.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at room temperature for 30 s. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4zc** as a colorless oil (37.8 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.1 (s, 1H), 7.70 – 7.62 (m, 2H), 7.50 – 7.40 (m, 3H), 7.39 – 7.34 (m, 1H), 7.30 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 3.93 (d, *J* = 7.8 Hz, 1H), 2.96 – 2.80 (m, 2H), 2.22 – 2.12 (m, 1H), 1.98 – 1.90 (m, 1H), 1.68 – 1.58 (m, 1H), 0.42 (s, 3H), 0.41 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 181.8, 137.9, 137.1, 134.1, 133.1, 129.4, 129.2, 128.6, 127.8, 127.0, 126.1, 46.2, 29.7, 24.4, 22.5, -4.2, -4.6 ppm. **HRMS** (ESI): calculated for $C_{19}H_{21}O_2Si^-$ [M-H]$^-$ 309.1316; found 309.1319.

3.2.31 3-(dimethyl(phenyl)silyl)-2,3-diphenylpropanoic acid (**4zd**)



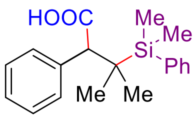
4zd

$C_{23}H_{24}O_2Si$

M = 360.53 g/mol

Prepared according to general procedure B from (*E*)-1,2-diphenylethene (36.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 °C and then the dried CO_2 was added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 °C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4zd** as gum (37.7 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 – 7.33 (m, 2H), 7.22 – 7.18 (m, 2H), 7.14 – 7.09 (m, 2H), 7.09 – 7.02 (m, 3H), 7.02 – 6.83 (m, 4H), 6.72 (d, *J* = 7.0 Hz, 2H), 4.06 (d, *J* = 12.7 Hz, 1H), 3.26 (d, *J* = 12.7 Hz, 1H), 0.26 (s, 3H), 0.20 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 179.1, 139.8, 137.9, 136.3, 134.4, 129.3, 129.1, 129.0, 128.1, 127.7, 127.4, 127.1, 124.6, 52.1, 38.6, -2.9, -4.6 ppm. **HRMS** (ESI): calculated for $C_{23}H_{23}O_2Si^-$ [M-H]$^-$ 359.1473; found 359.1469.

3.2.32 3-(dimethyl(phenyl)silyl)-3-methyl-2-phenylbutanoic acid (**4ze**)



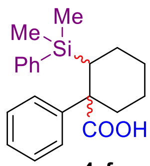
4ze

$C_{19}H_{24}O_2Si$

M = 312.48 g/mol

Prepared according to general procedure B from *β*-dimethylstyrene (26.4 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.4 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 °C for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4ze** as gum (28.3 mg, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.46 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 6H), 3.59 (s, 1H), 1.17 (s, 3H), 0.94 (s, 3H), 0.27 (s, 3H), 0.20 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 179.2, 137.1, 135.3, 134.8, 130.6, 129.1, 127.9, 127.5, 127.5, 56.9, 24.6, 21.8, 21.0, -4.6, -5.0 ppm. **HRMS** (ESI): calculated for $C_{19}H_{23}O_2Si^-$ $[M-H]^-$ 311.1473; found 311.1468.

3.2.33 2-(dimethyl(phenyl)silyl)-1-phenylcyclohexane-1-carboxylic acid (**4zf**)



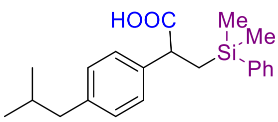
4zf

$C_{21}H_{26}O_2Si$

M = 338.52 g/mol

Prepared according to general procedure B from (*E*)-1,2-diphenylethene (36.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. Then, the direct bubbling of dry CO_2 through the reaction mixture, stirred at -20 ^{o}C for 2 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **4zf** as a colorless oil (28.7 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 – 7.41 (m, 2H), 7.41 – 7.32 (m, 2H), 7.32 – 7.30 (m, 3H), 7.30 – 7.25 (m, 3H), 2.59 (dd, *J* = 12.6, 3.1 Hz, 1H), 2.53 (d, *J* = 3.3 Hz, 1H), 2.04 (td, *J* = 12.8, 3.8 Hz, 1H), 1.96 (dt, *J* = 13.1, 3.3 Hz, 1H), 1.87 (dt, *J* = 7.7, 2.9 Hz, 2H), 1.61 (dd, *J* = 9.8, 6.3 Hz, 1H), 1.53 (d, *J* = 13.2 Hz, 1H), 1.37 (s, 1H), 0.22 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.9, 141.8, 140.0, 133.6, 128.4, 128.3, 127.5, 126.9, 126.2, 53.5, 32.6, 29.8, 27.0, 24.1, 23.4, -0.38, -0.74 ppm. **HRMS** (ESI): calculated for $C_{21}H_{25}O_2Si^-$ $[M-H]^-$ 337.1629; found 337.1632.

3.2.34 3-(dimethyl(phenyl)silyl)-2-(4-isobutylphenyl)propanoic acid (**5a**)



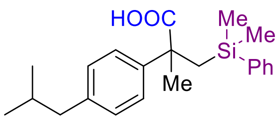
5a

$C_{21}H_{28}O_2Si$

M = 340.54 g/mol

Prepared according to general procedure B from 1-isobutyl-4-vinylbenzene (32.5 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (52.8 mg, 0.20 mmol, 1.0 equiv.), ^tBuOK (44.9 mg, 0.40 mmol, 2.0 equiv.), stirred for 30 min. The solution was cooled to -20 °C and then the dried CO_2 was added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 °C for 3 min. After the reaction finished (The reaction solution gradually fades), 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **5a** as gum (49.0 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.19 – 7.12 (m, 2H), 7.08 – 7.01 (m, 2H), 3.60 – 3.52 (m, 1H), 2.43 (d, J = 7.2 Hz, 2H), 1.89 – 1.76 (m, 1H), 1.61 (dd, J = 14.8, 7.2 Hz, 1H), 1.37 (dd, J = 14.8, 8.6 Hz, 1H), 0.88 (d, J = 6.6 Hz, 6H), 0.11 (d, J = 2.0 Hz, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 180.2, 141.0, 138.3, 137.3, 133.6, 129.3, 129.1, 127.8, 127.8, 46.7, 45.1, 30.2, 22.4, 22.4, 20.4, -2.7, -3.1 ppm. **HRMS** (ESI): calculated for $C_{21}H_{27}O_2Si^-$ [M-H]$^-$ 339.1786; found 339.1780.

3.2.35 3-(dimethyl(phenyl)silyl)-2-(4-isobutylphenyl)-2-methylpropanoic acid (**5b**)



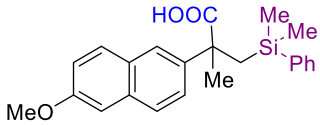
5b

$C_{22}H_{30}O_2Si$

M = 354.57 g/mol

Prepared according to general procedure B from 2-methoxy-6-(prop-1-en-2-yl)naphthalene (34.9 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^tBuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 °C and then the dried CO_2 was added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 °C for 3 min. After the reaction finished (The reaction solution gradually fades), 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **5b** as gum (65.5 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.45 (m, 2H), 7.40 – 7.26 (m, 5H), 7.16 – 7.02 (m, 2H), 2.48 (d, J = 6.6 Hz, 2H), 1.96 – 1.84 (m, 1H), 1.82 – 1.72 (m, 1H), 1.72 – 1.62 (m, 1H), 1.56 (s, 3H), 0.99 – 0.87 (m, 6H), 0.25 – 0.02 (m, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 183.5, 141.9, 140.3, 139.7, 133.6, 129.1, 128.9, 127.7, 125.8, 48.2, 45.0, 30.2, 28.1, 25.3, 22.4, -1.5, -1.6 ppm. **HRMS** (ESI): calculated for $C_{22}H_{29}O_2Si^-$ [M-H]$^-$ 353.1942; found 353.1935.

3.2.36 3-(dimethyl(phenyl)silyl)-2-(6-methoxynaphthalen-2-yl)-2-methylpropanoic acid (**5c**)



5c

$C_{23}H_{26}O_3Si$

M = 378.54 g/mol

Prepared according to general procedure B from 2-methoxy-6-(prop-1-en-2-yl)naphthalene (40.0 mg, 0.20 mmol, 1.0 equiv.), $PhMe_2SiBpin$ (63.0 mg, 0.24 mmol, 1.2 equiv.), ^{t}BuOK (53.8 mg, 0.48 mmol, 2.4 equiv.), stirred for 30 min. The solution was cooled to -20 °C and then the dried CO_2 was added to the reaction mixture through a balloon. The reaction mixture was stirred at -20 °C for 3 min. After the reaction finished, 1M HCl solution (~0.5 mL) was added to the reaction mixture, and the organic phase was separated. The aqueous layer was extracted with EtOAc (3×5 mL). Then, the organic layers were combined, dried over anhydrous sodium sulfate, and filtered. After the removal of the solvent under reduced pressure, the crude material was purified by preparative TLC (petroleum ether/ethyl acetate = 1:1) to afford **5c** as gum (49.2 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 – 7.73 (m, 1H), 7.72 – 7.64 (m, 2H), 7.54 – 7.49 (m, 1H), 7.48 – 7.40 (m, 2H), 7.34 – 7.27 (m, 3H), 7.34 – 7.27 (m, 3H), 7.34 – 7.27 (m, 3H), 7.17 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.12 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H), 1.88 (d, *J* = 14.7 Hz, 1H), 1.77 (d, *J* = 14.7 Hz, 1H), 1.66 (s, 3H), 0.21 (s, 3H), 0.18 (s, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 182.8, 157.8, 139.7, 139.5, 133.6, 133.4, 129.7, 128.9, 128.7, 127.7, 126.9, 125.3, 124.3, 118.9, 105.5, 55.3, 48.5, 27.9, 25.4, -1.5, -1.6 ppm. **HRMS** (ESI): calculated for $C_{23}H_{25}O_3Si^-$ $[M-H]^-$ 377.1578; found 377.1572.

4. Computational Investigations

4.1 Computational Details

All calculations were performed with the Gaussian 16 package[5]. The 3D structures of the optimized species were generated using CYLview[6]. Geometry optimizations were performed at M06-2X[7]/6-31G(d,p) (def2-TZVP for K atoms) level of theory in conjugation with the polarizable continuum model (PCM)[8] solvation model for tetrahydrofuran. Vibrational frequencies were calculated for all the geometries to provide thermal corrections to the Gibbs free energies at 298.15 K and 1.0 atm, and to confirm whether the optimized geometry corresponds to a minimum or a transition state (TS). Intrinsic reaction coordinate (IRC) calculations were performed to verify whether a TS connects the correct minimum structures. To get more accurate energies, single-point energy calculations were done with the same functional and solvation model using the cc-pVTZ basis set (def2-QZVP for K atom). Free energy barriers here are defined as the free energy difference between the transition state and the lowest-energy stationary point before it along the reaction pathways.

NOTE: The crystallographic evidence from reported benzyl potassium-THF complexes reveals that the potassium ion in benzyl potassium adopts a distinctive sandwich-like acoordinate geometry, interacting simultaneously with the aromatic ring and THF molecules.[9-10] Guided by this structural insight, we employed THF as the coordination solvent for potassium ions (as shown in Figure S18-S19) and recalculated the complete potential energy surface for the ^{t}BuOK-mediated selective 1,2-silacarboxylation of arylalkenes. Notably, the additional computational results are in excellent agreement with those obtained from the simplified model. To facilitate reader reference, we have incorporated both sets of computational results into the revised ESI (see Figures S16-S19 for details).

4.2 DFT Calculations on the ^{t}BuOK-Mediated 1,2-Silylcarboxylation of Arylalkenes

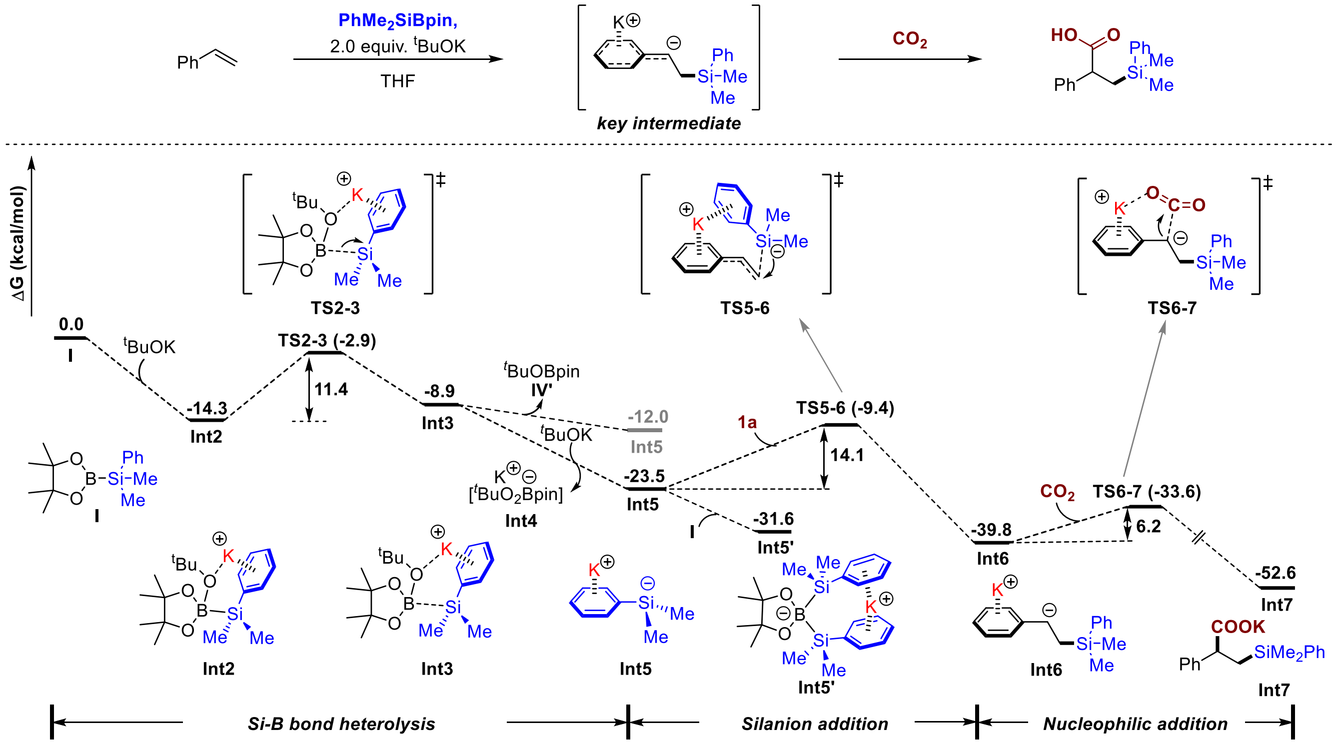


Figure S16. Gibbs free energy profile for the ^{t}BuOK-mediated selective 1,2-silylcarboxylation reaction of styrene.

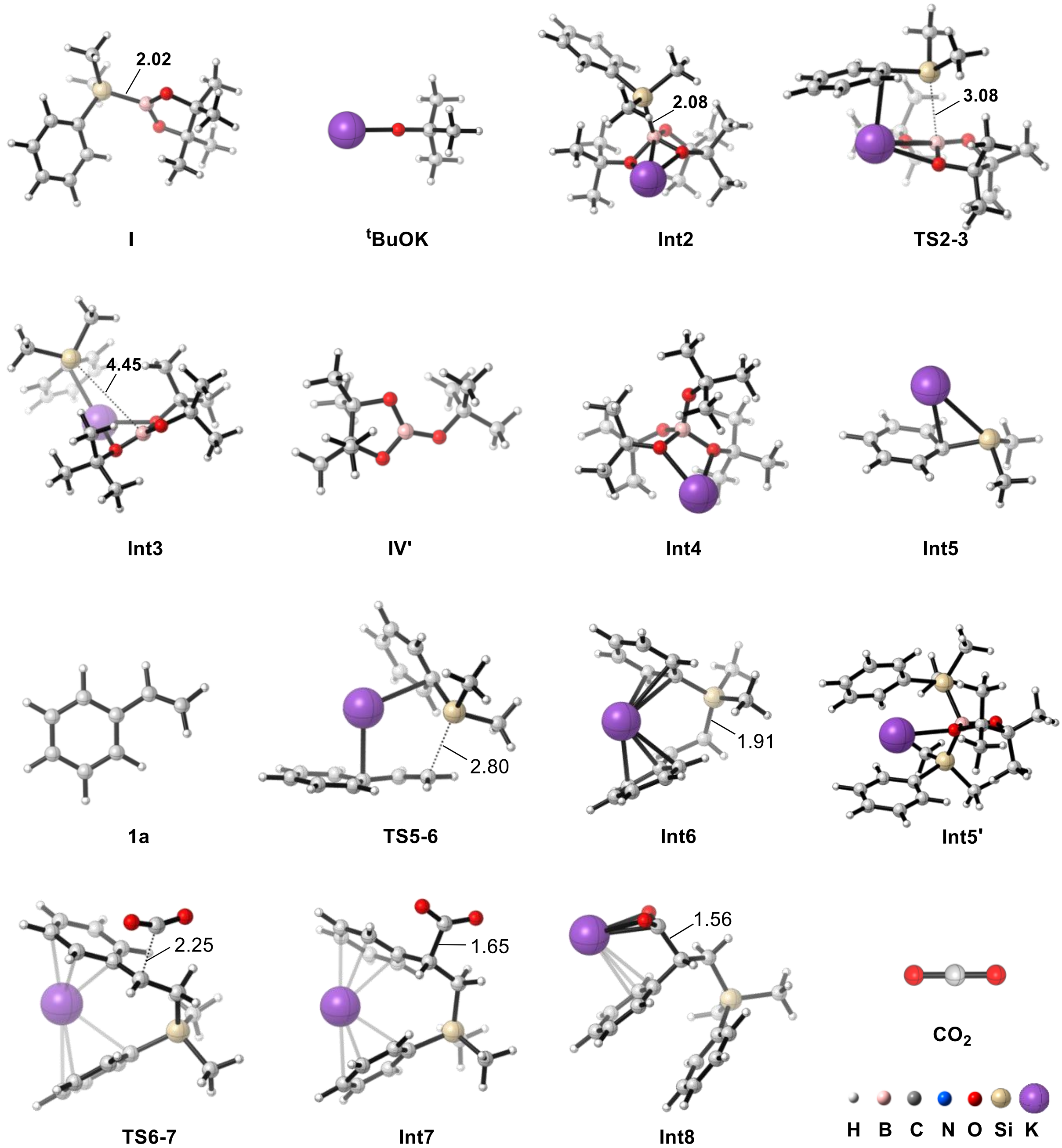


Figure S17. 3D structures of the species involved in the ^{t}BuOK-mediated selective 1,2-silylcarboxylation reaction of styrene. Selected distances were shown in Å.

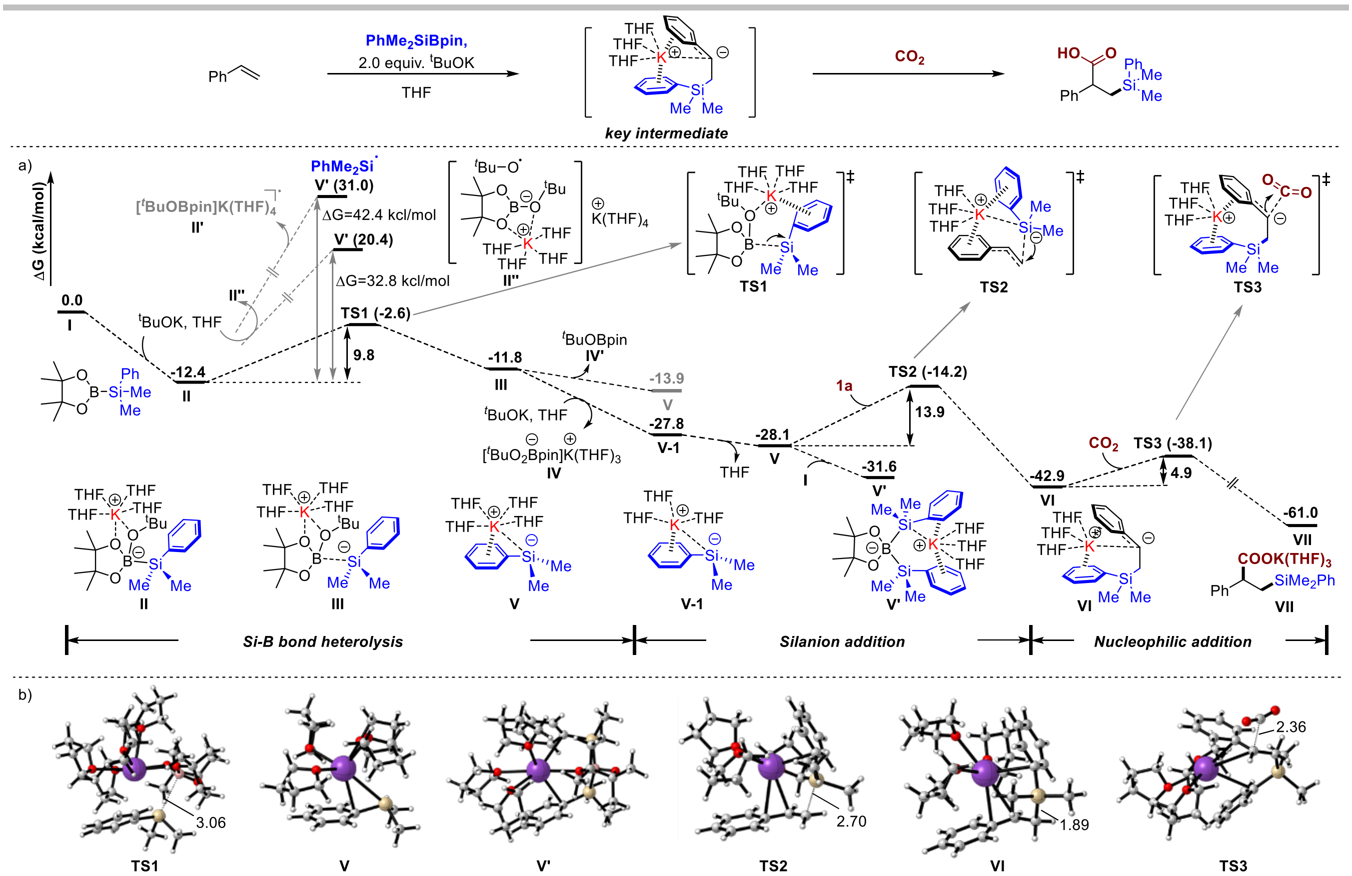


Figure S18. Gibbs free energy profile for the ^{t}BuOK-mediated selective 1,2-silylcarboxylation reaction of styrene (with THF).

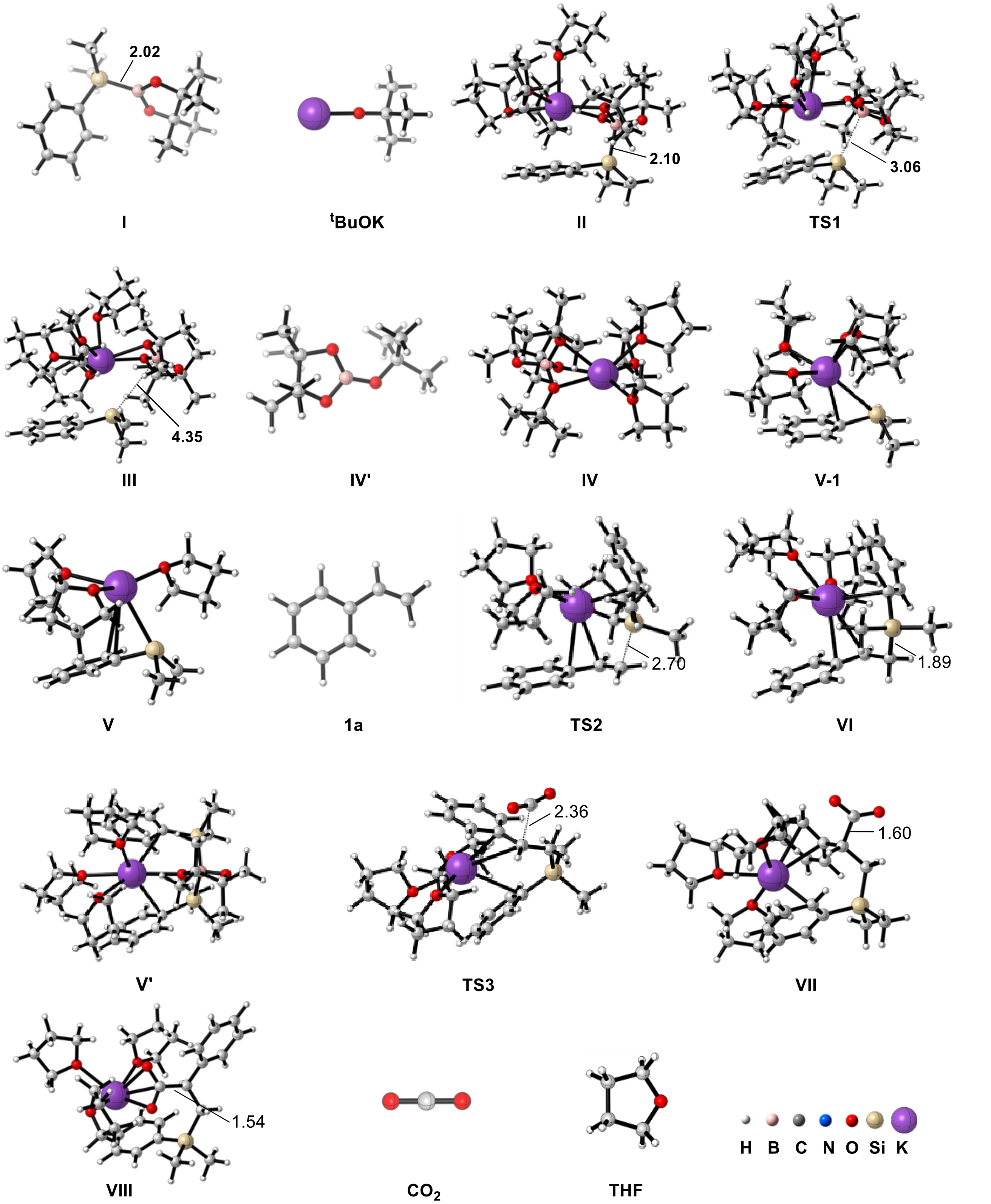
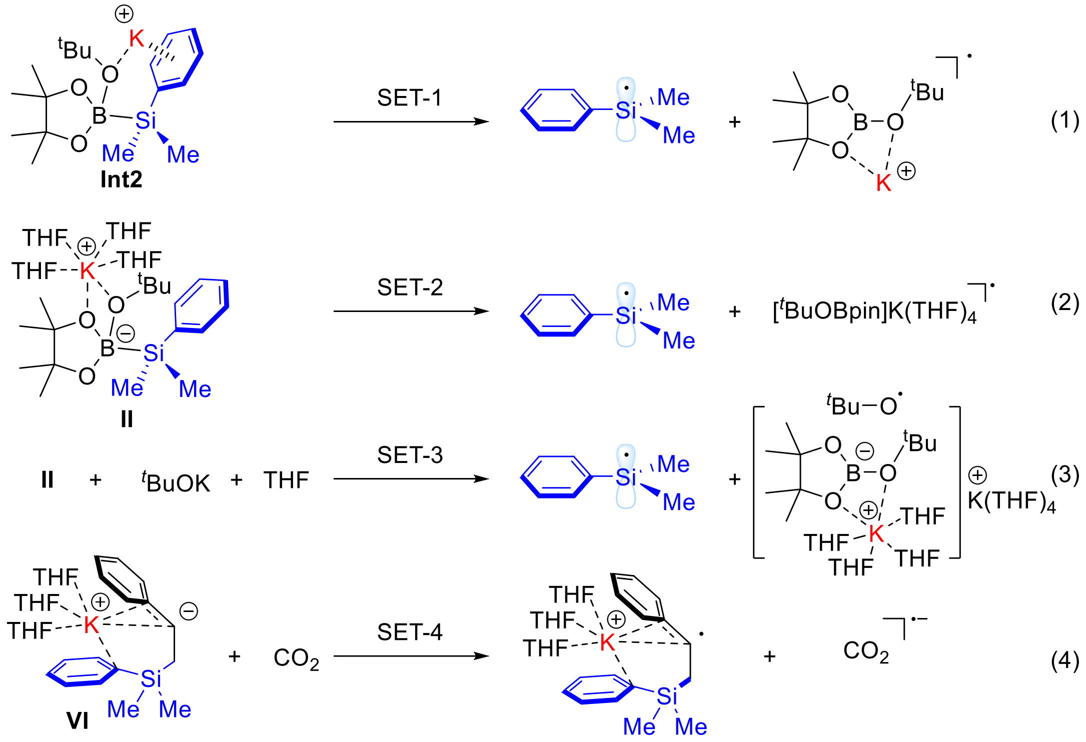


Figure S19. 3D structures of the species involved in the ^{t}BuOK-mediated selective 1,2-silylcarboxylation reaction of styrene (with THF). Selected distances were shown in Å.

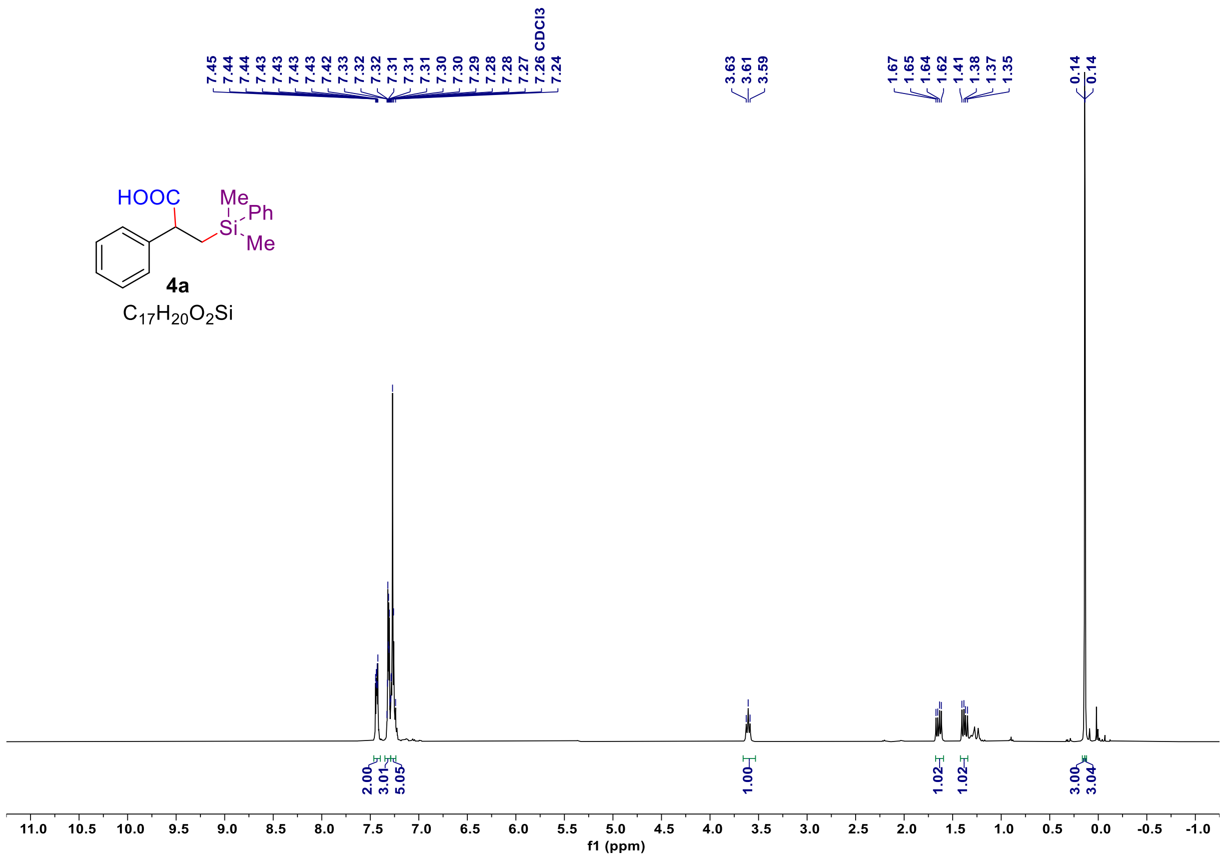


Reaction		△G (kcal/mol)
(1)	SET-1	**42.5**
(2)	SET-2	**43.4**
(3)	SET-3	**32.8**
(4)	SET-4	**86.5**

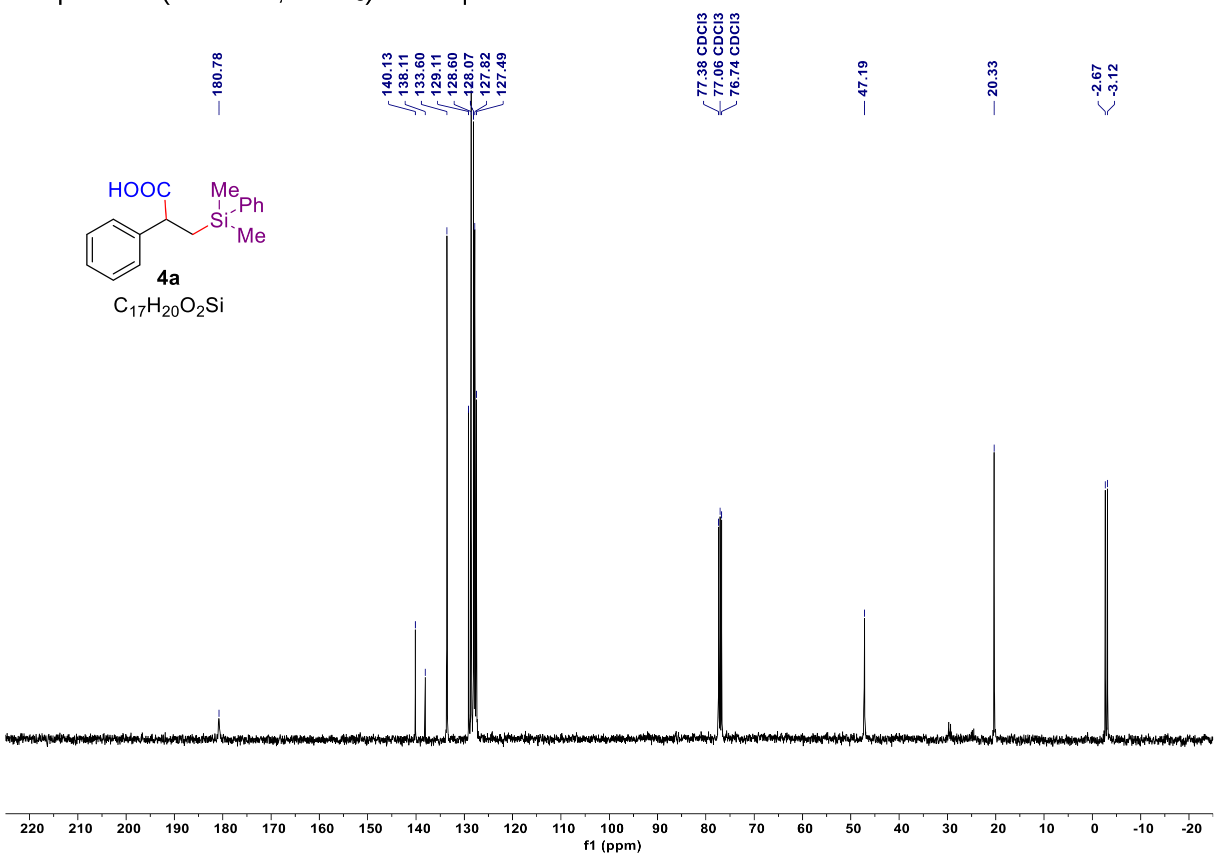
Figure S20. Computed reaction energies for the generation of silyl radical via the SET processes between ^{t}BuOK and $PhMe_2SiBpin$.

As shown in Figure S17, the direct generation of silyl radical via the single electron transfer (SET) from intermediate **II** (with or without THF) or intermediate **II** with ^{t}BuOK are endergonic by 42.5, 43.4, and 32.8 kcal/mol, respectively. And the SET processes between carbanion **VI** and CO_2 is also thermodynamically unfavorable (being endergonic by 86.5 kcal/mol). Thus, SET mechanisms could be excluded.

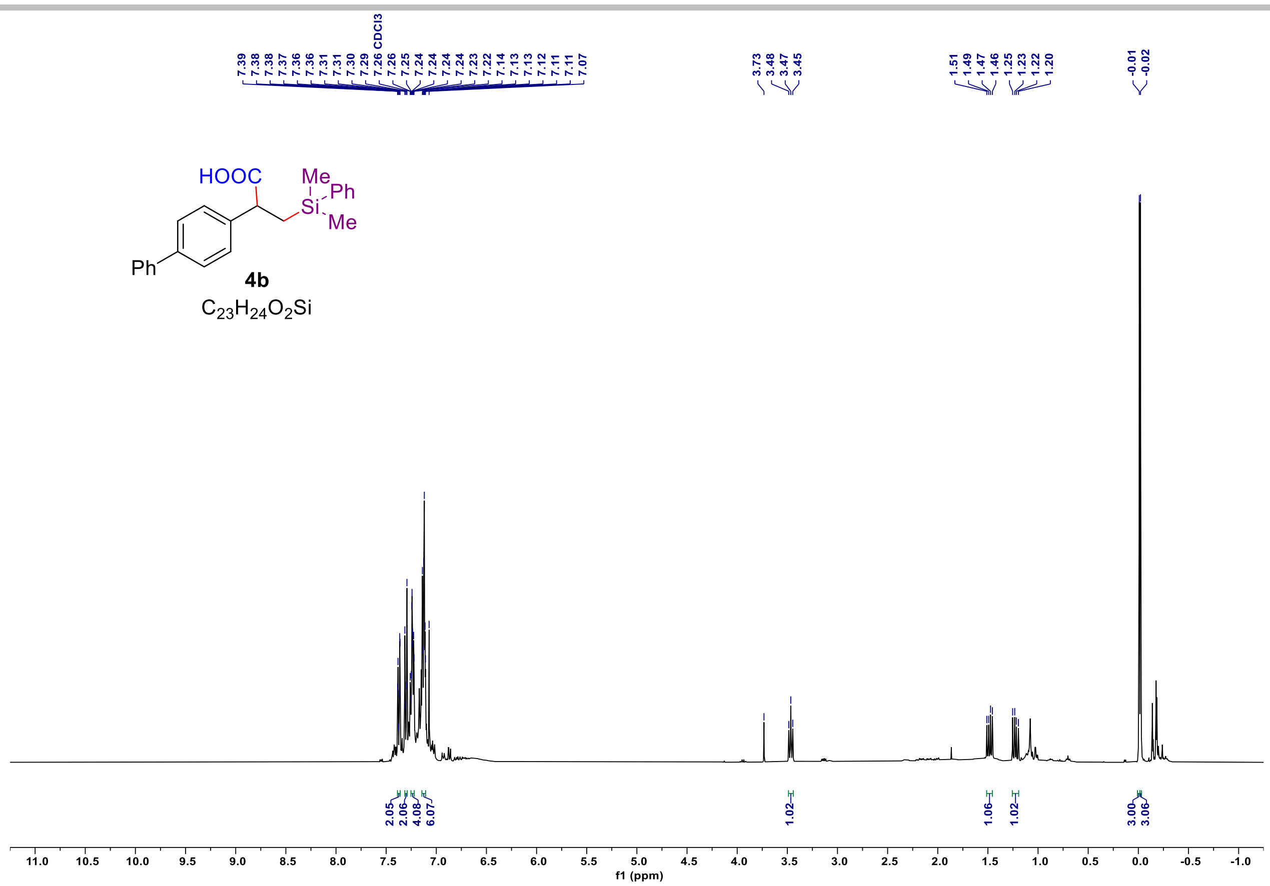
5. NMR Spectra



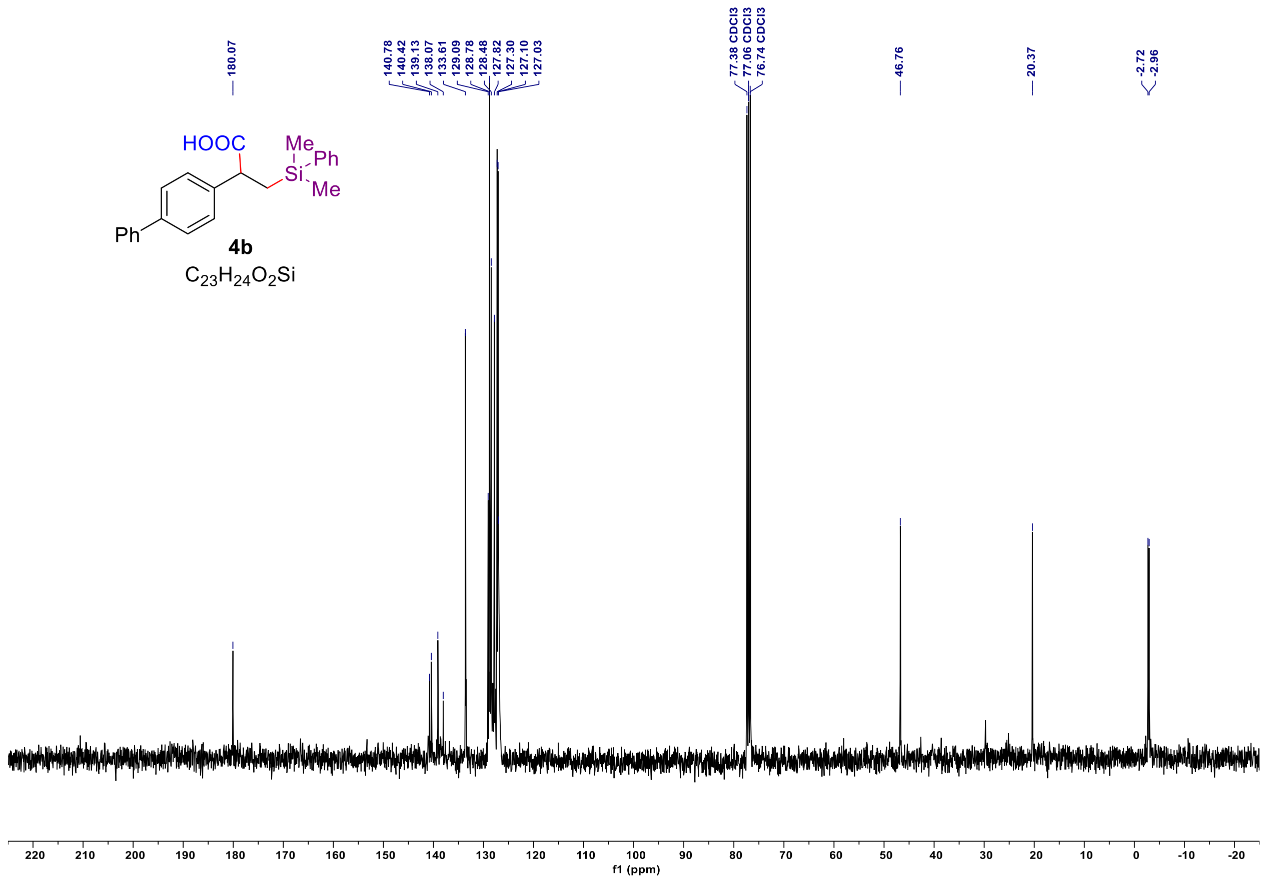
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4a.**



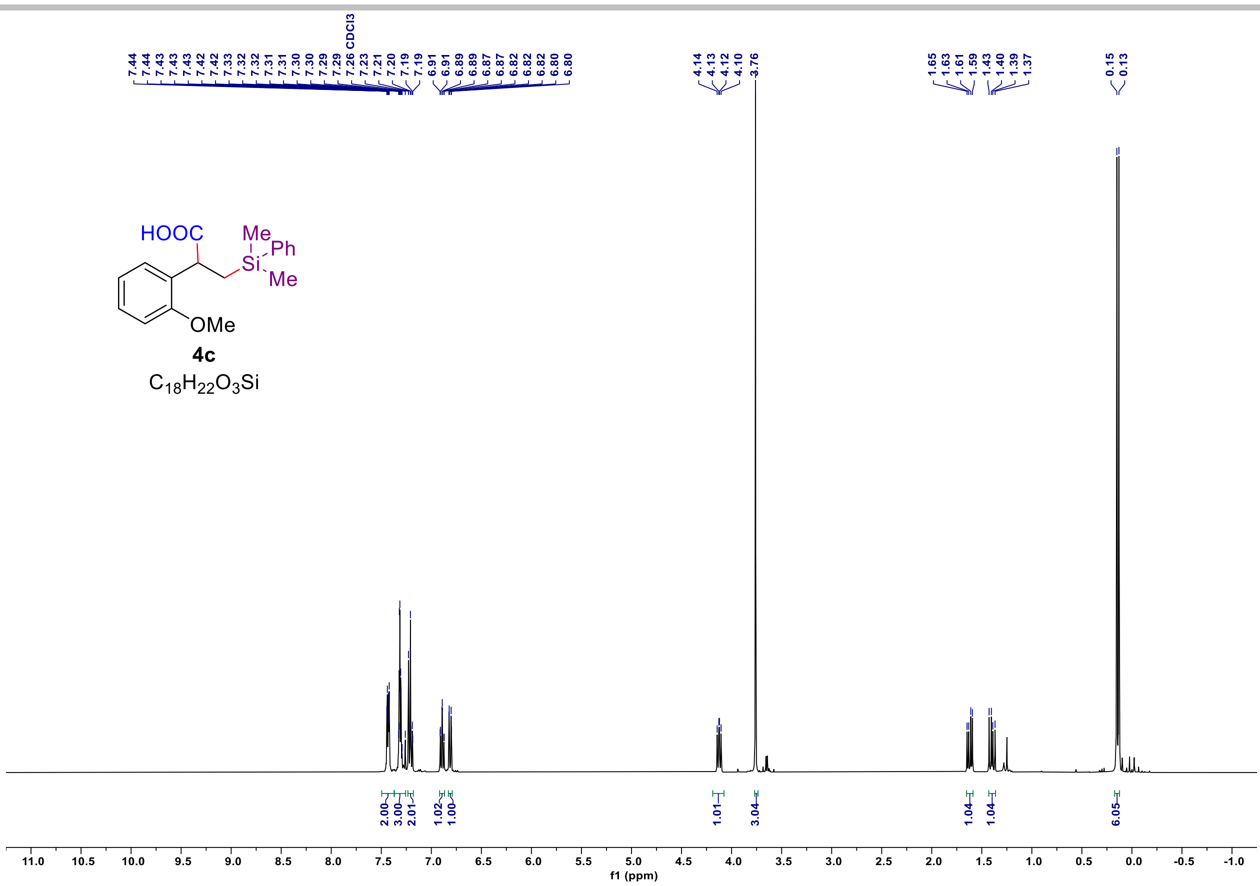
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4a.**



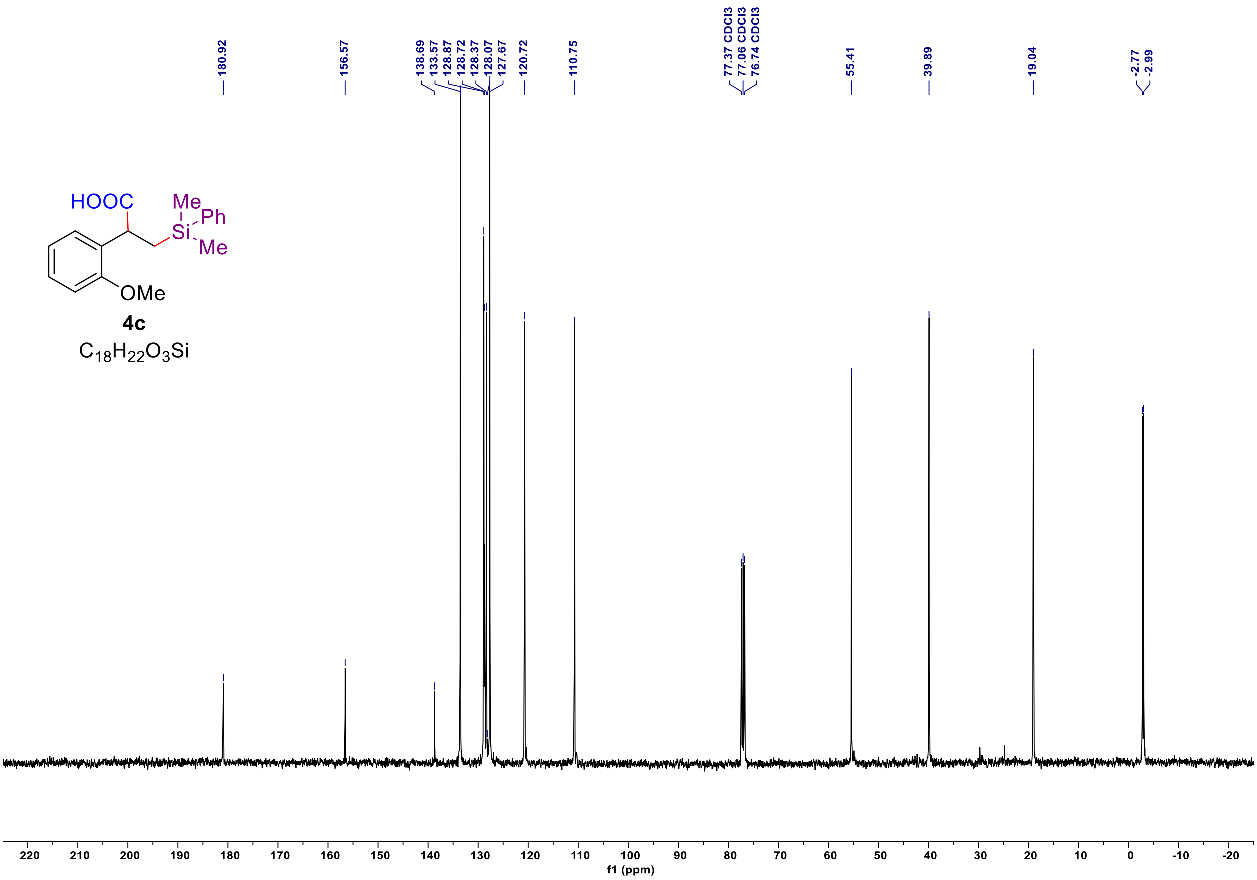
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4b.**



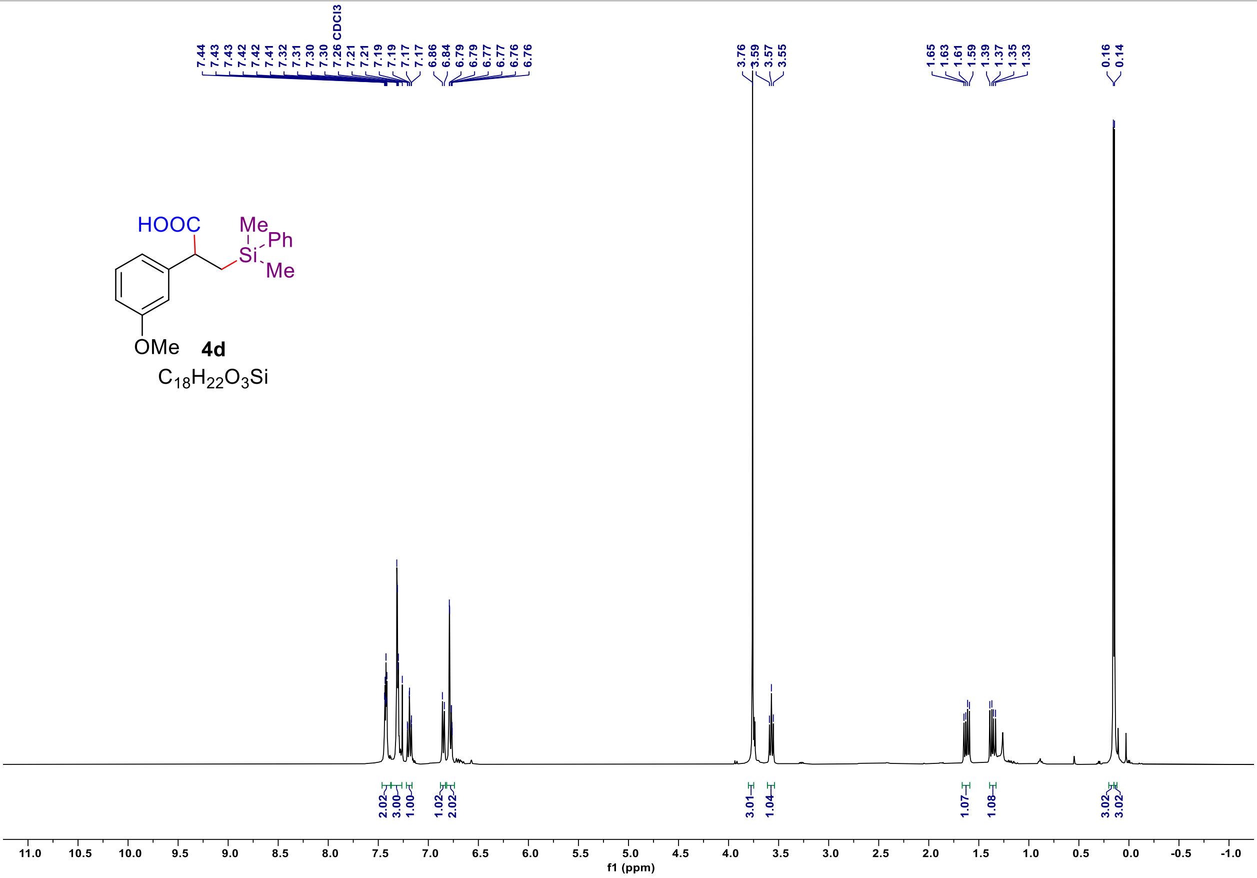
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4b.**



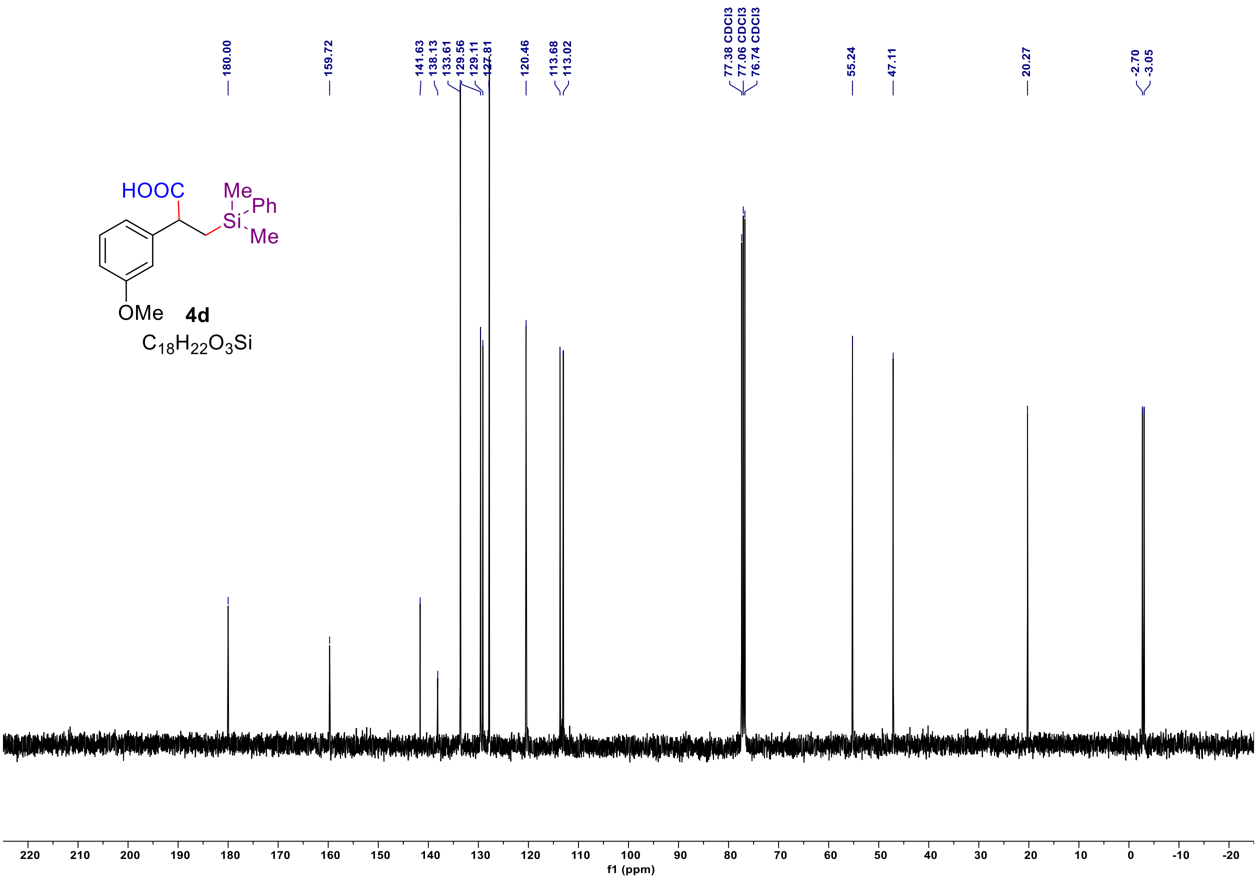
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4c.**



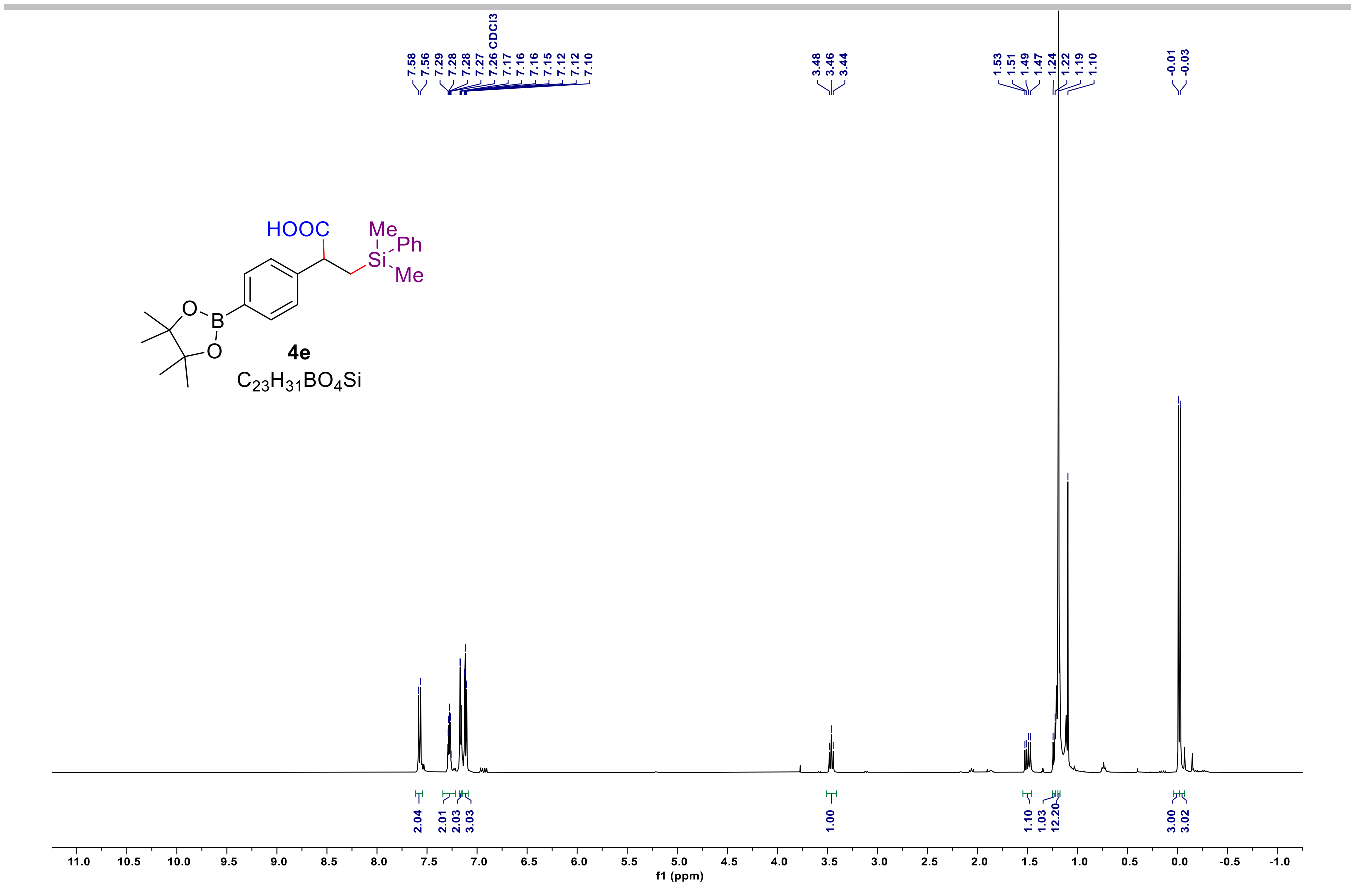
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4c.**



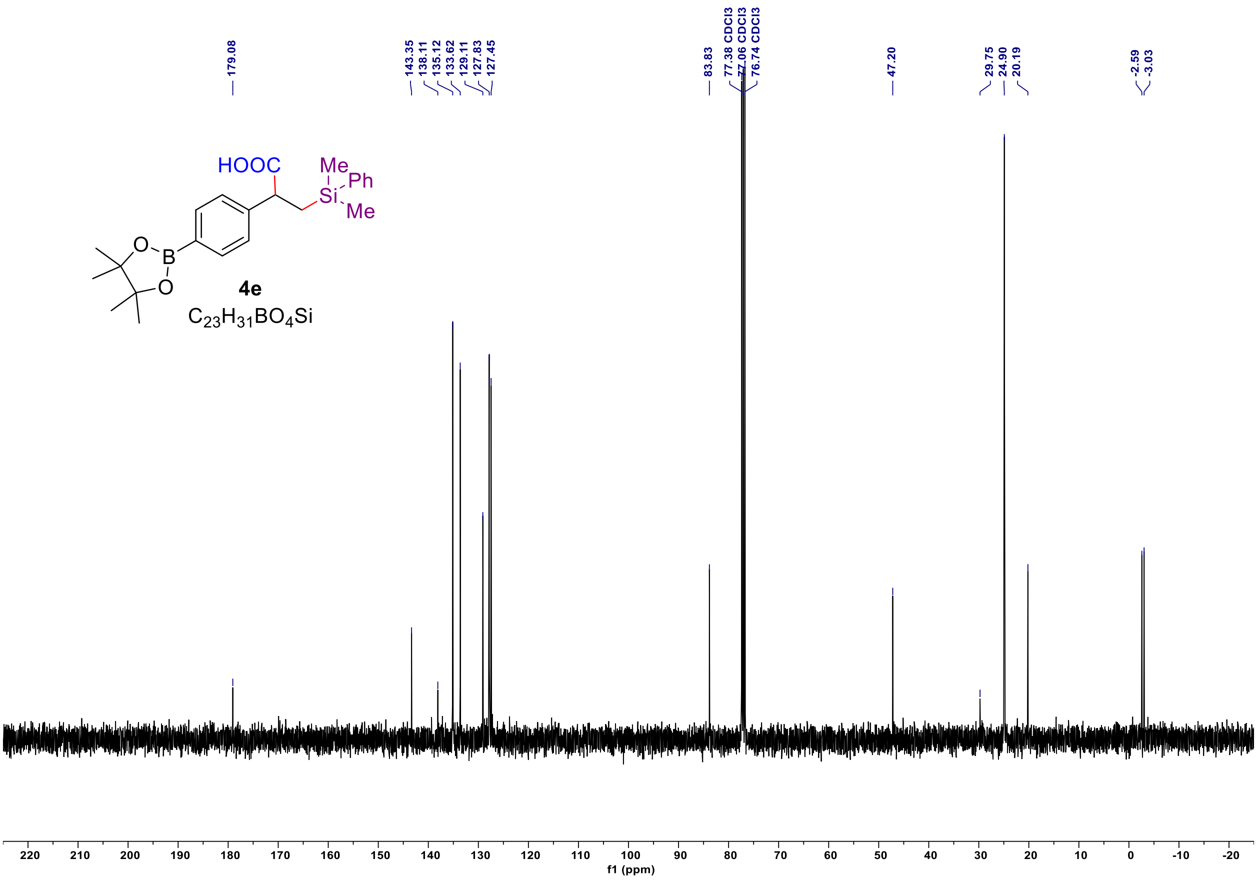
[1]H NMR spectrum (400 MHz, $CDCl_3$) of compound **4d.**



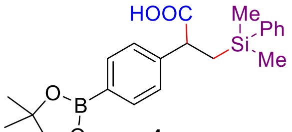
[13]C{[1]H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4d.**



^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4e.**

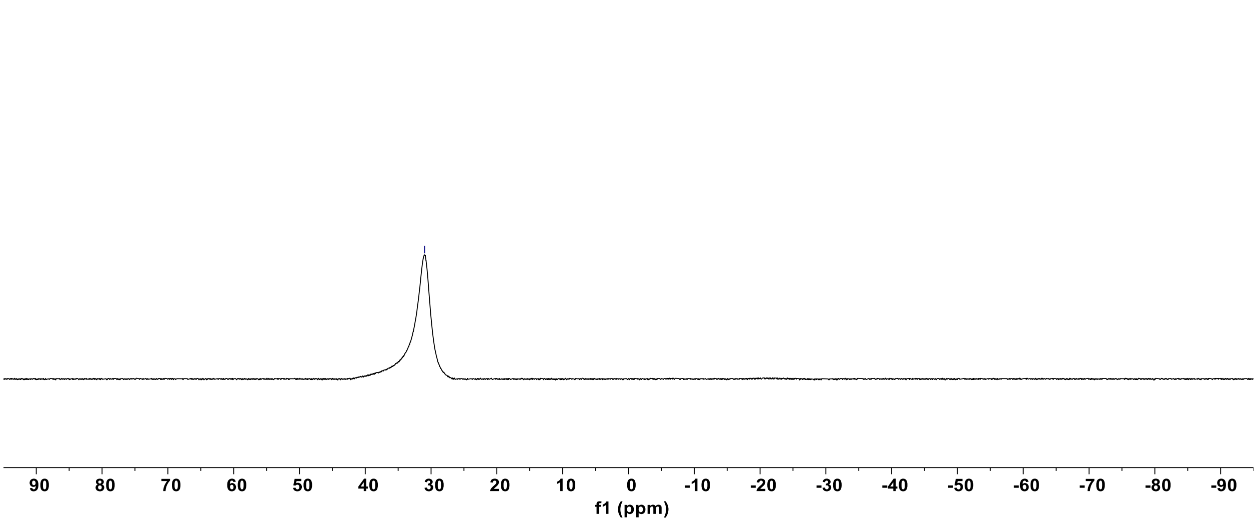


^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4e.**

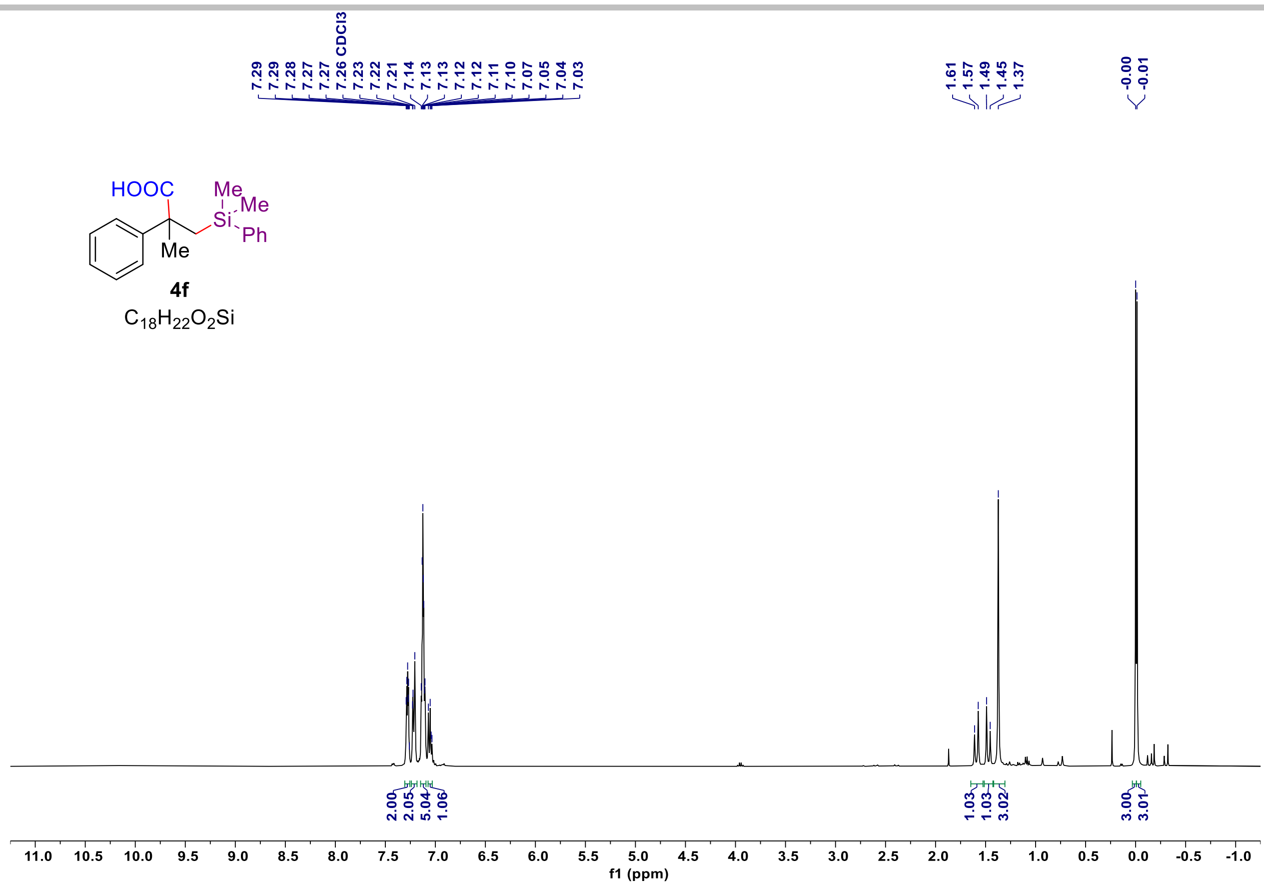


4e

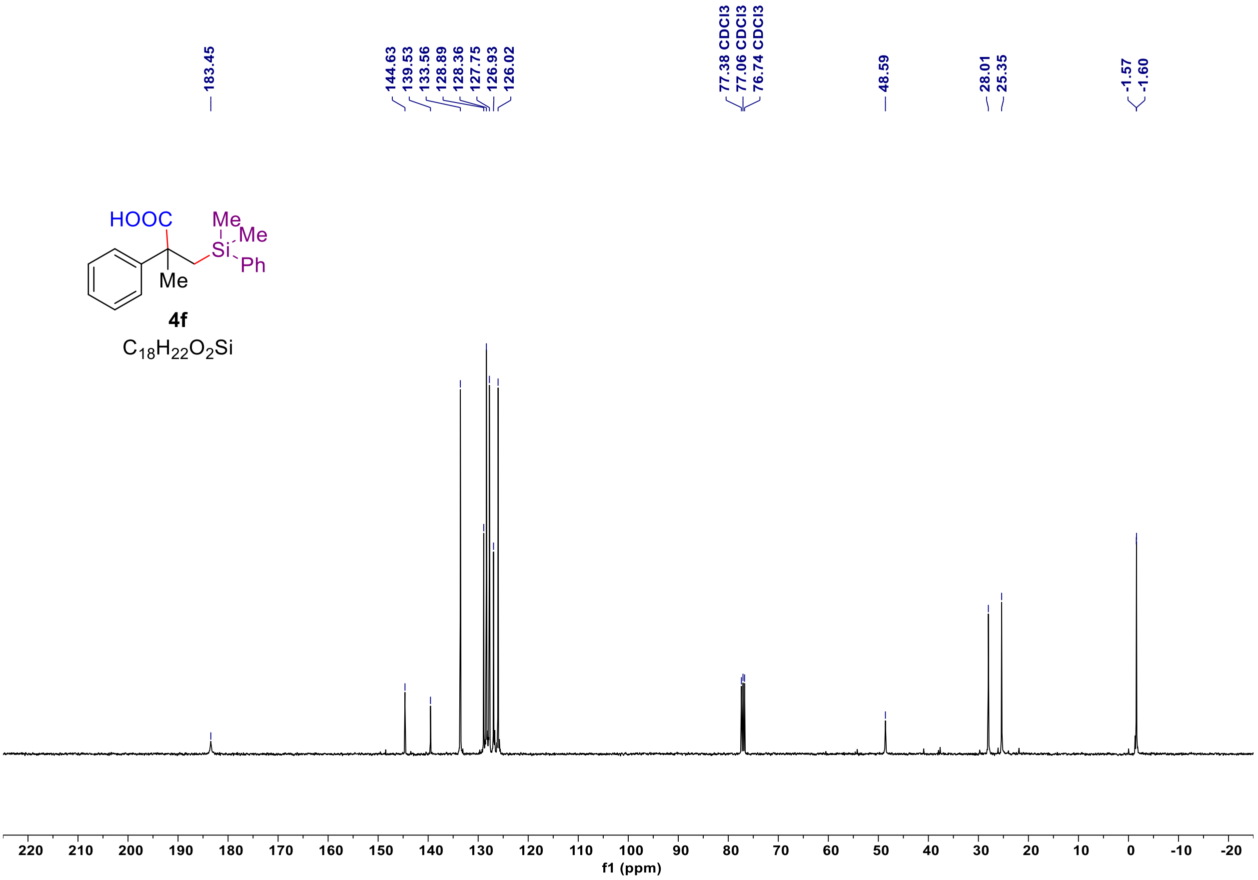
$C_{23}H_{31}BO_4Si$



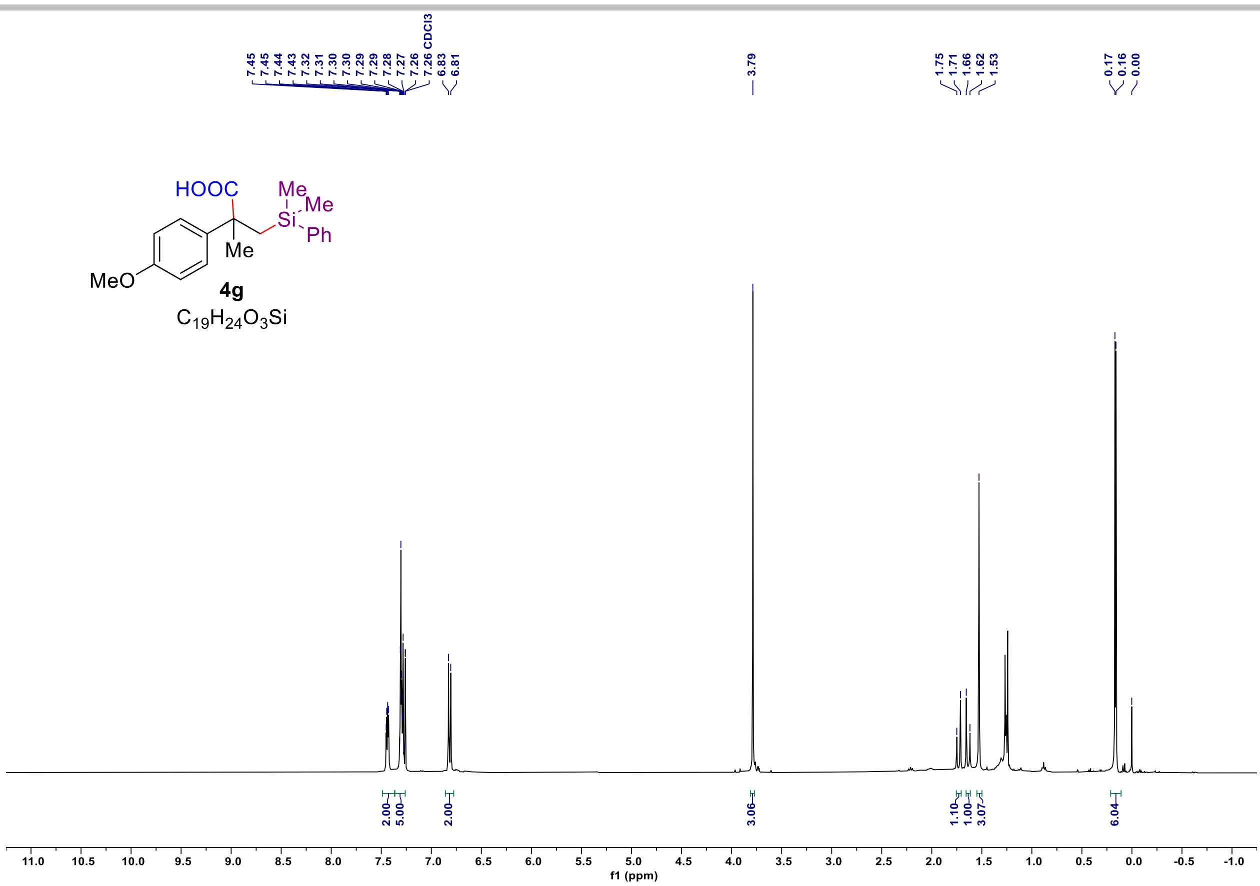
^{11}B{^{1}H} NMR spectrum (128 MHz, $CDCl_3$) of compound **4e.**



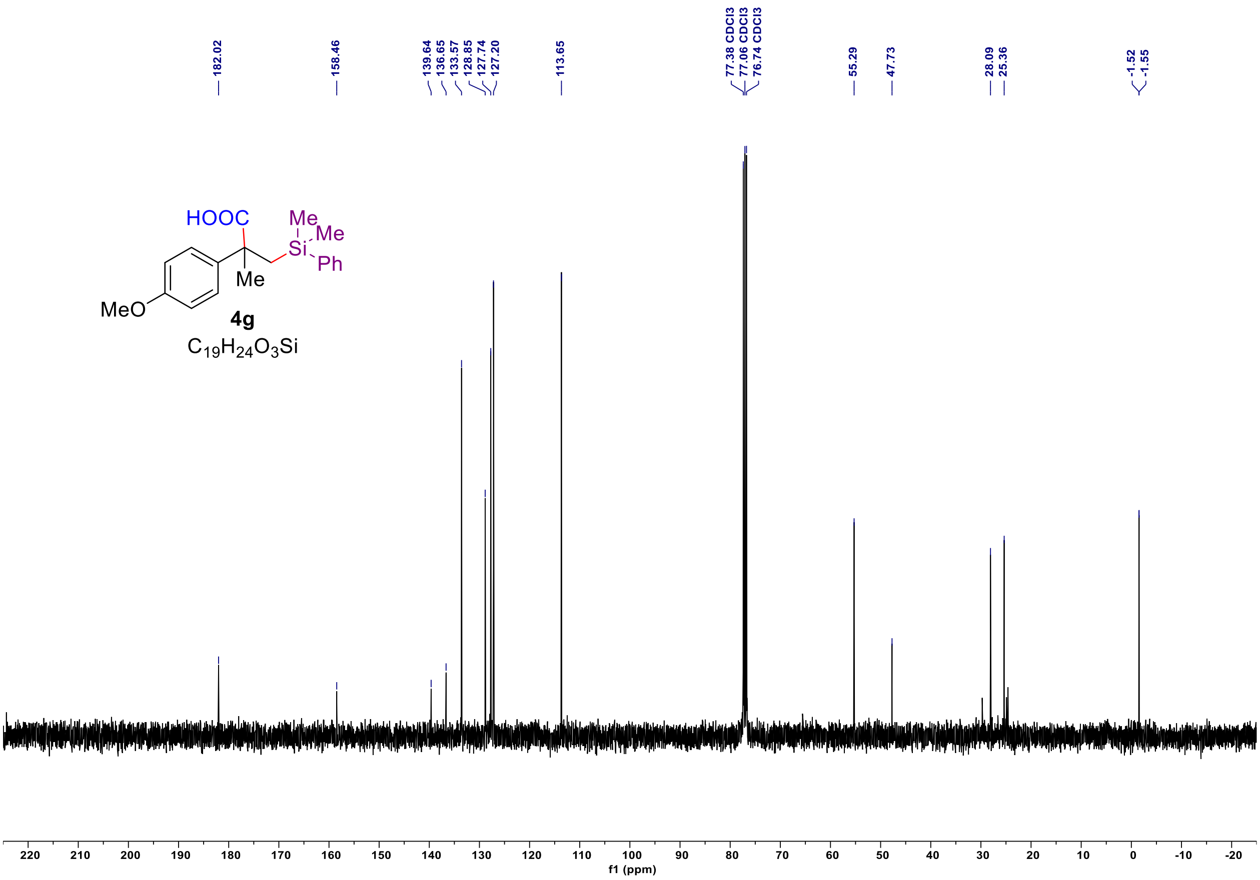
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4f.**



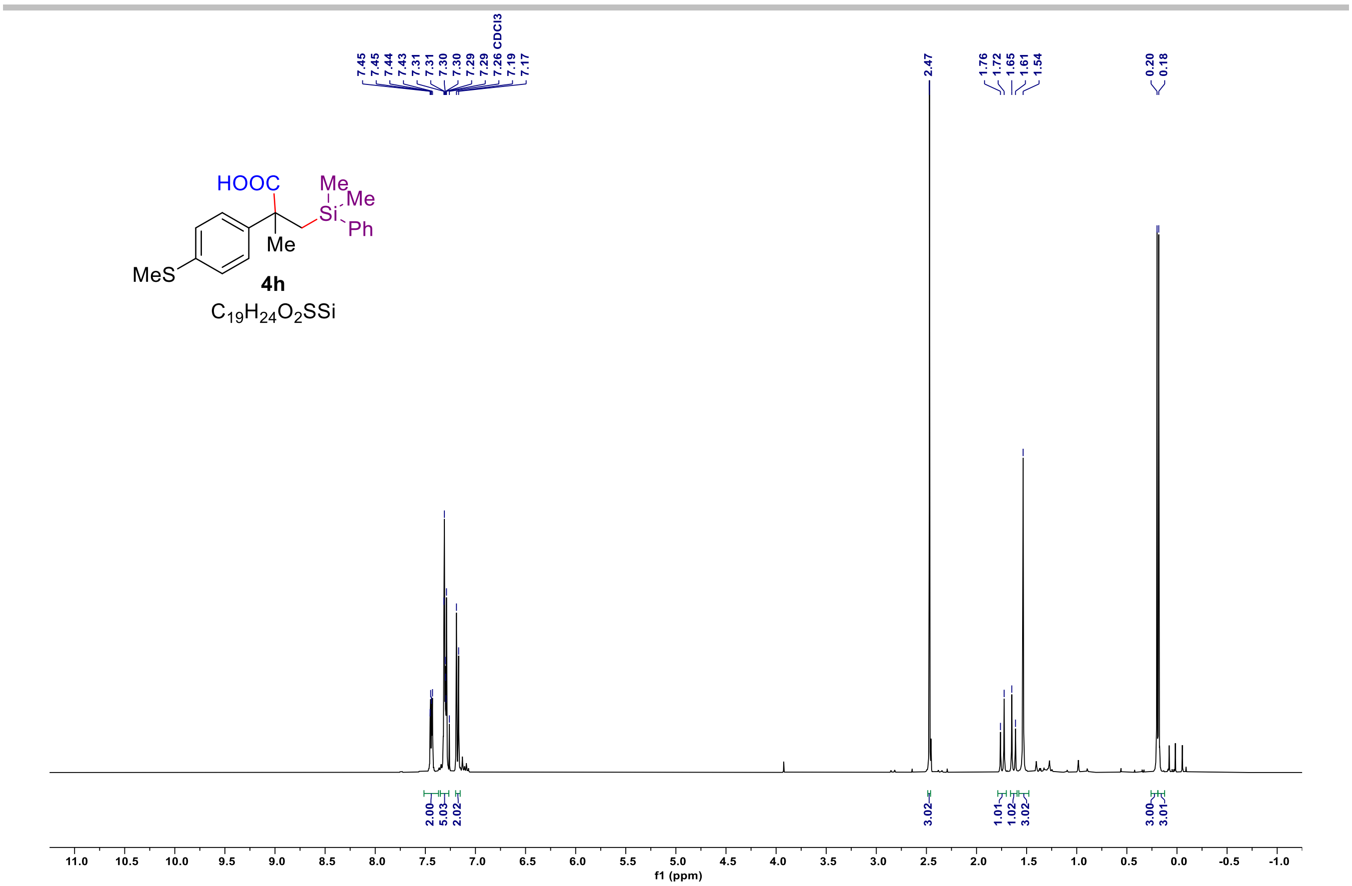
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4f.**



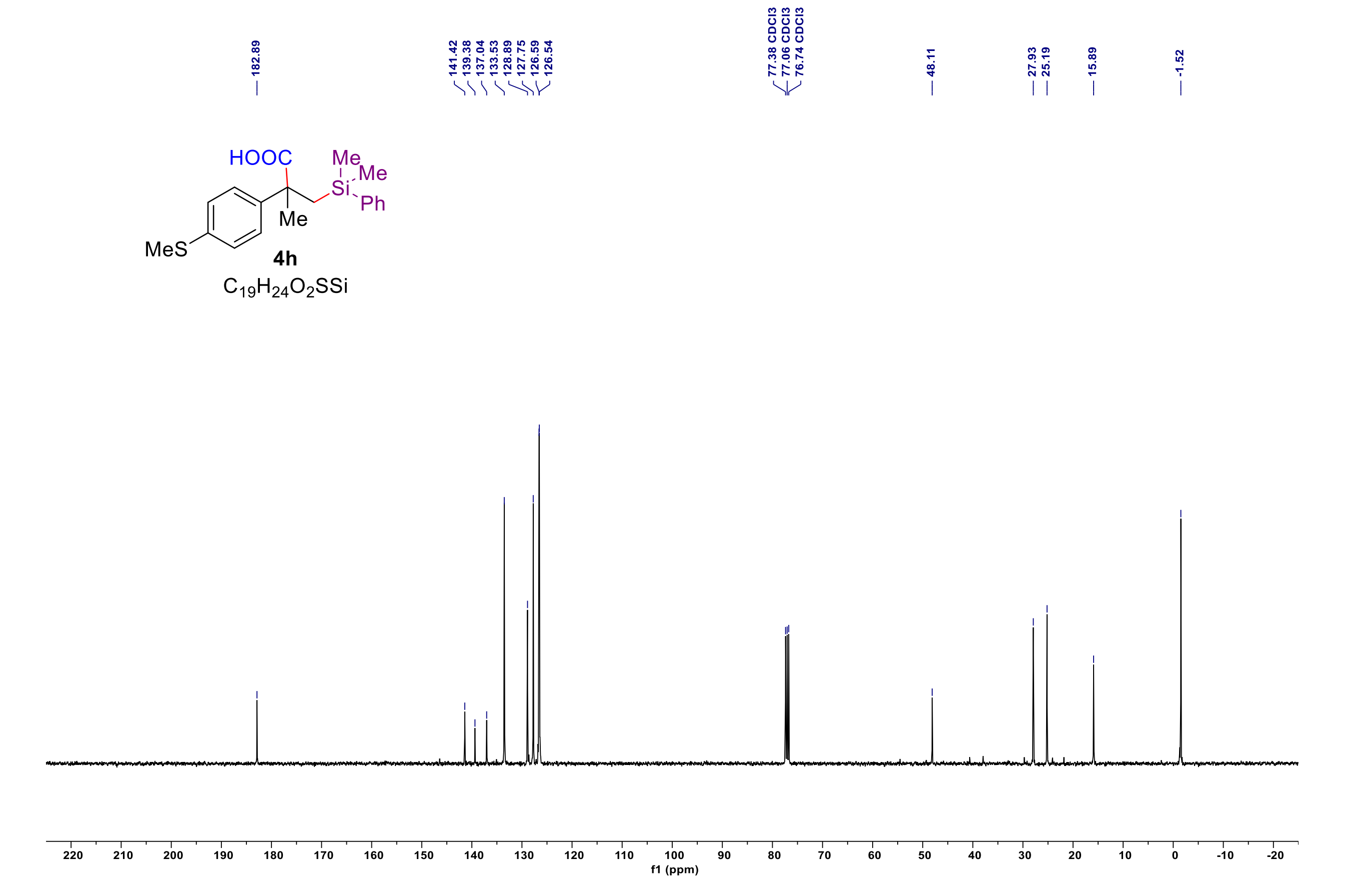
^{1}**H NMR** spectrum (400 MHz, CDCl$_3$) of compound **4g.**



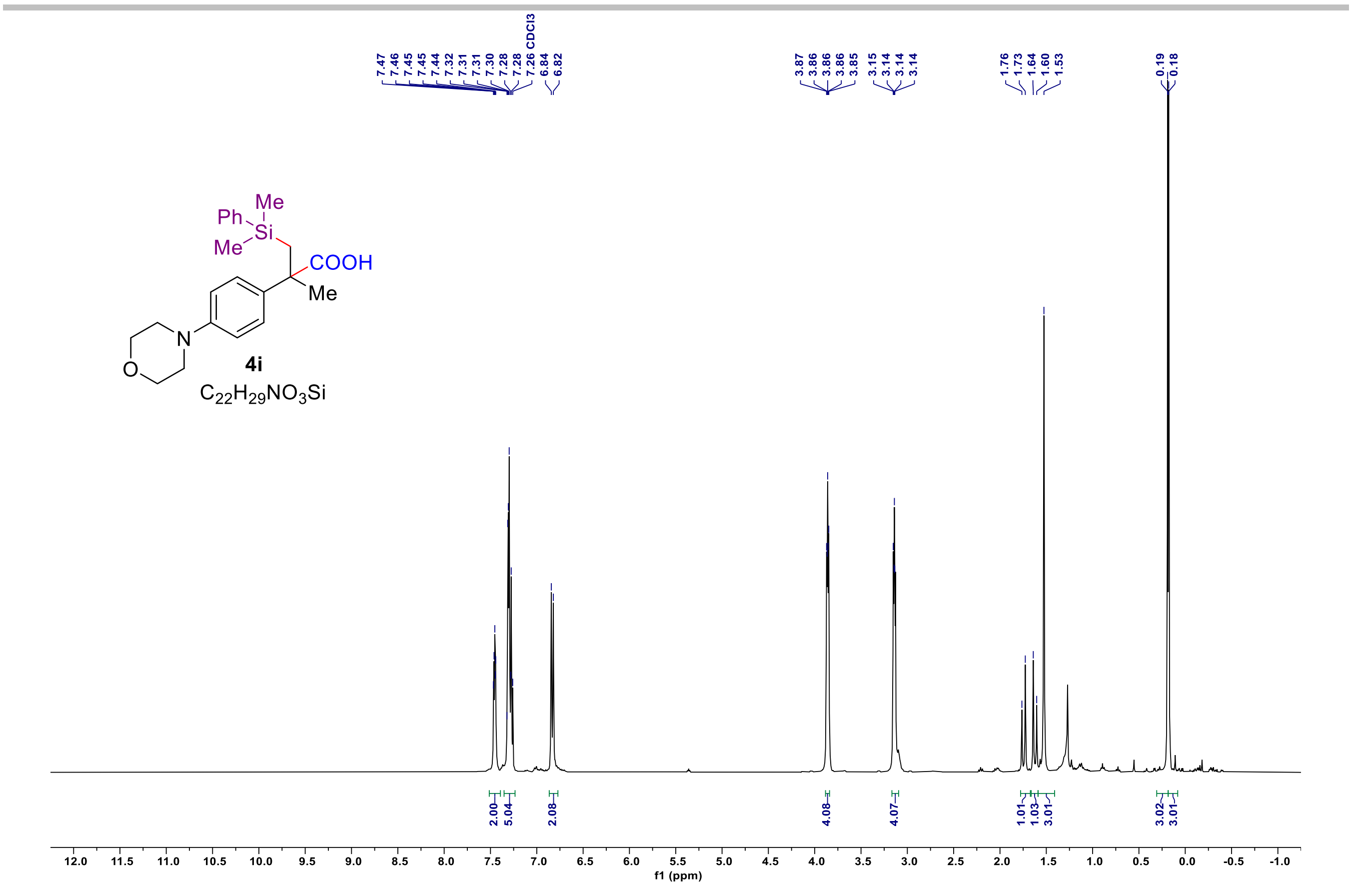
^{13}**C{^{1}H} NMR** spectrum (100 MHz, CDCl$_3$) of compound **4g.**



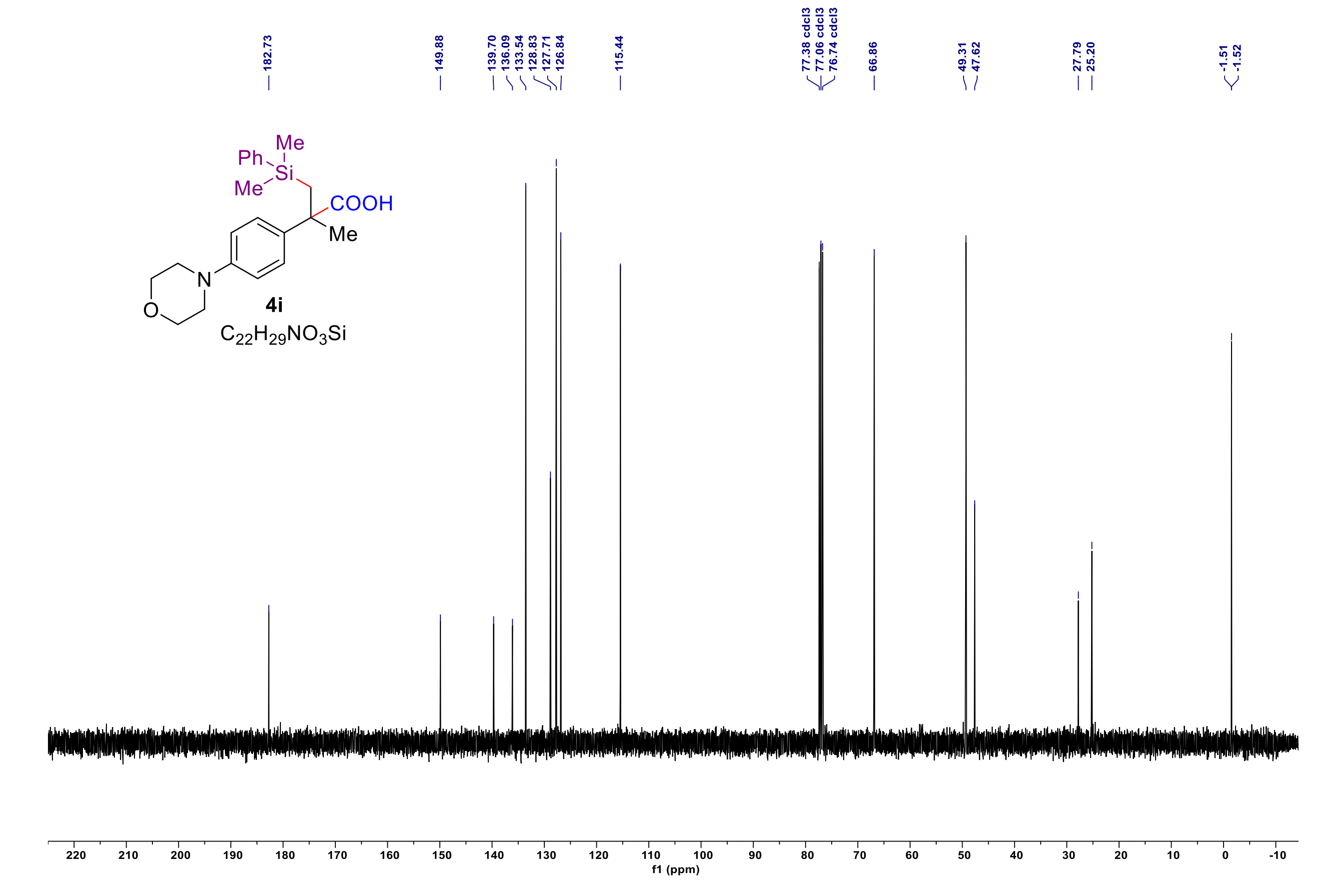
¹H NMR spectrum (400 MHz, $CDCl_3$) of compound **4h.**



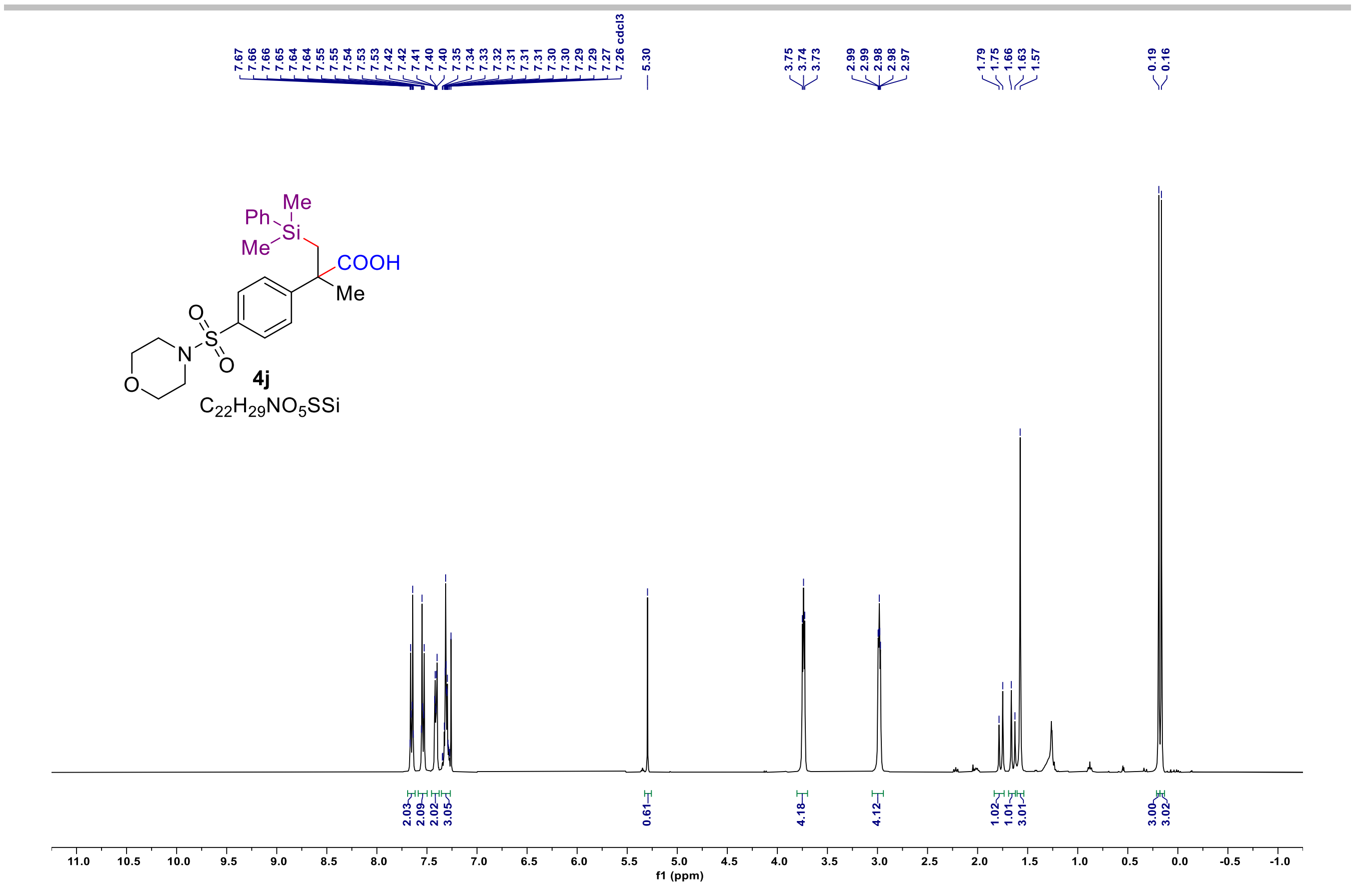
¹³C{¹H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4h.**



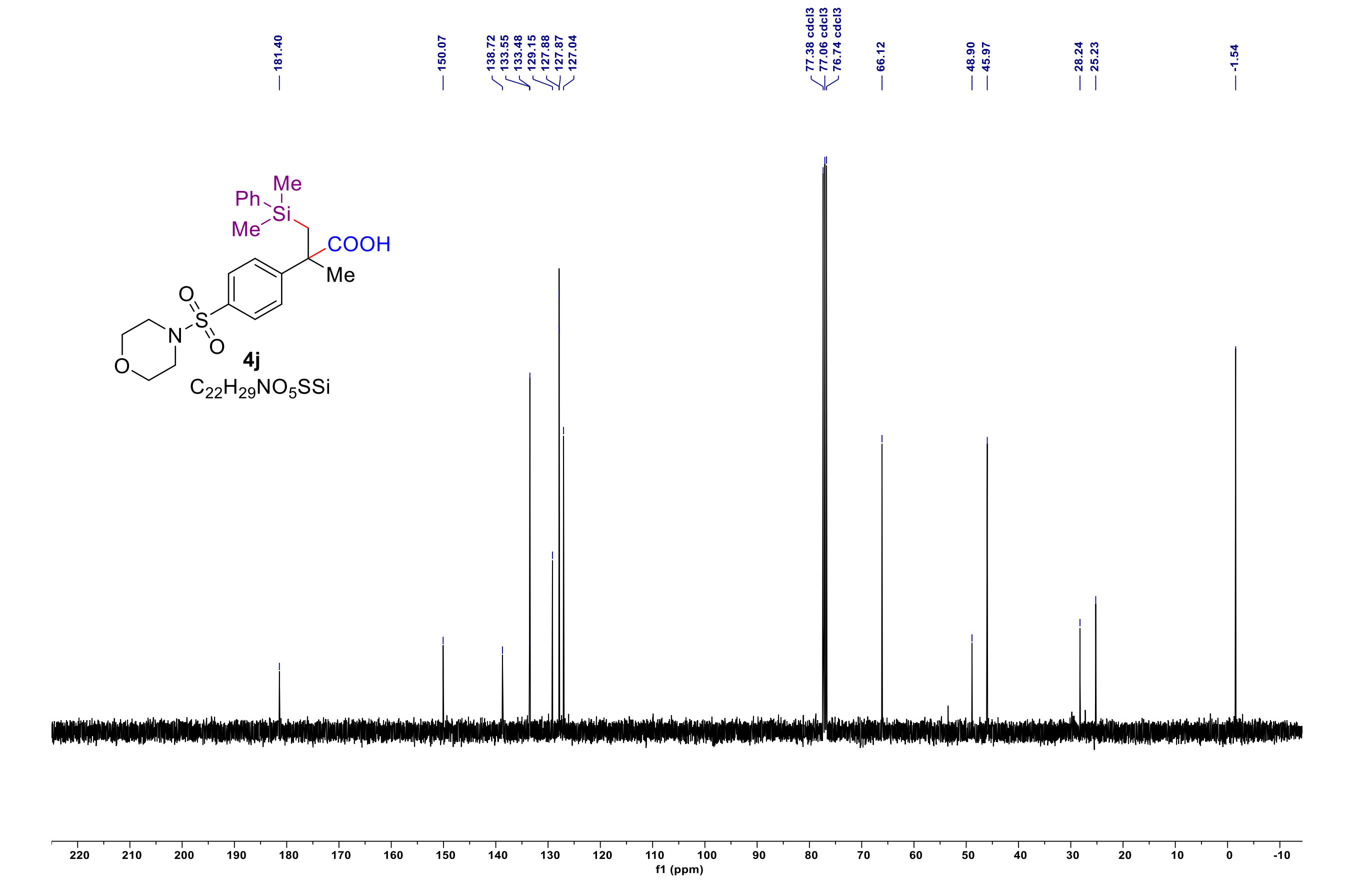
^{1}**H NMR** spectrum (400 MHz, CDCl$_3$) of compound **4i.**



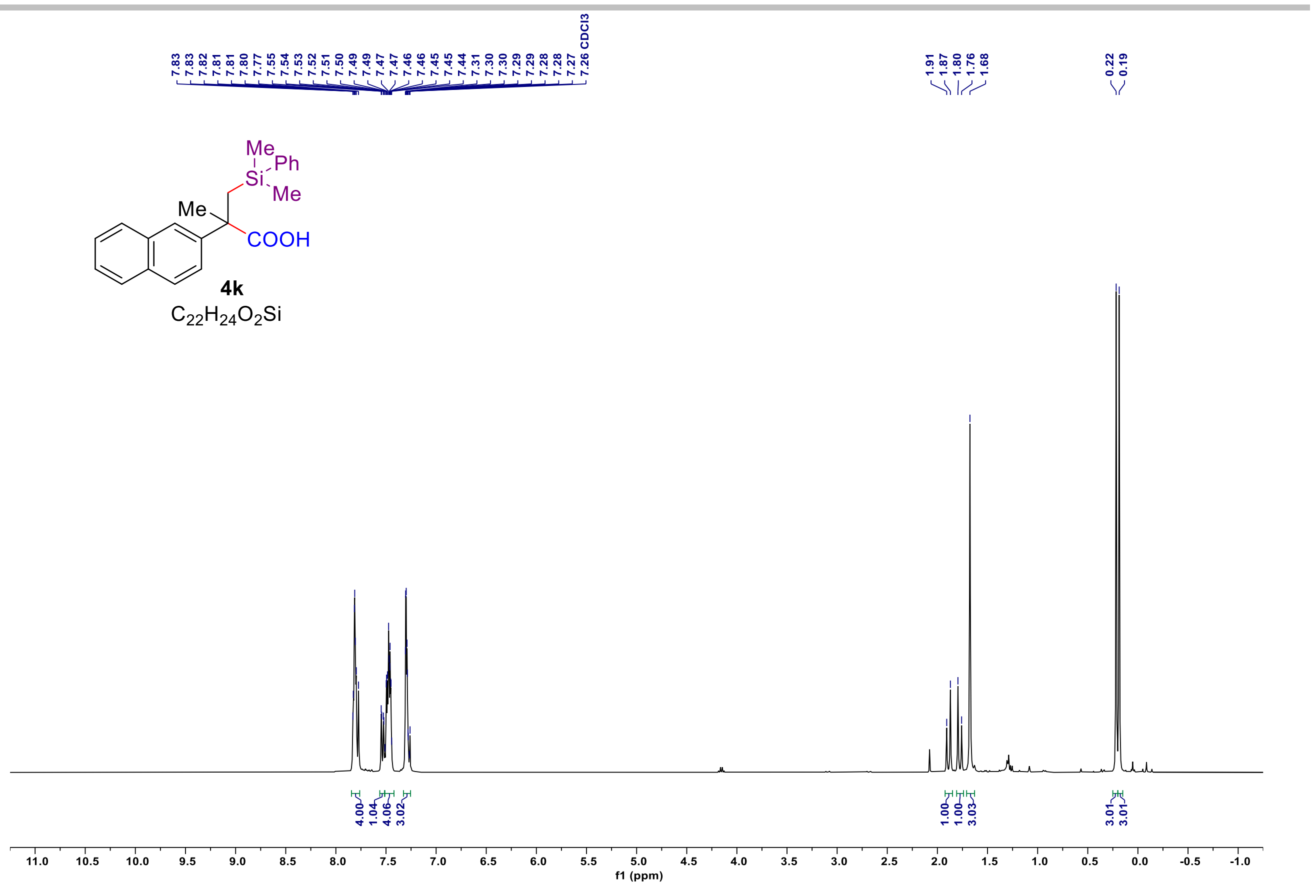
^{13}**C{^{1}H} NMR** spectrum (100 MHz, CDCl$_3$) of compound **4i. gao-27-81 或 82chR.**



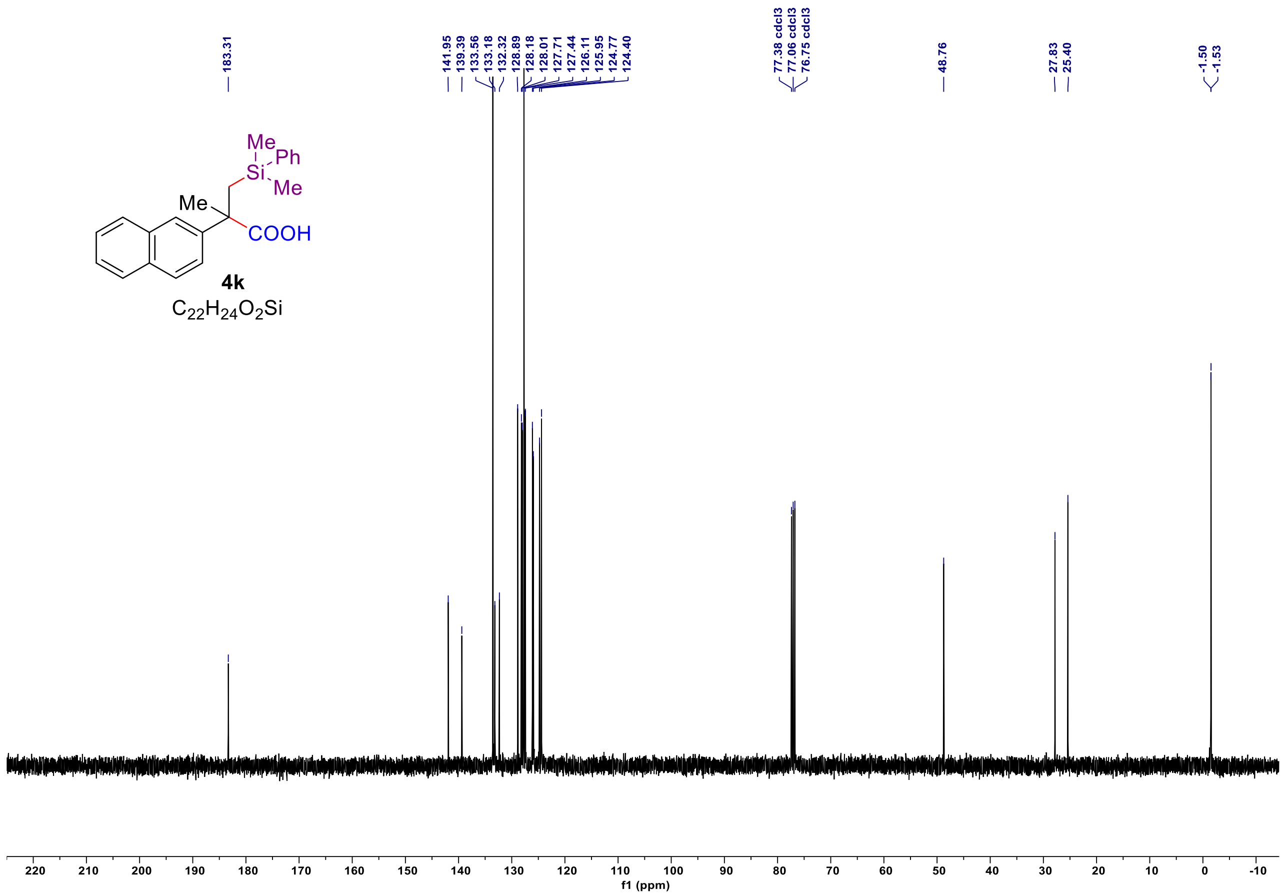
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4j.**



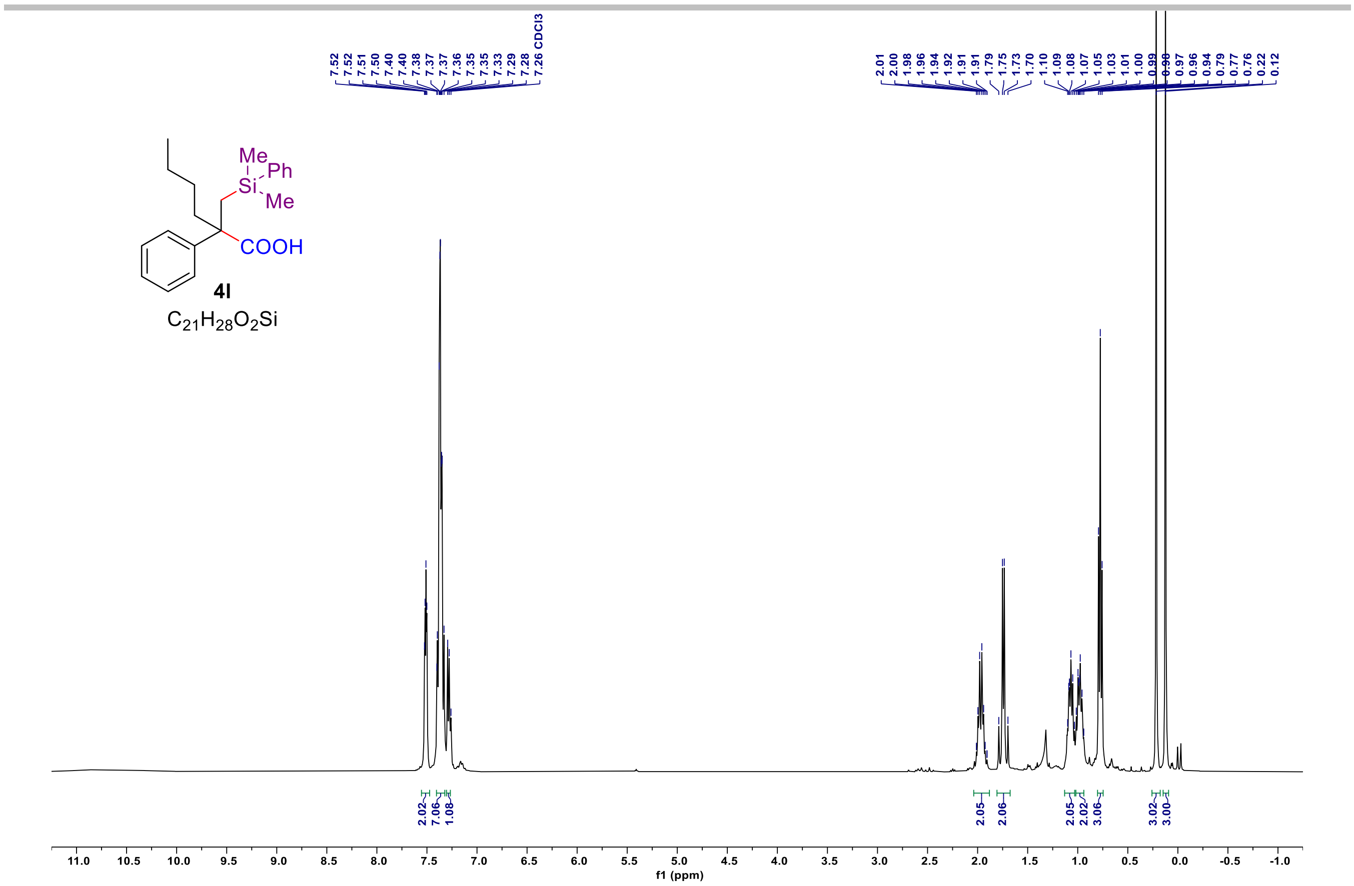
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4j. gao-27-114ch.**



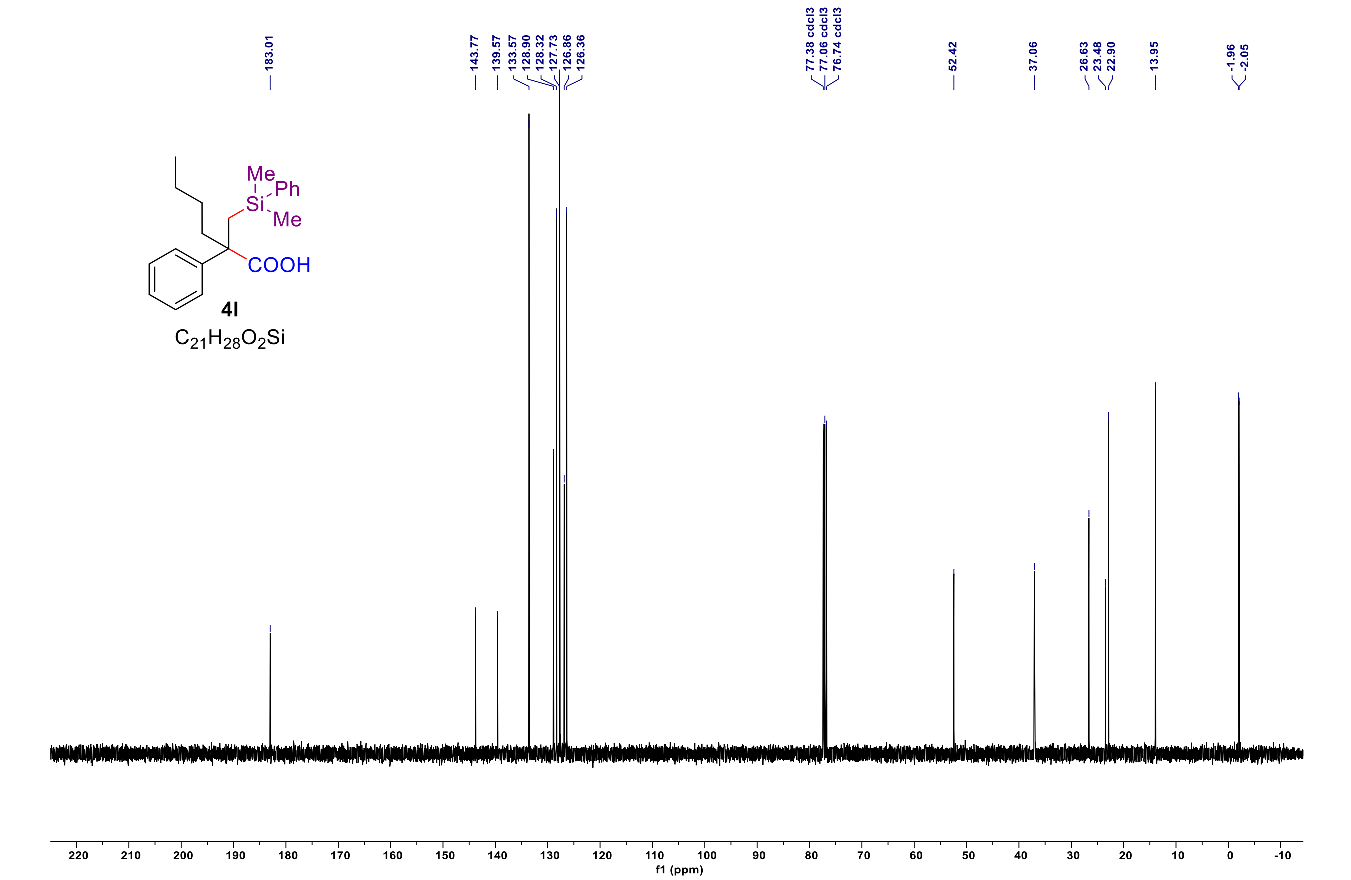
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4k.**



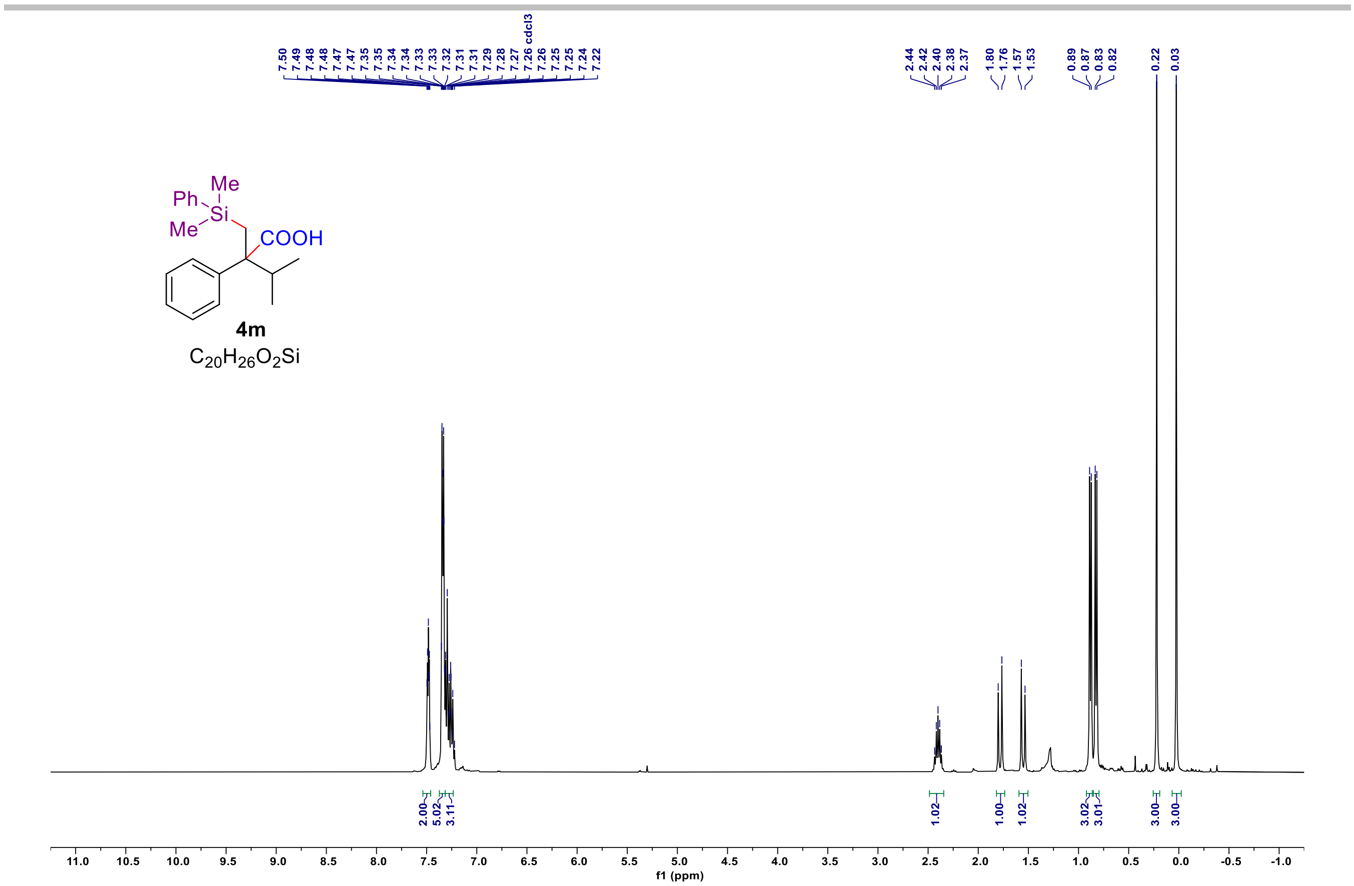
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4k. gao-27-109ch.**



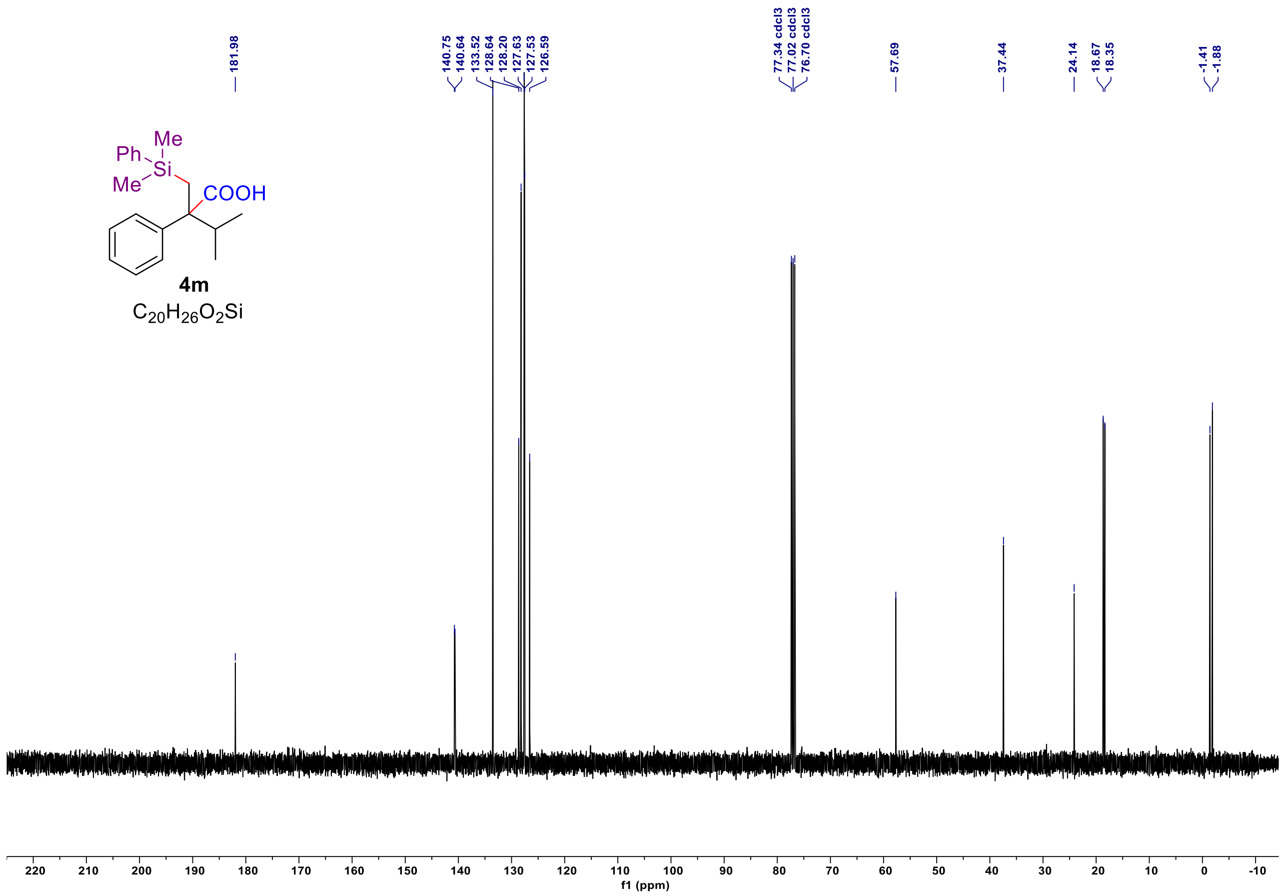
¹H NMR spectrum (400 MHz, CDCl₃) of compound **4l.**



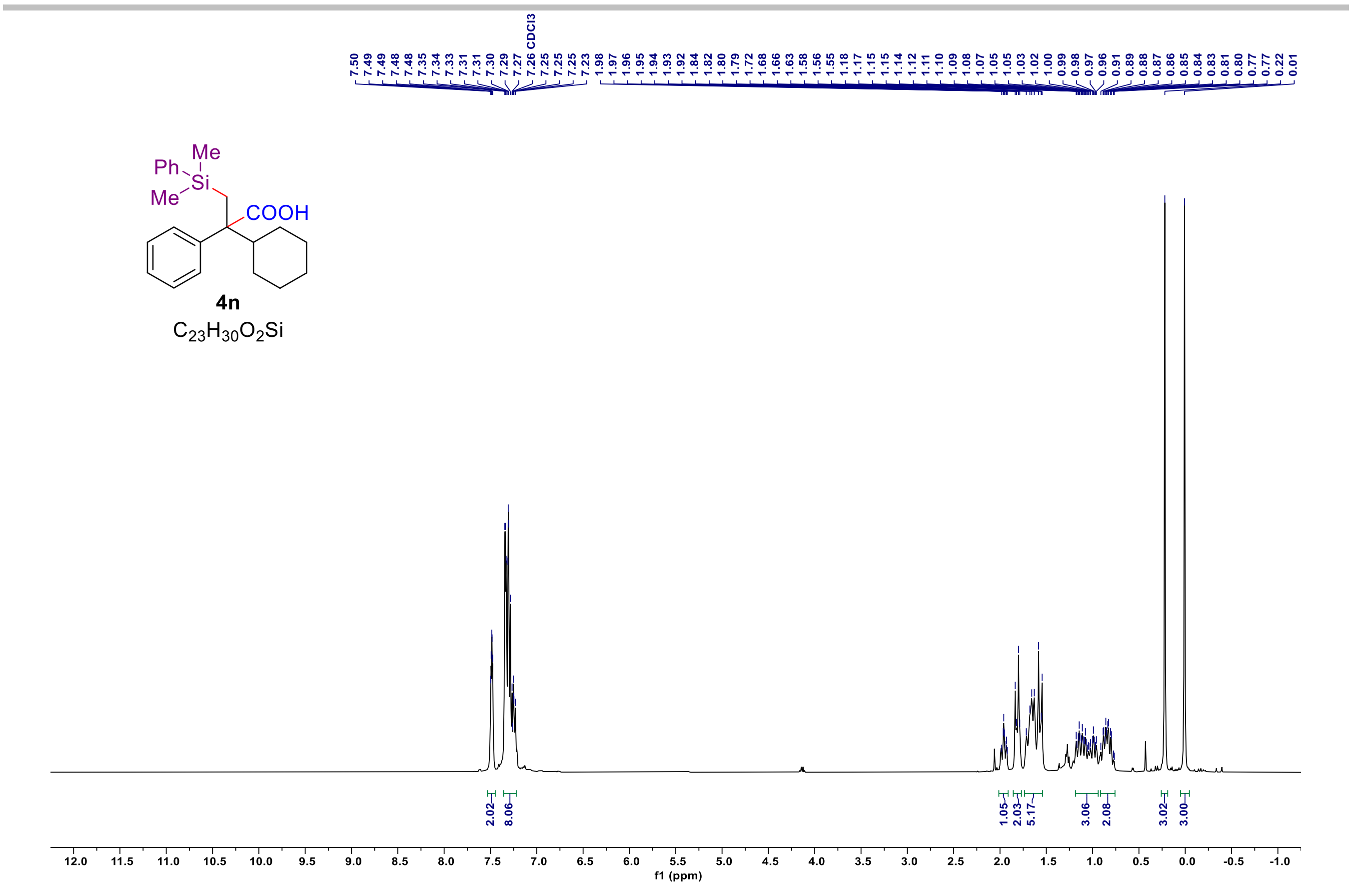
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl₃) of compound **4l. gao-27-110ch.**



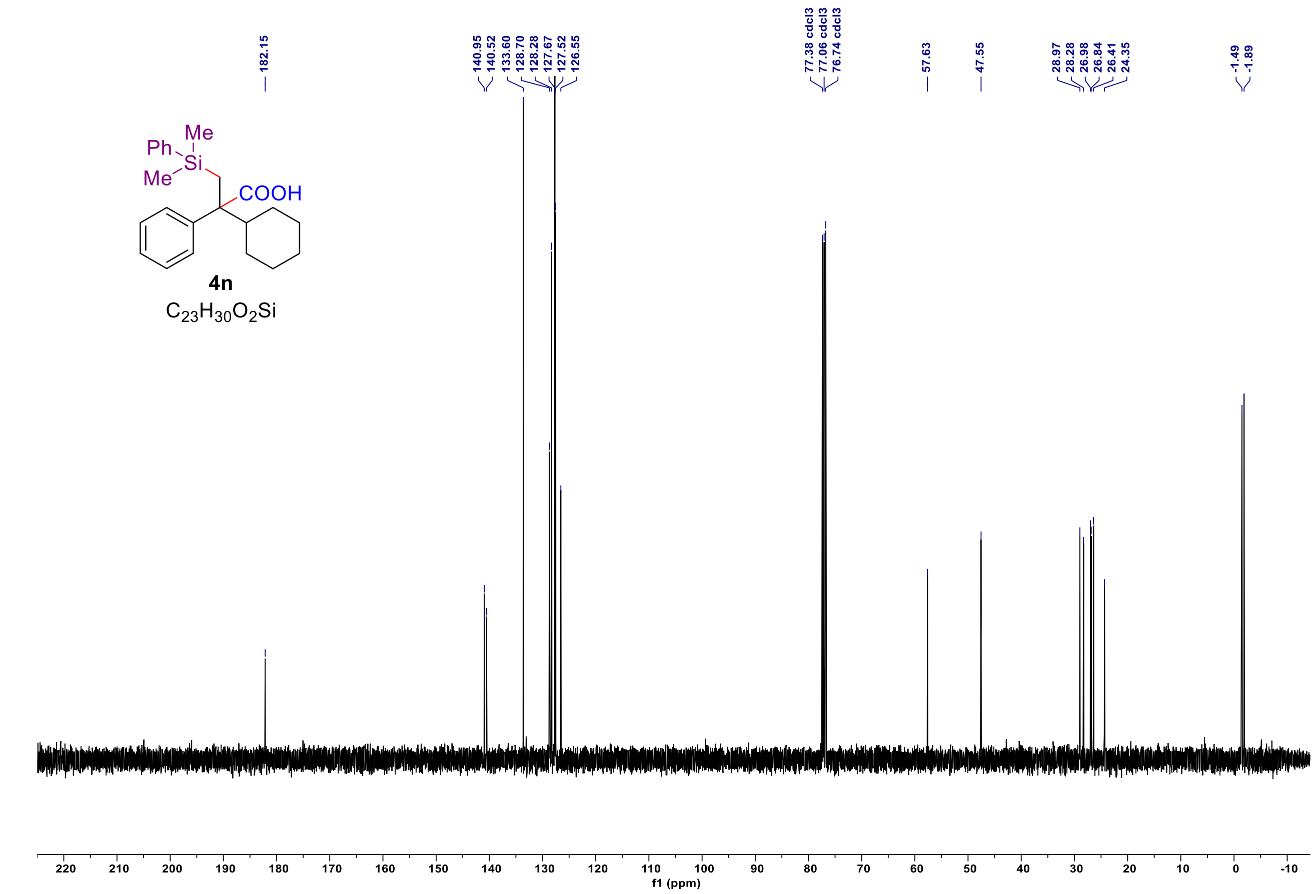
^{1}**H NMR** spectrum (400 MHz, CDCl3) of compound **4m.**



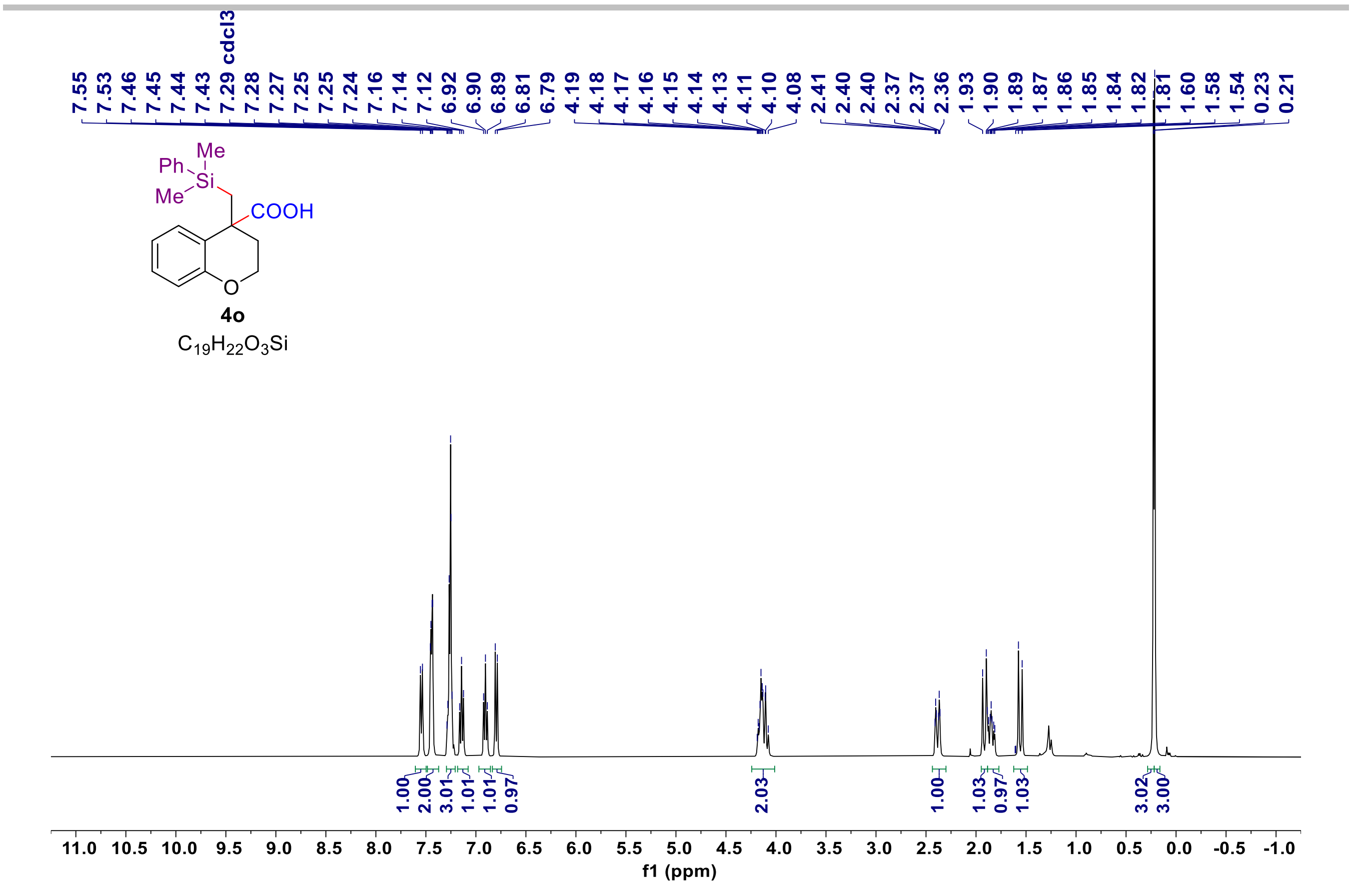
^{13}**C{^{1}H} NMR** spectrum (100 MHz, CDCl3) of compound **4m. gao-27-107ch.**



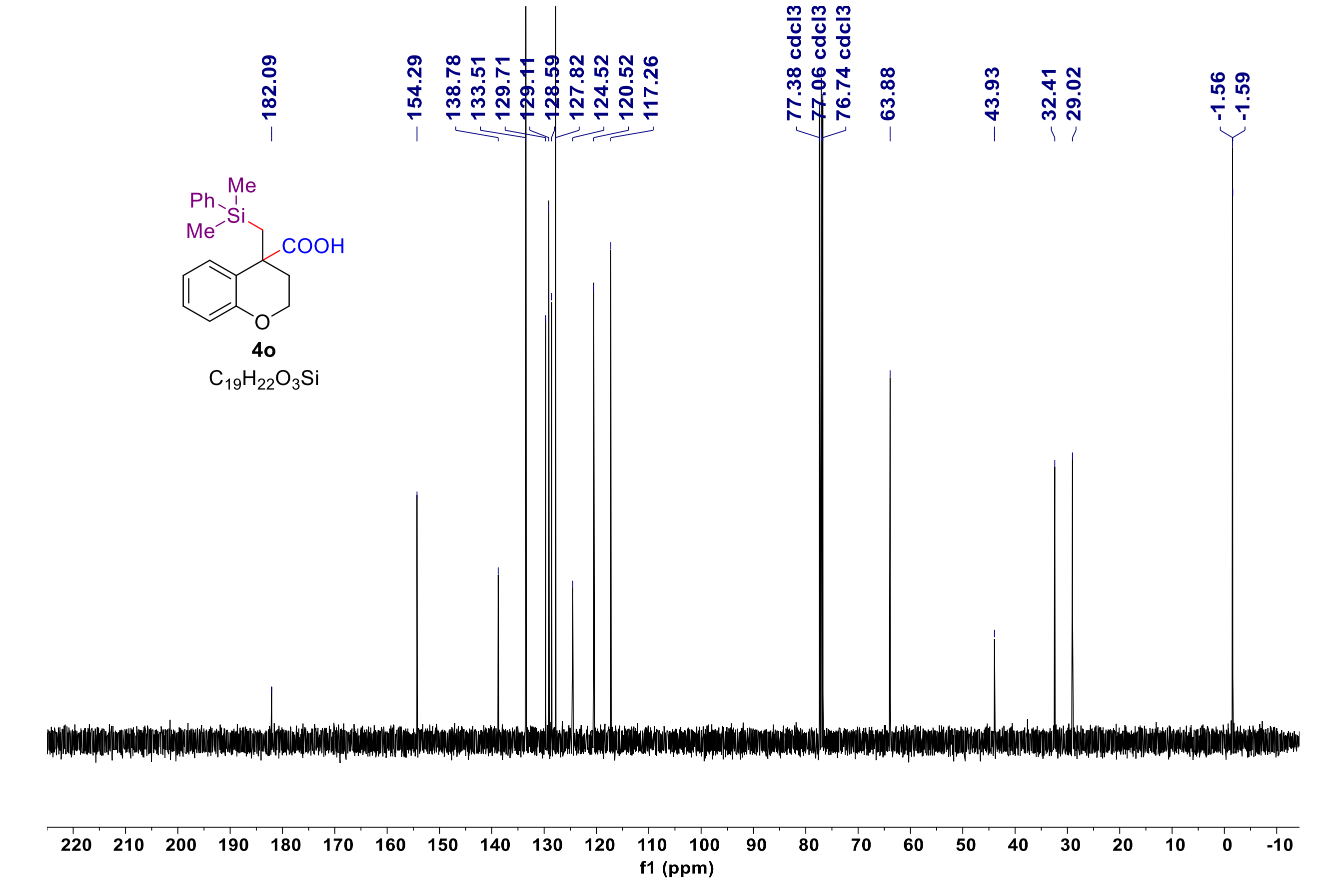
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4n.**



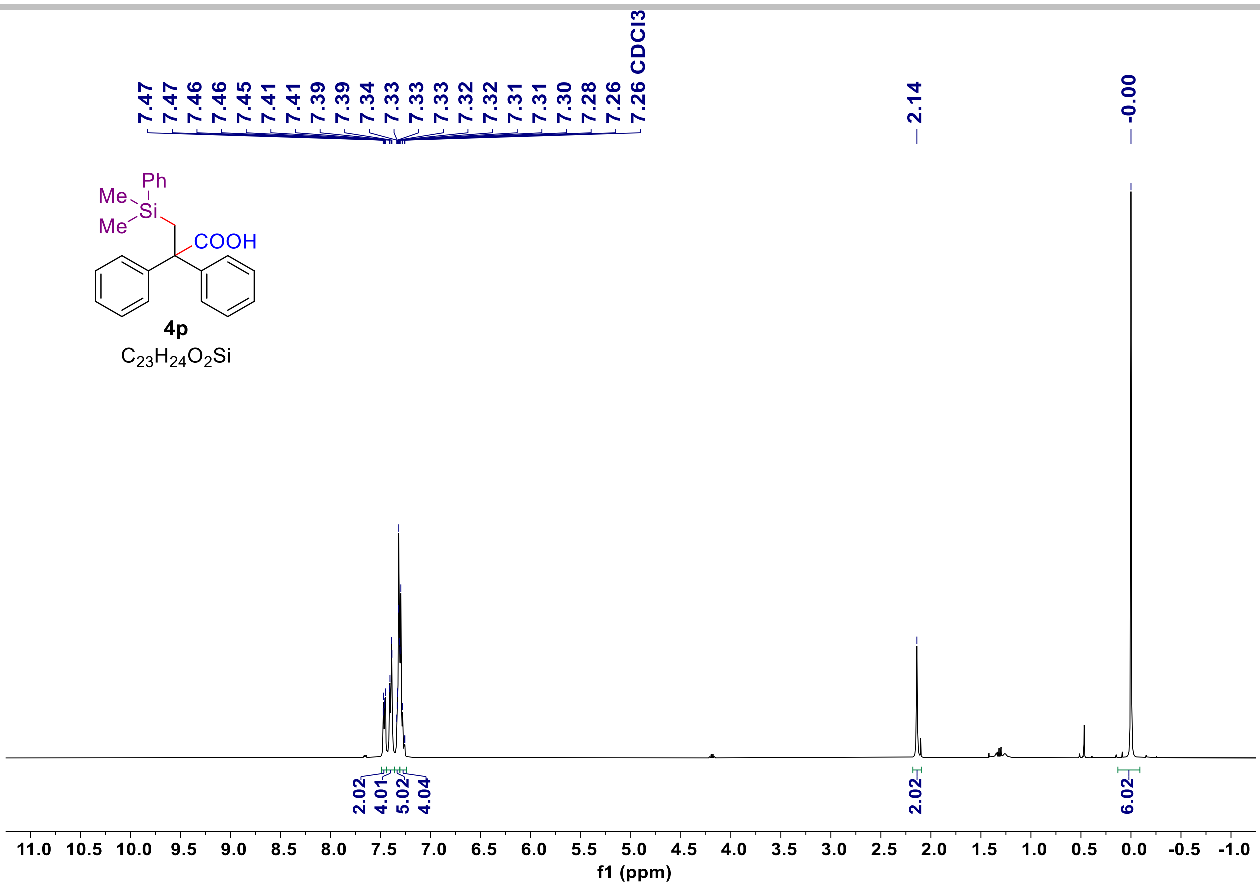
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4n. gao-27-106ch.**



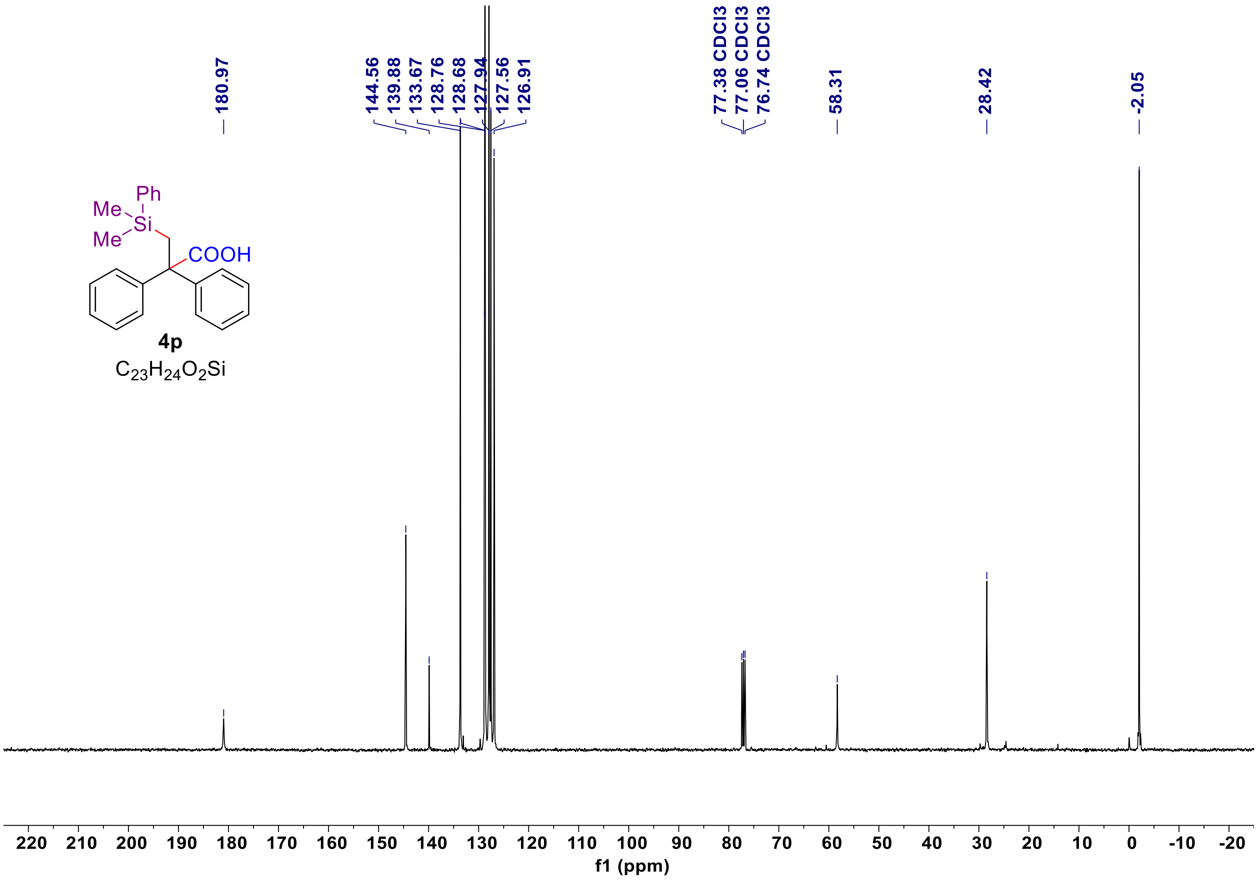
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4o.**



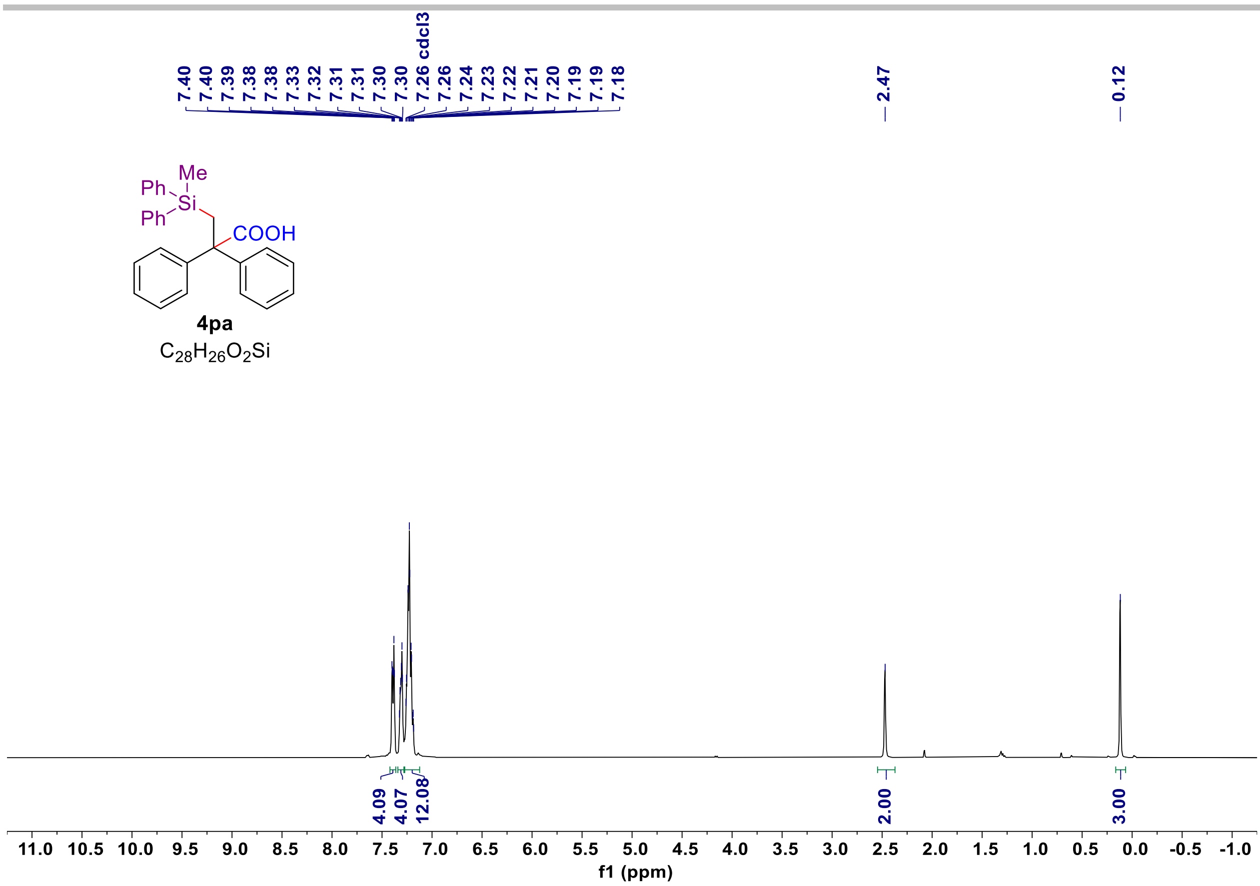
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4o. gao-27-83ch.**



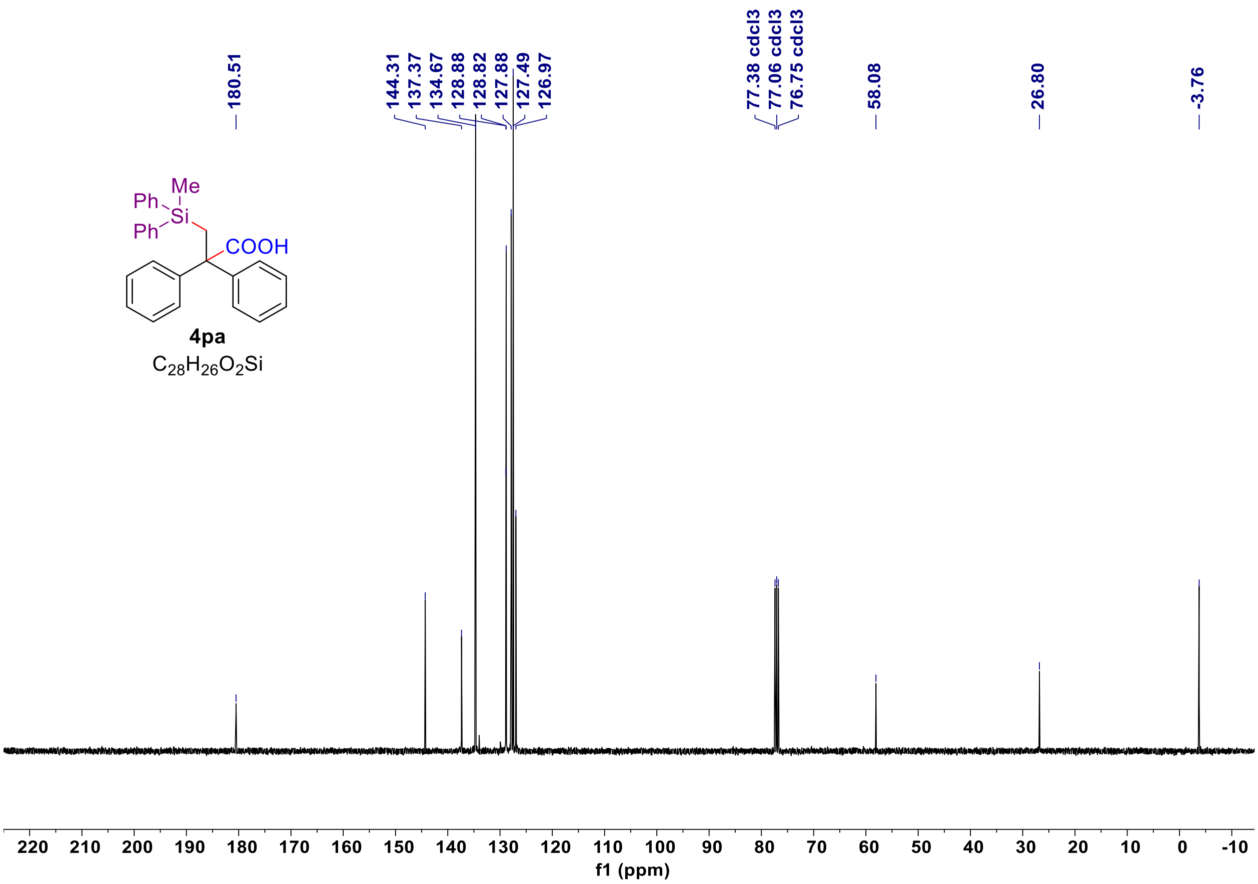
[1]H NMR spectrum (400 MHz, $CDCl_3$) of compound **4p.**



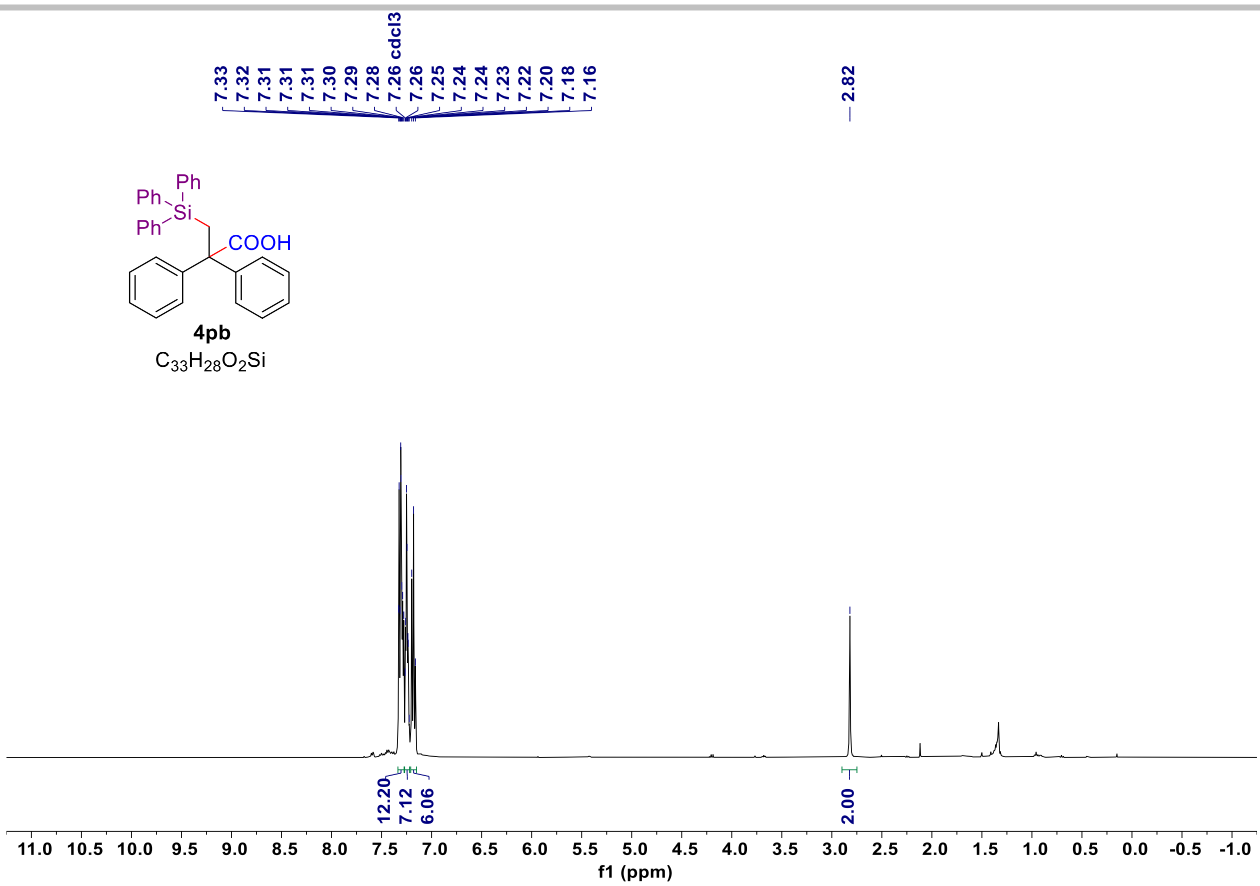
[13]C{[1]H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4p. gao-22-127chr.**



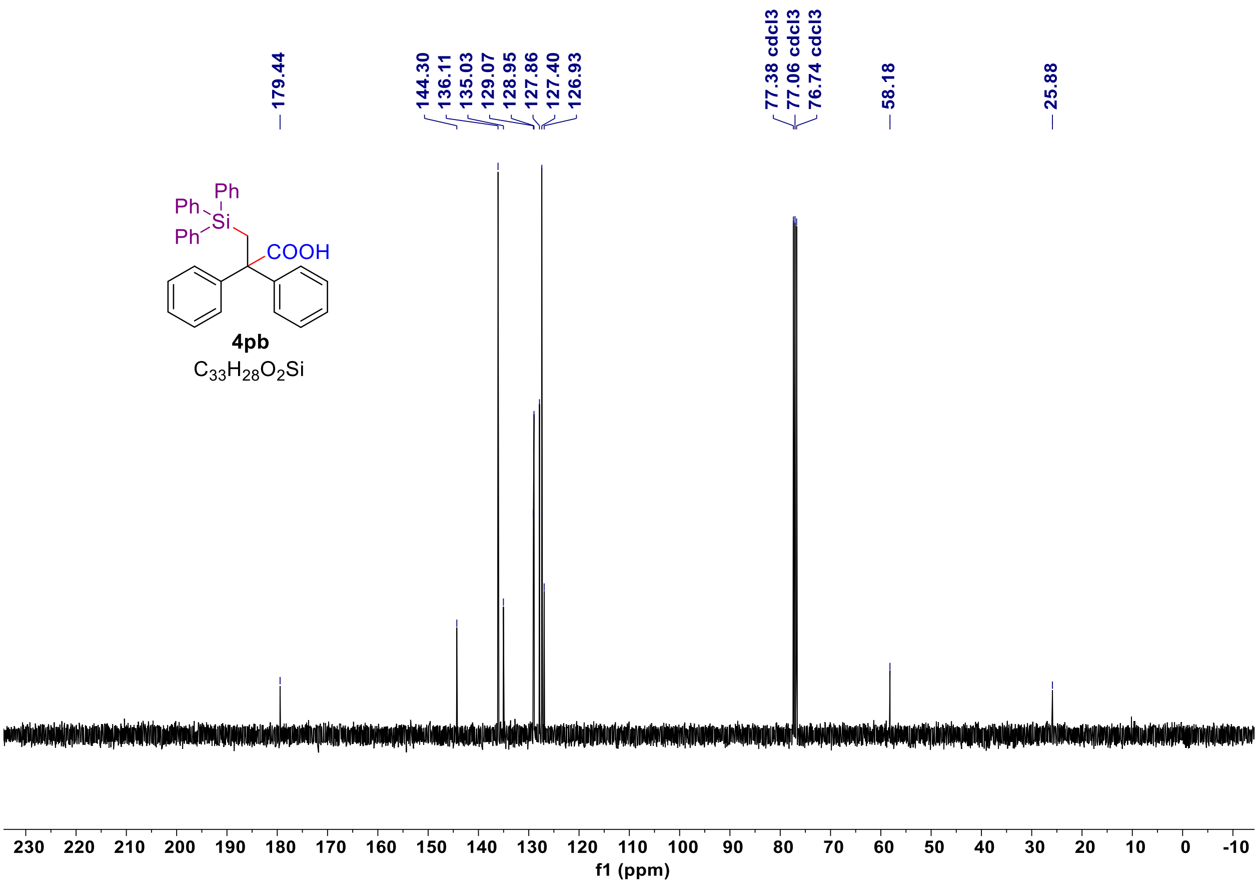
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4pa.**



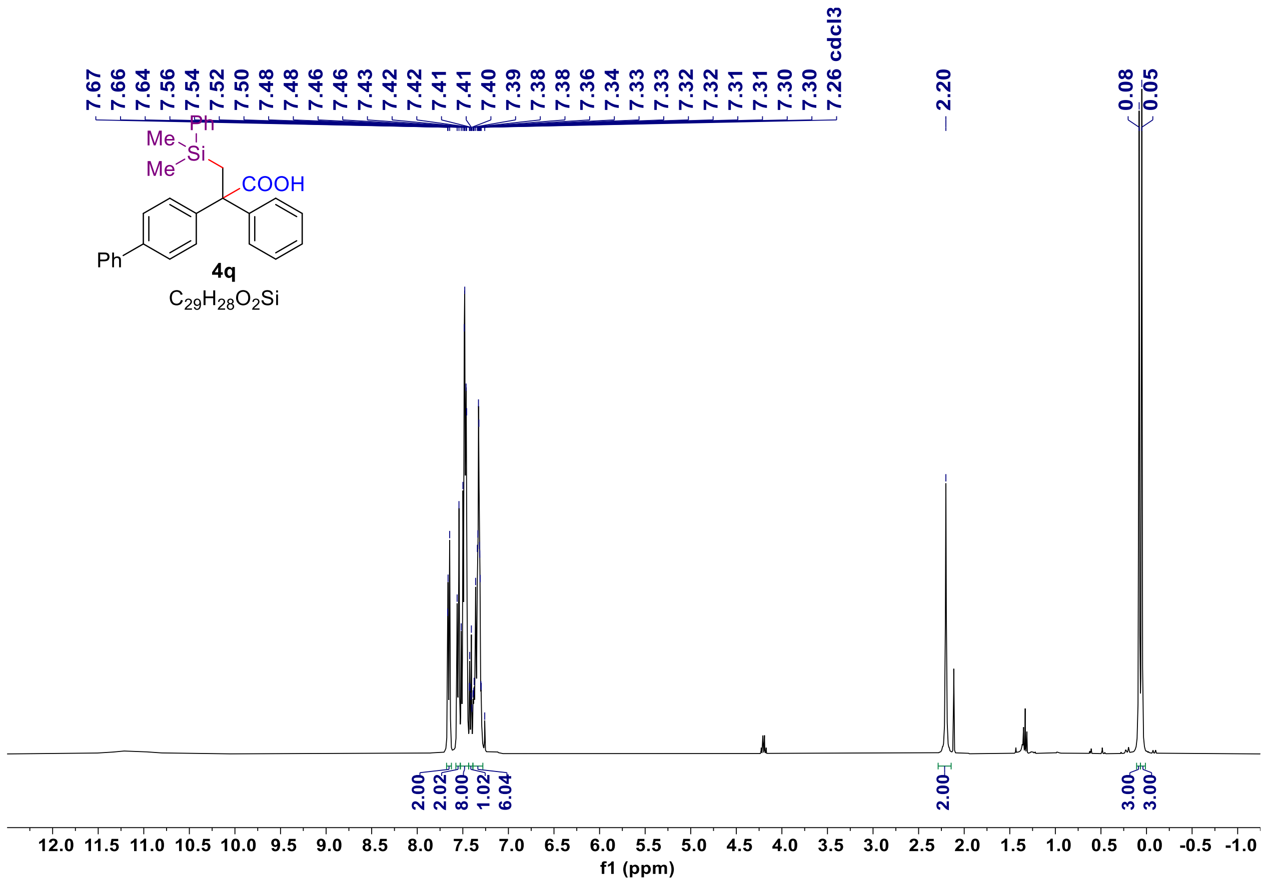
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4pa. gao-241120.**



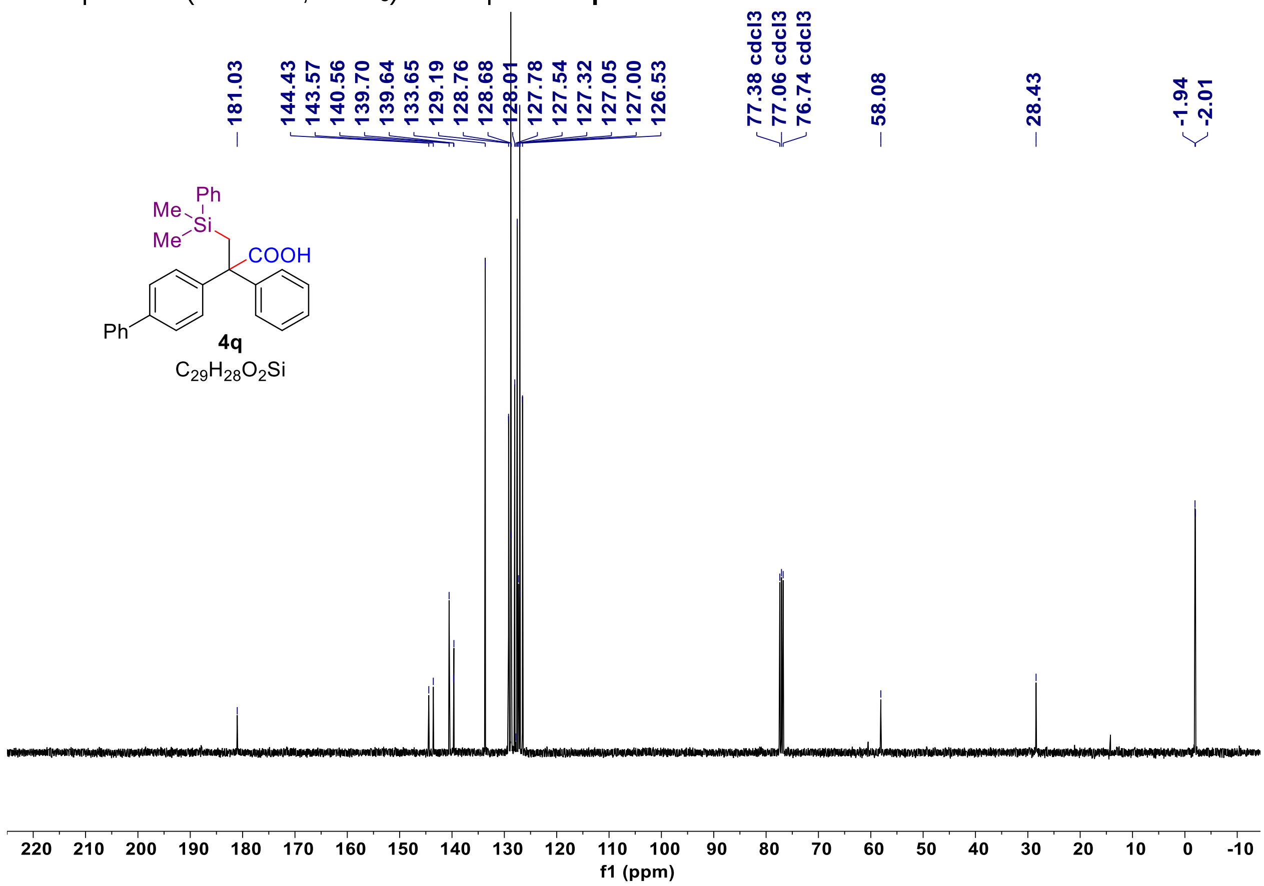
[1]H NMR spectrum (400 MHz, $CDCl_3$) of compound **4pb.**



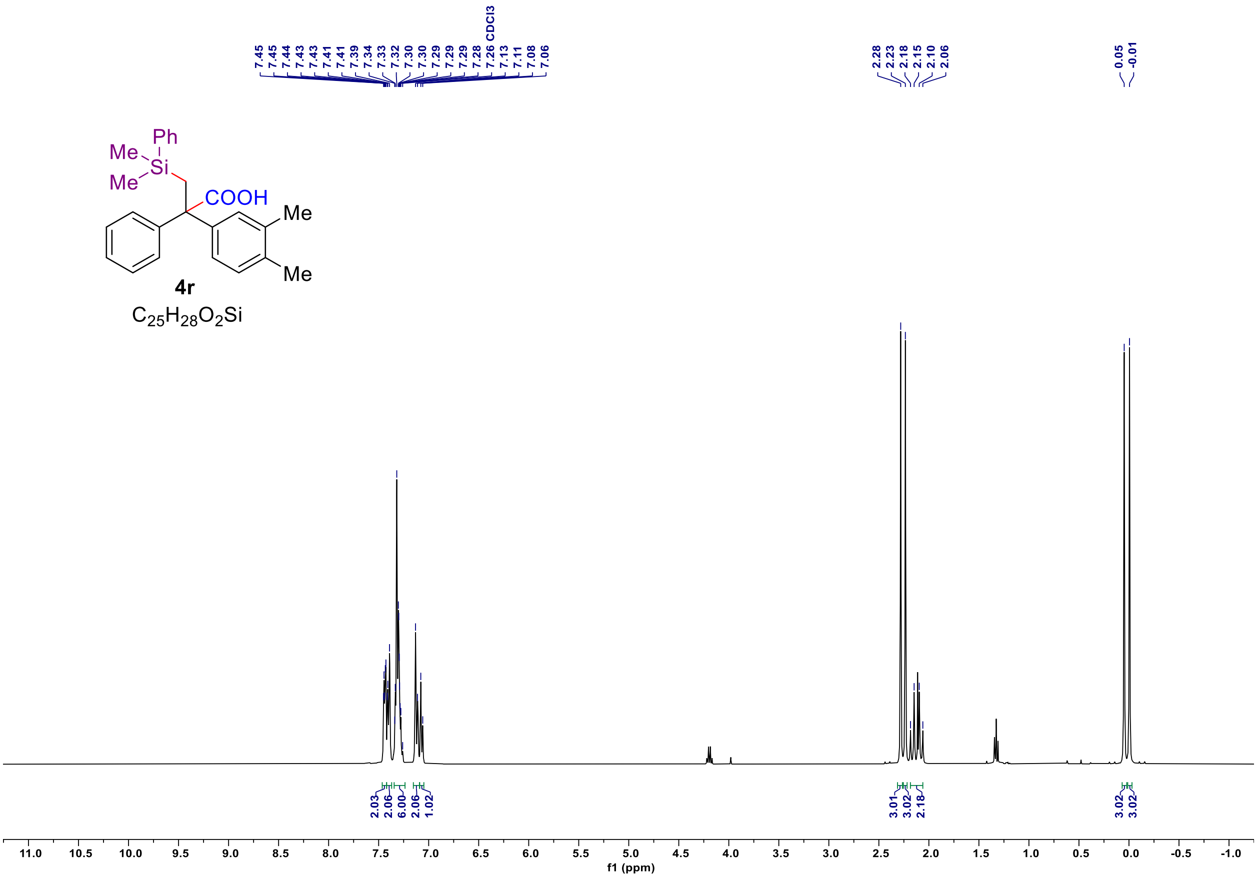
[13]C{[1]H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4pb. gao-241121.**



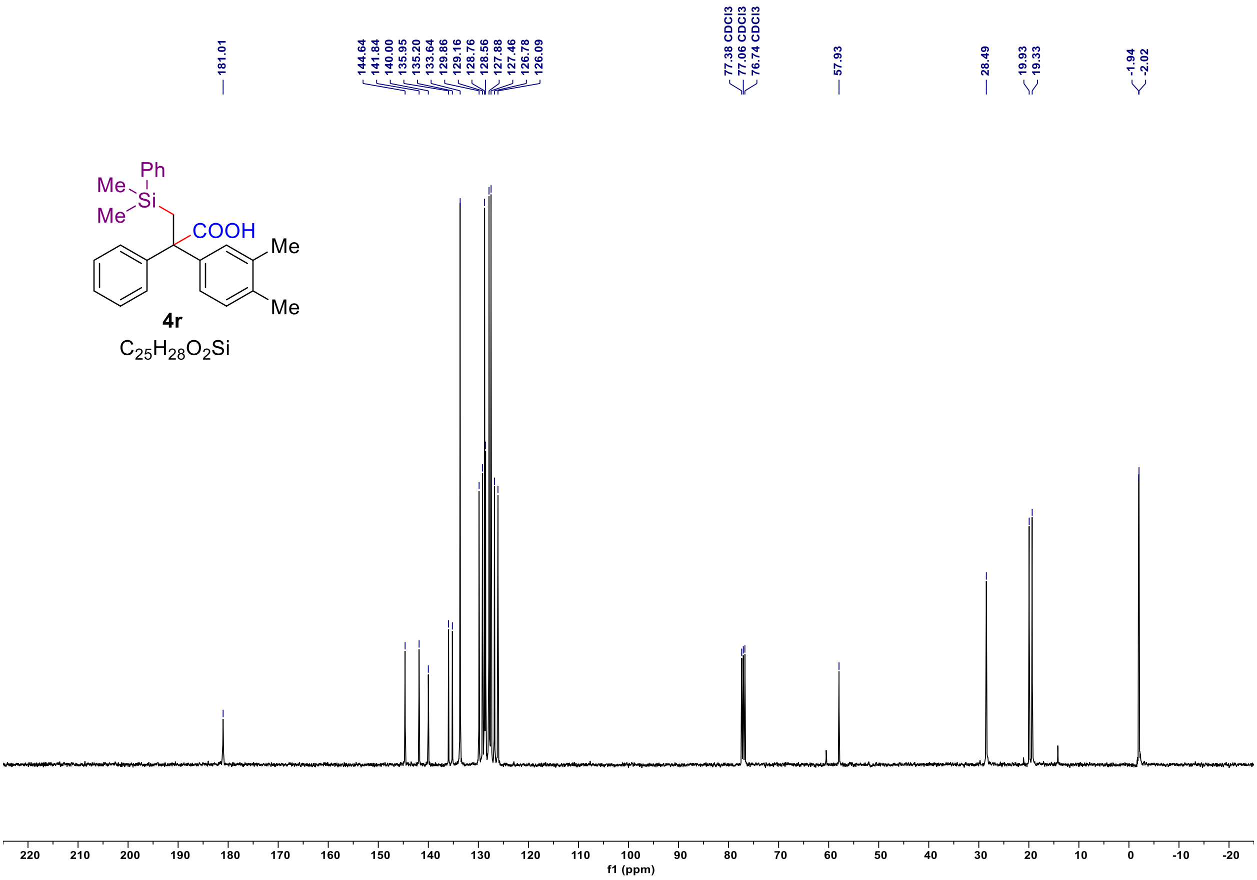
[1]H NMR spectrum (400 MHz, $CDCl_3$) of compound **4q.**



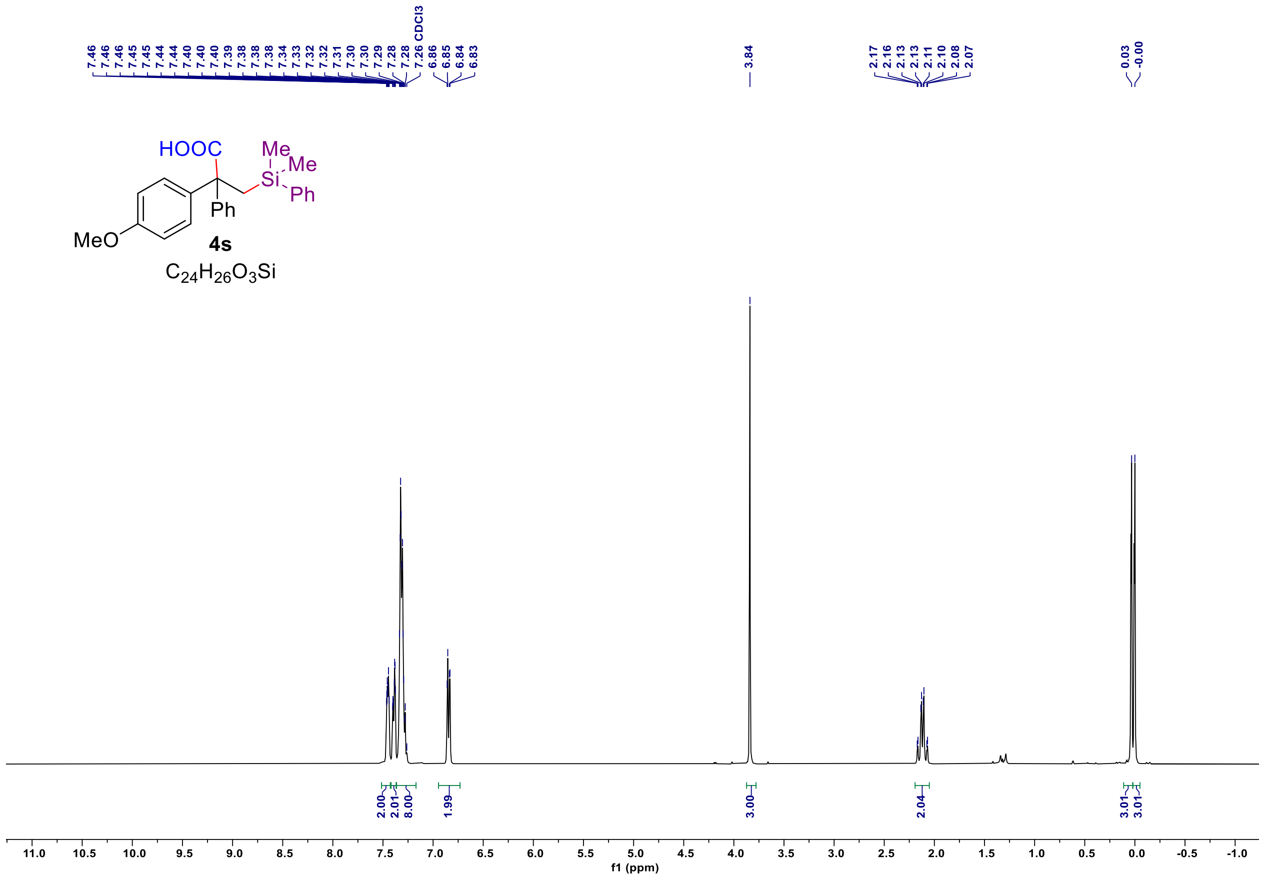
[13]C{[1]H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4q. gao-27-119ch.**



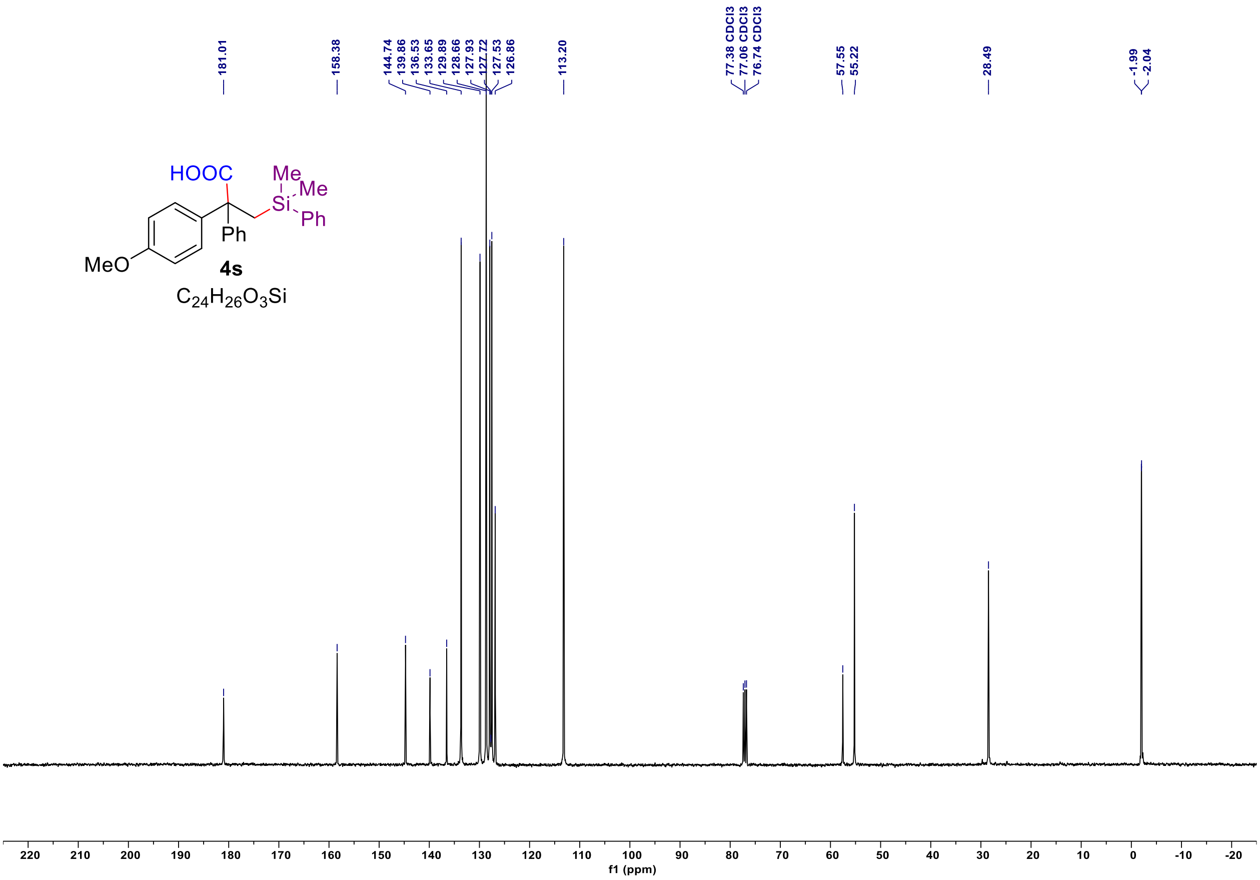
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4r.**



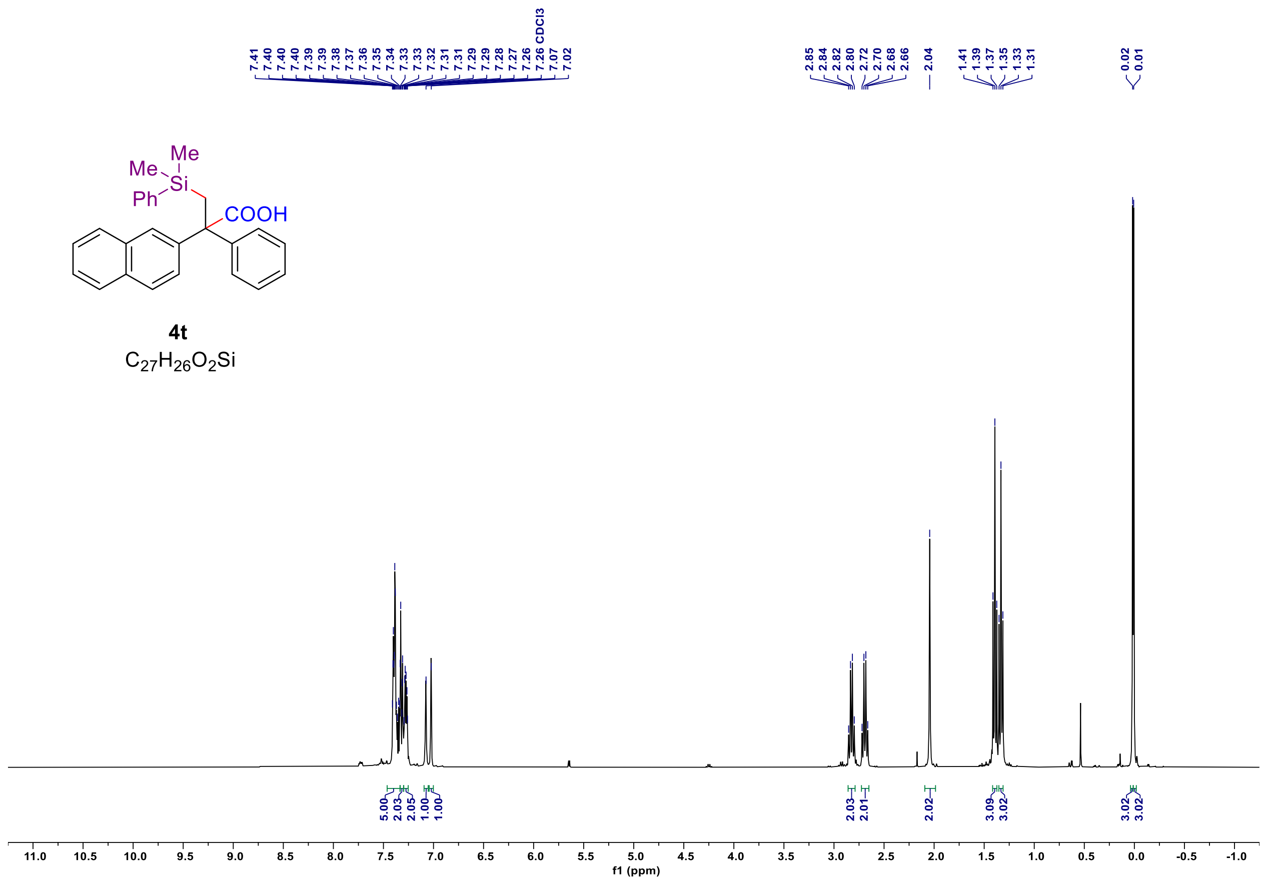
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4r. gao-27-43ch.**



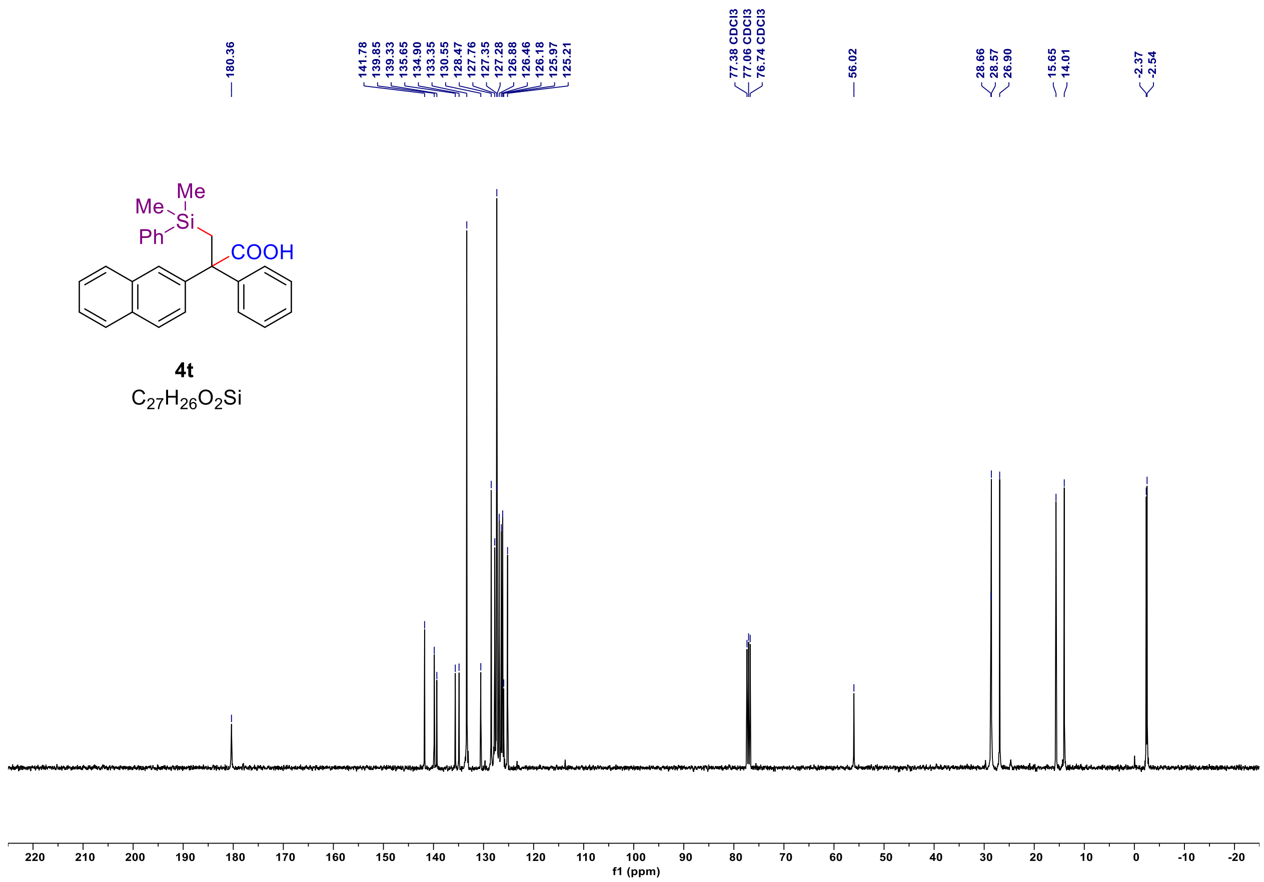
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4s.**



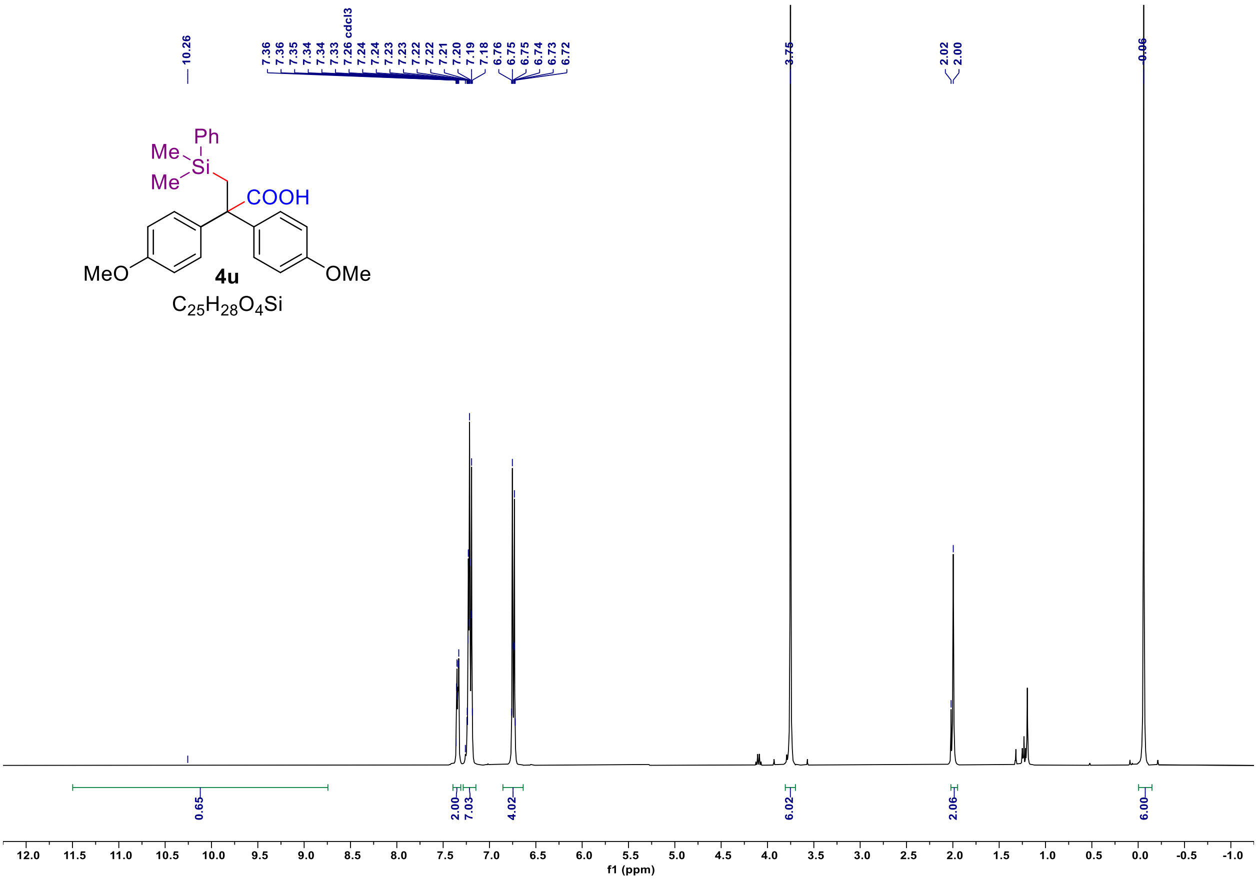
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4s. gao-27-3ch.**



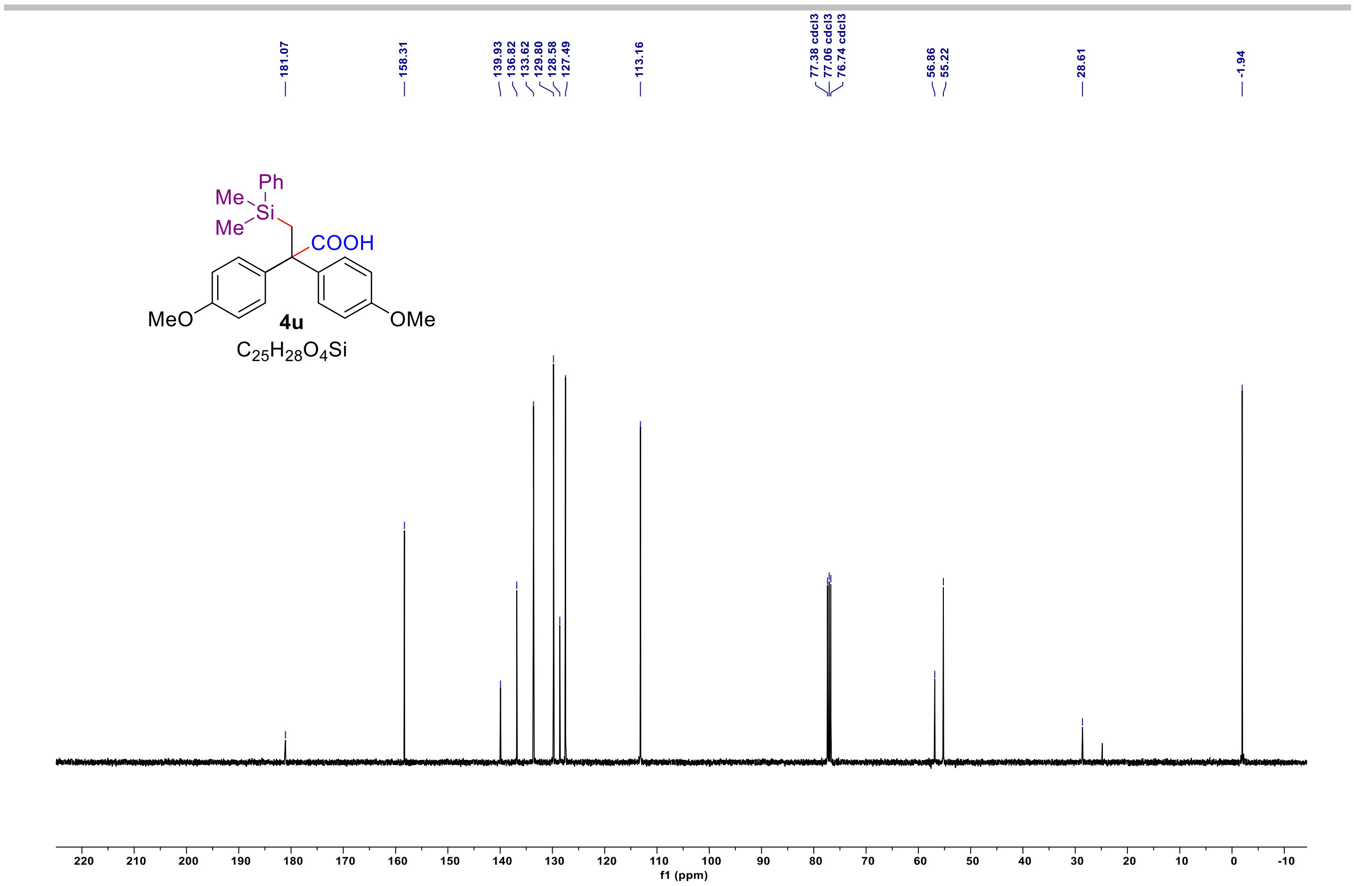
¹H NMR spectrum (400 MHz, $CDCl_3$) of compound **4t.**



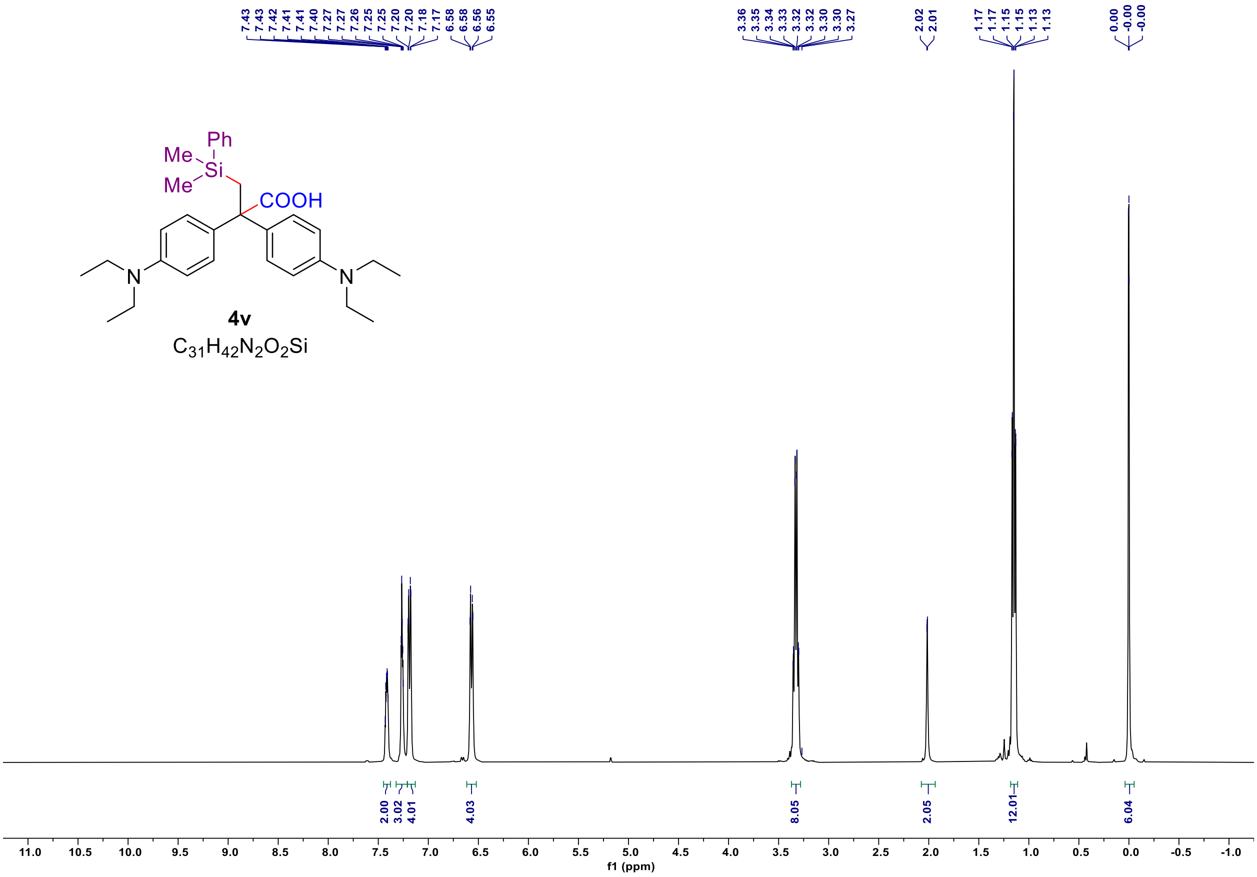
$^{13}C\{^{1}H\}$ **NMR** spectrum (100 MHz, $CDCl_3$) of compound **4t. gao-27-118ch**



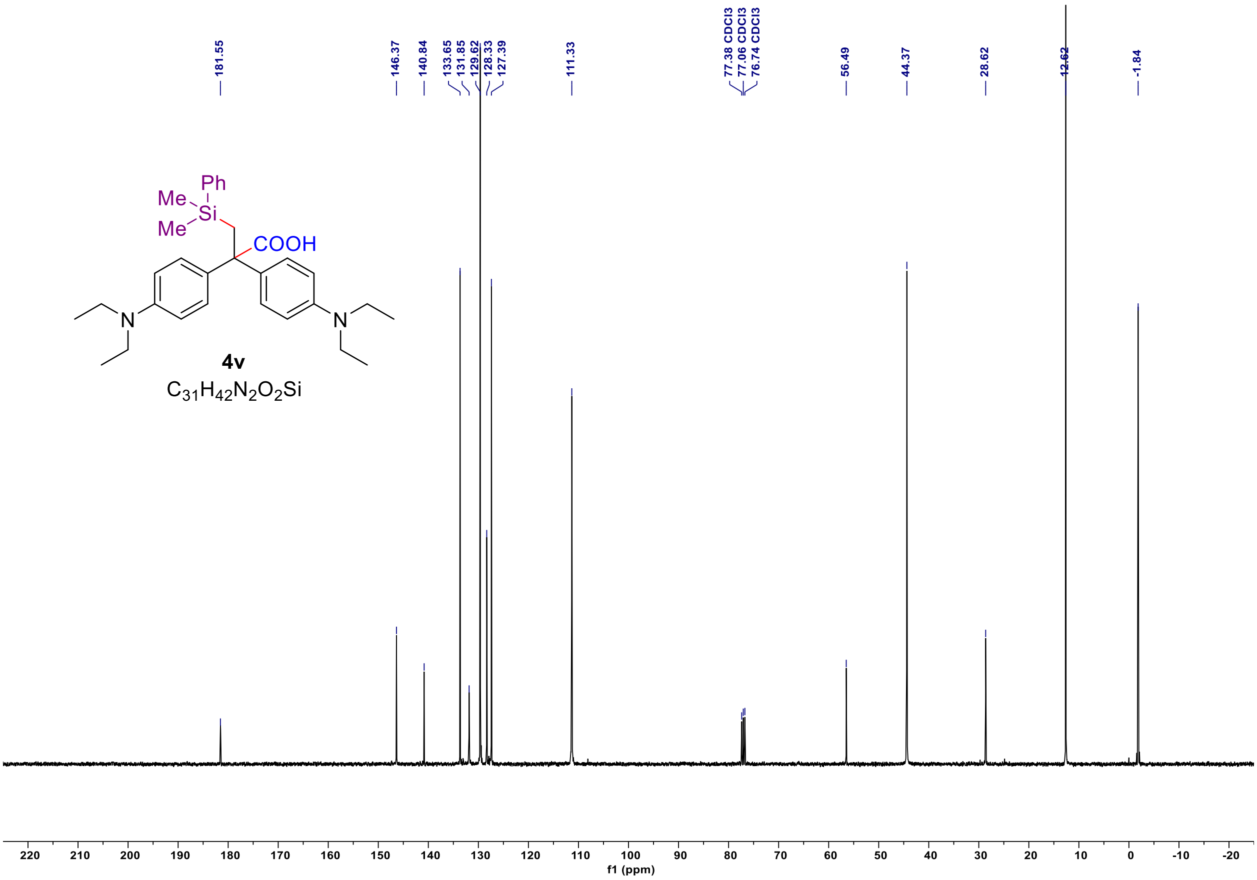
^{1}H **NMR** spectrum (400 MHz, $CDCl_3$) of compound **4u.**



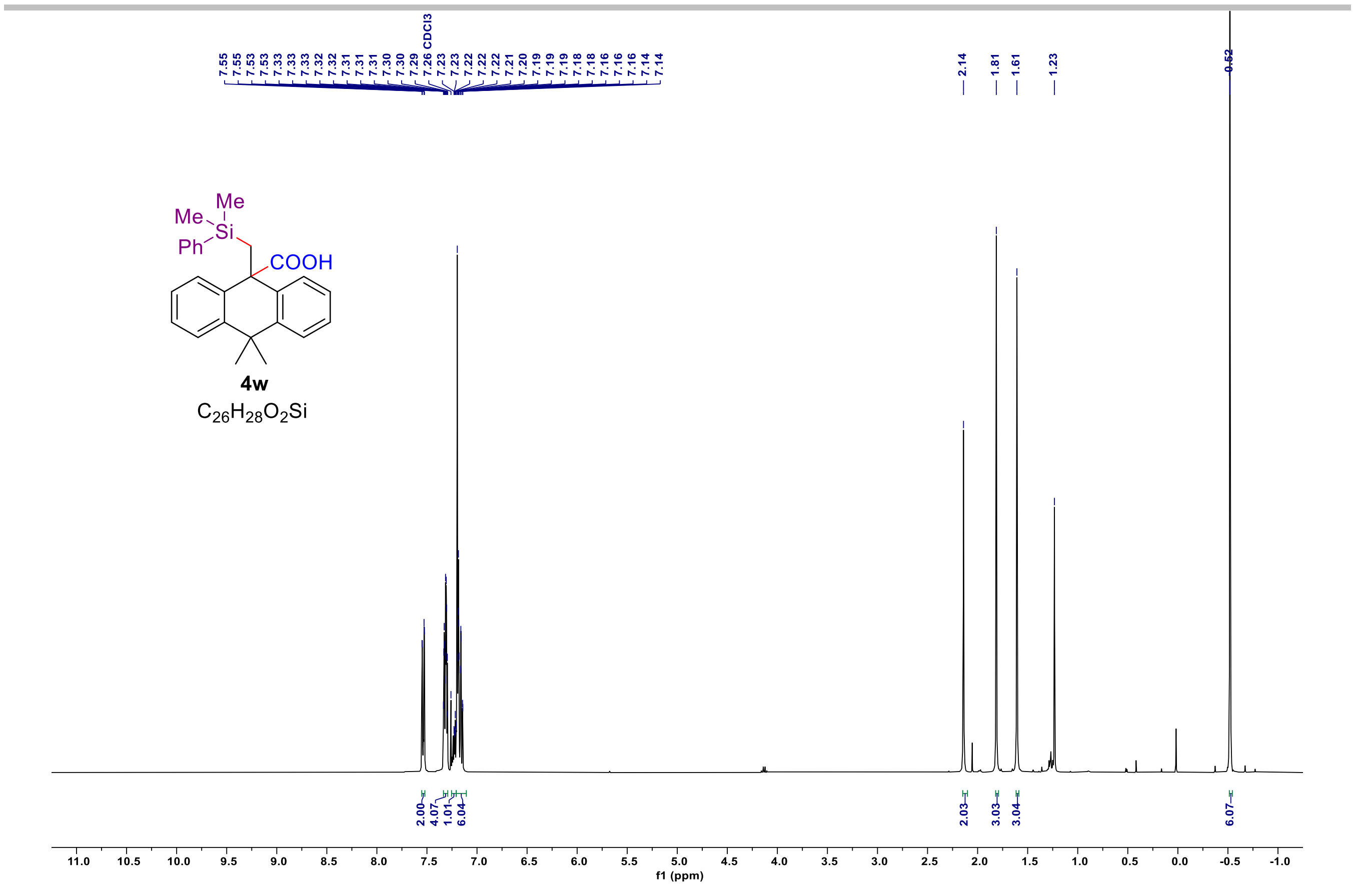
$^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4u.**



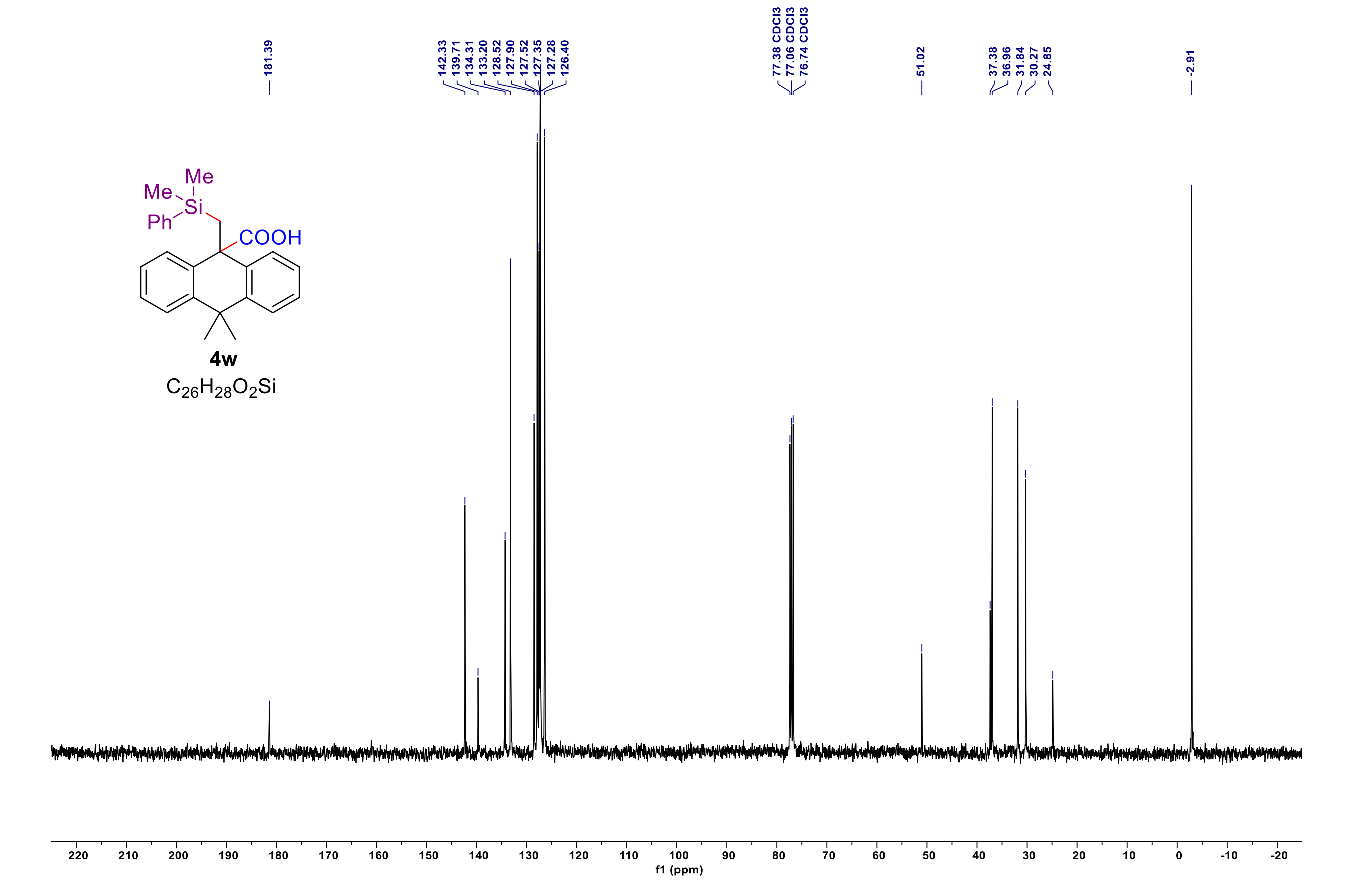
¹H NMR spectrum (400 MHz, $CDCl_3$) of compound **4v.**



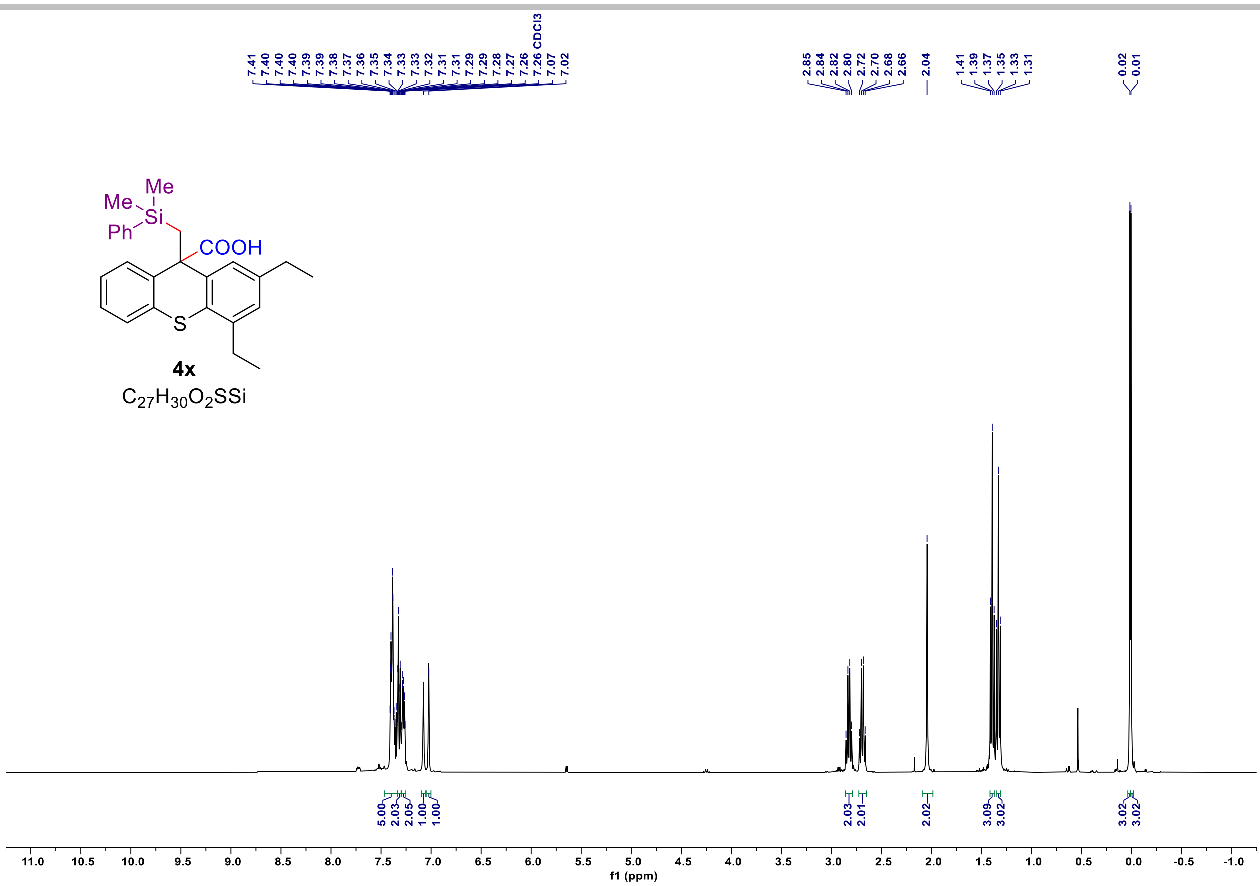
¹³C{¹H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4v.**



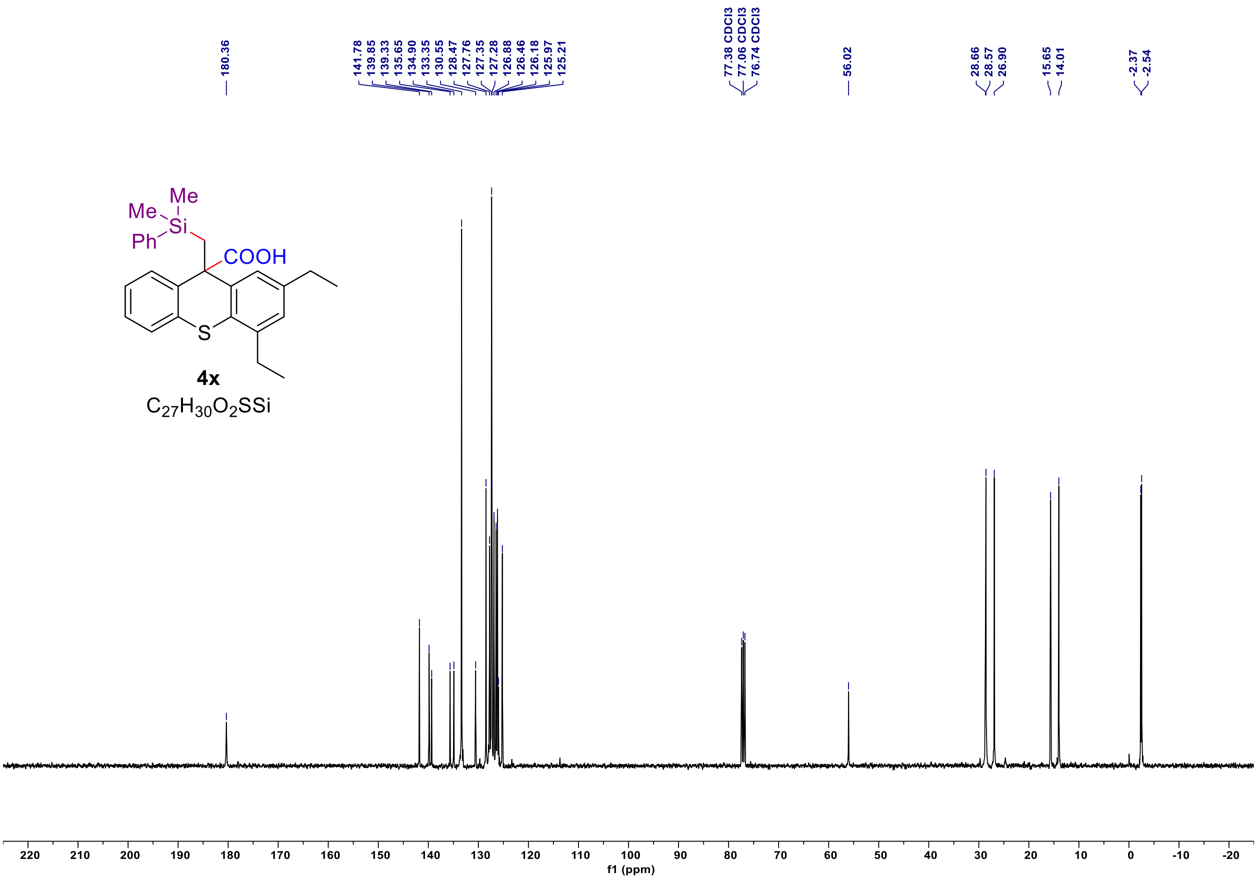
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4w.**



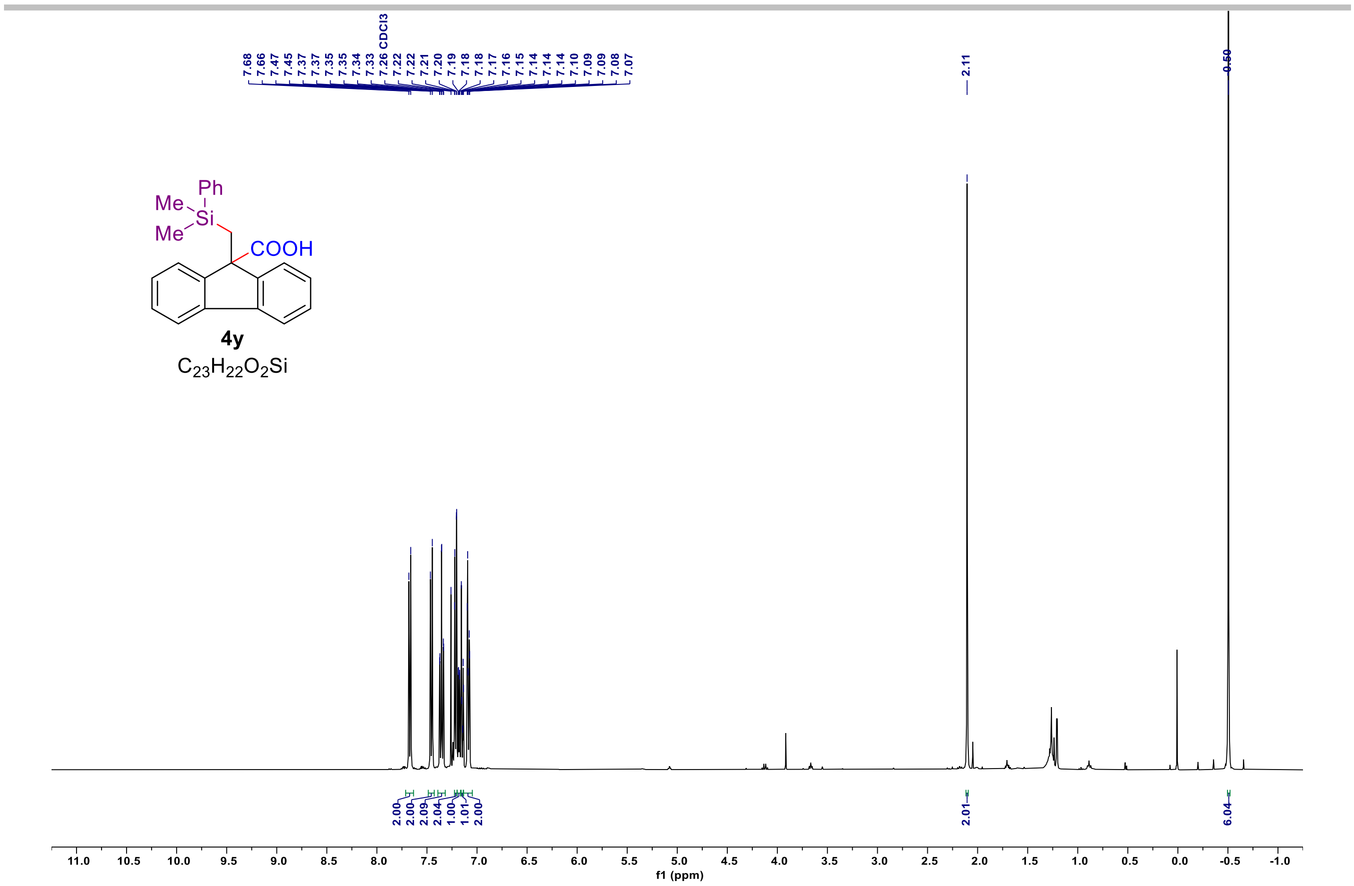
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4w. gao-27-5ch**



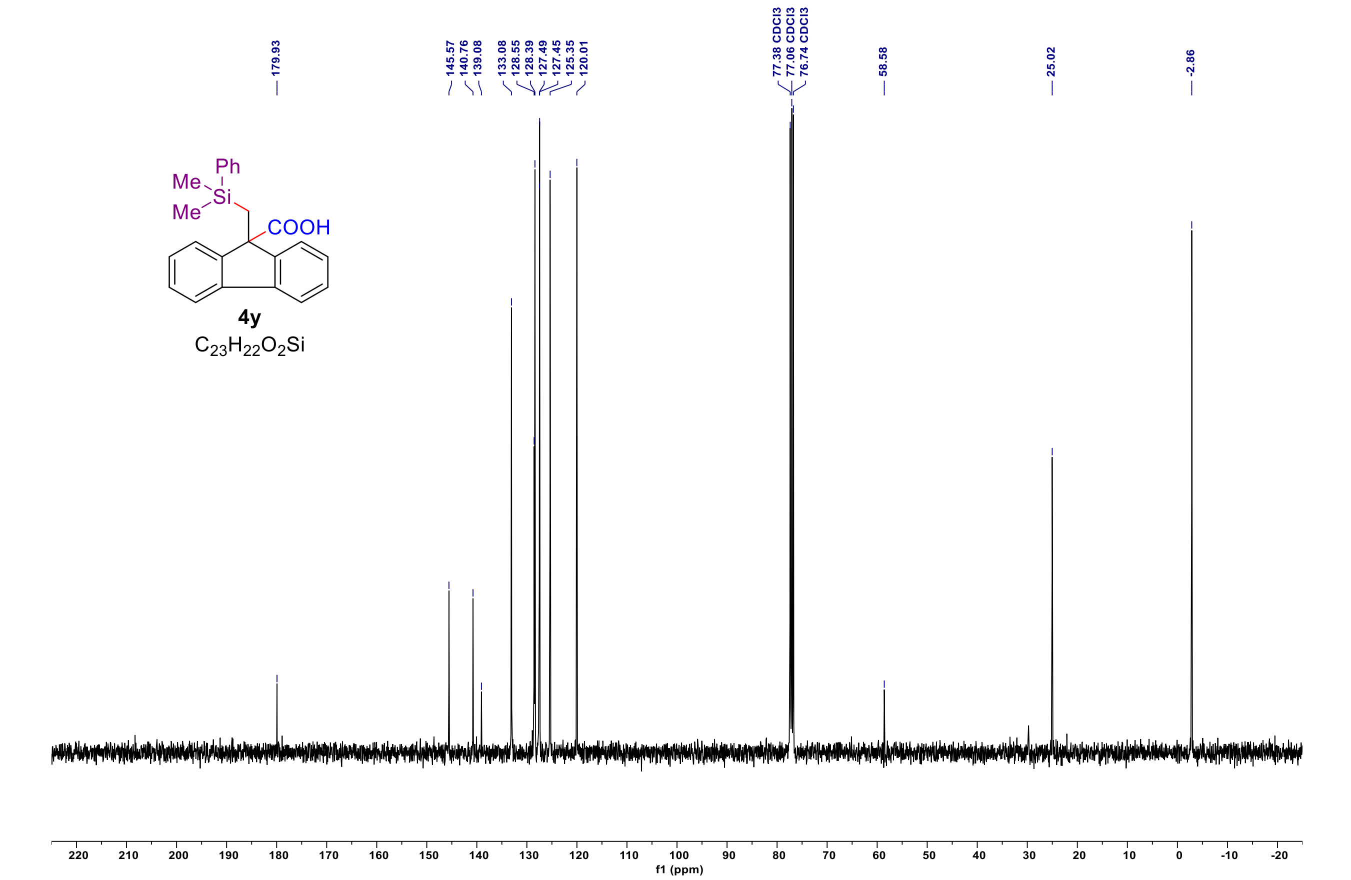
[1]**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4x.**



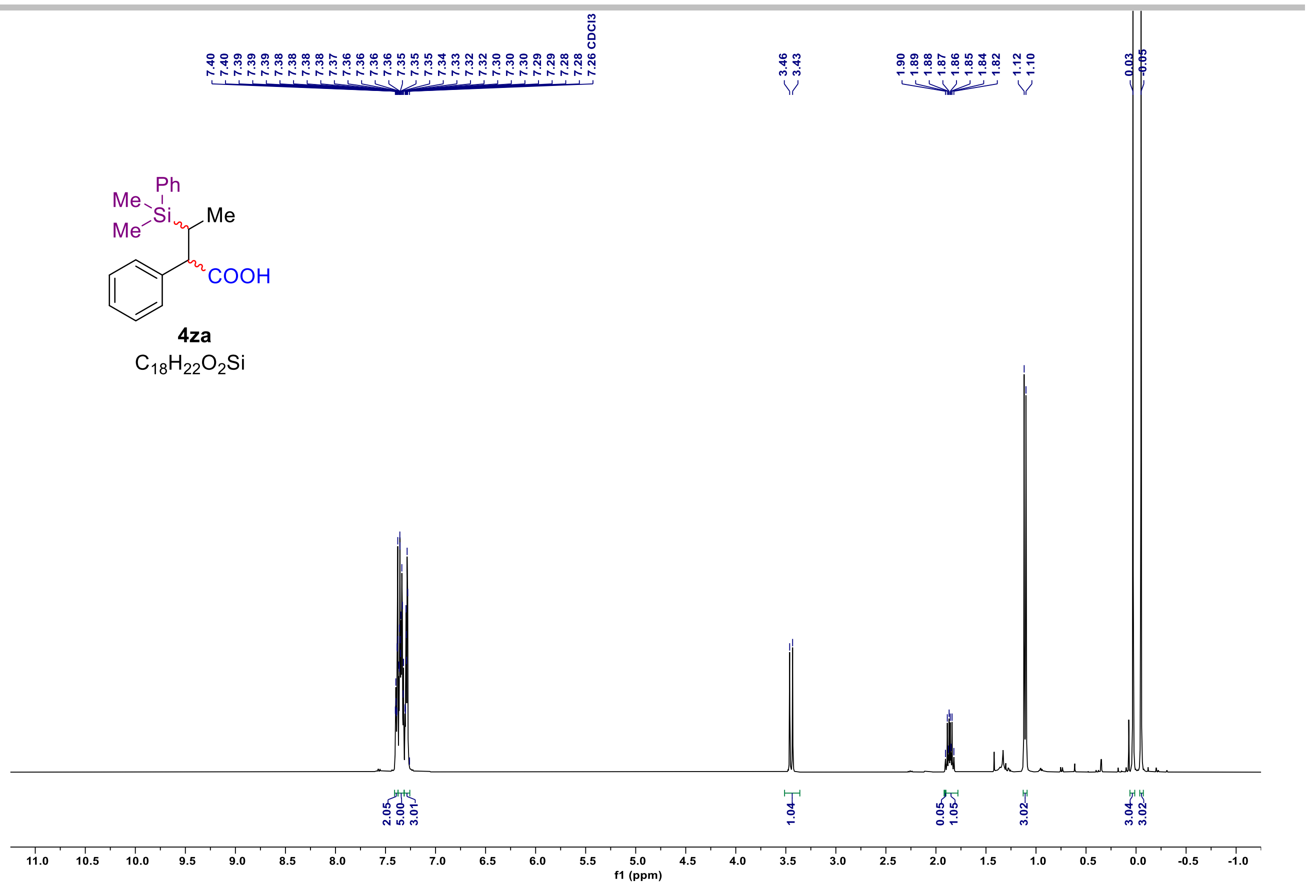
[13]**C{[1]H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4x. gao-27-4ch**



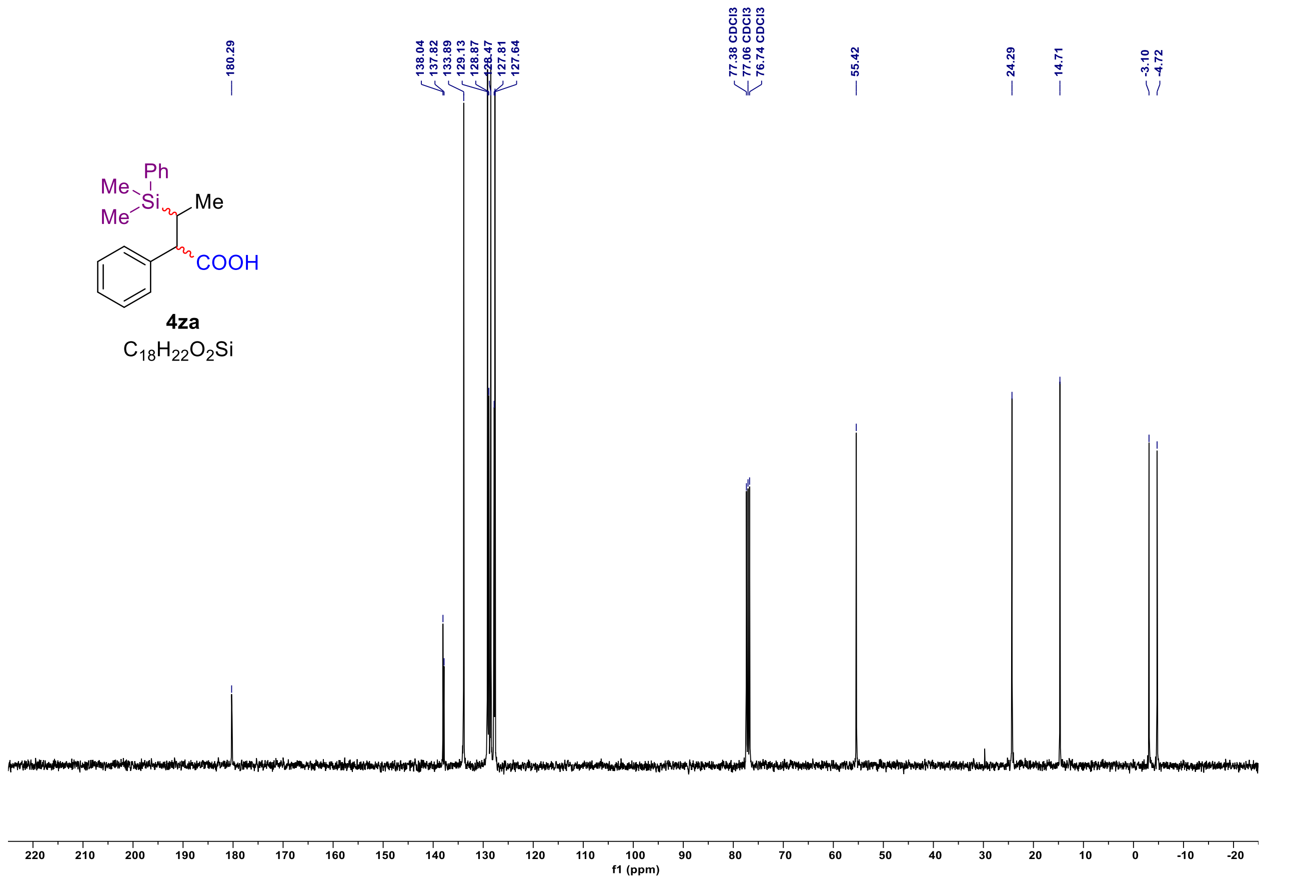
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4y.**



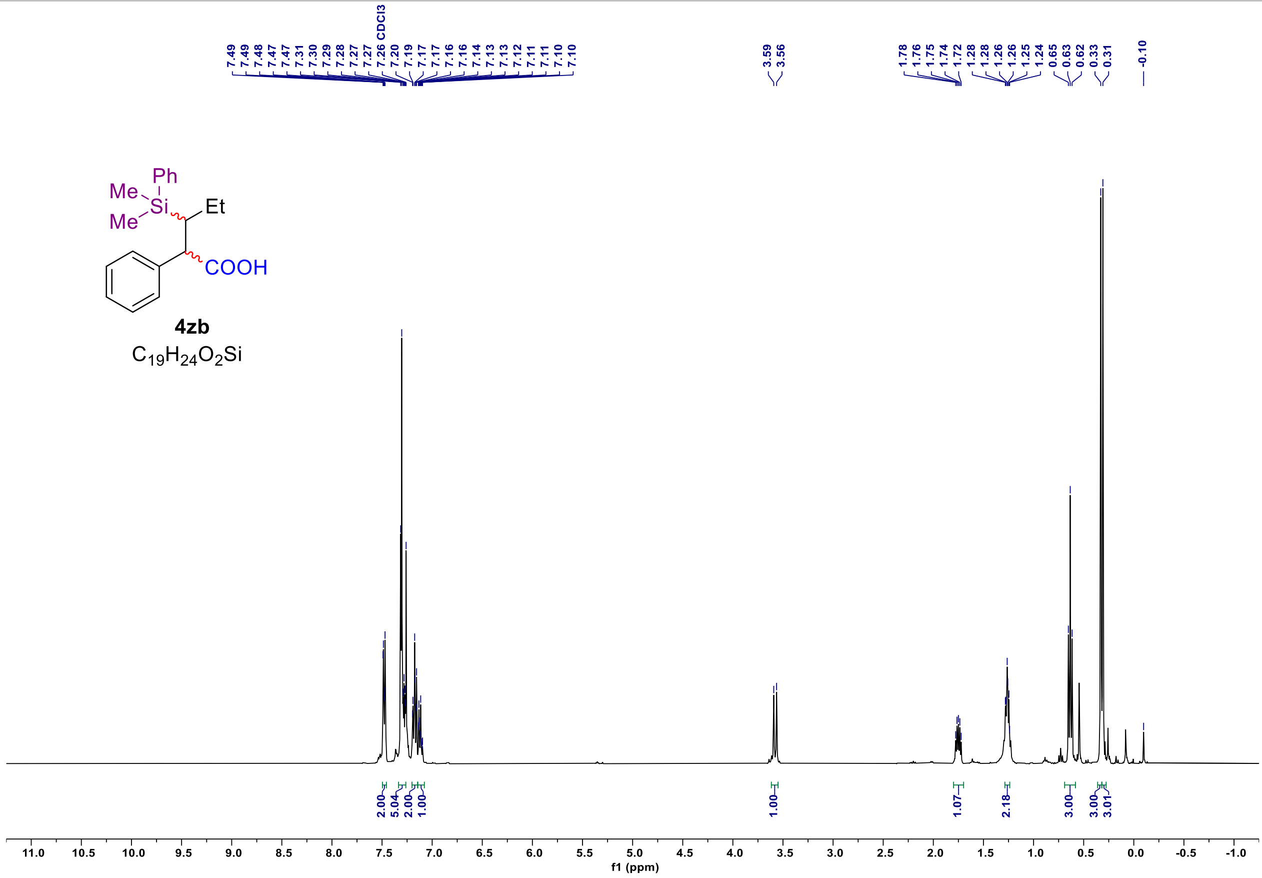
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4y. gao-27-7ch2.**



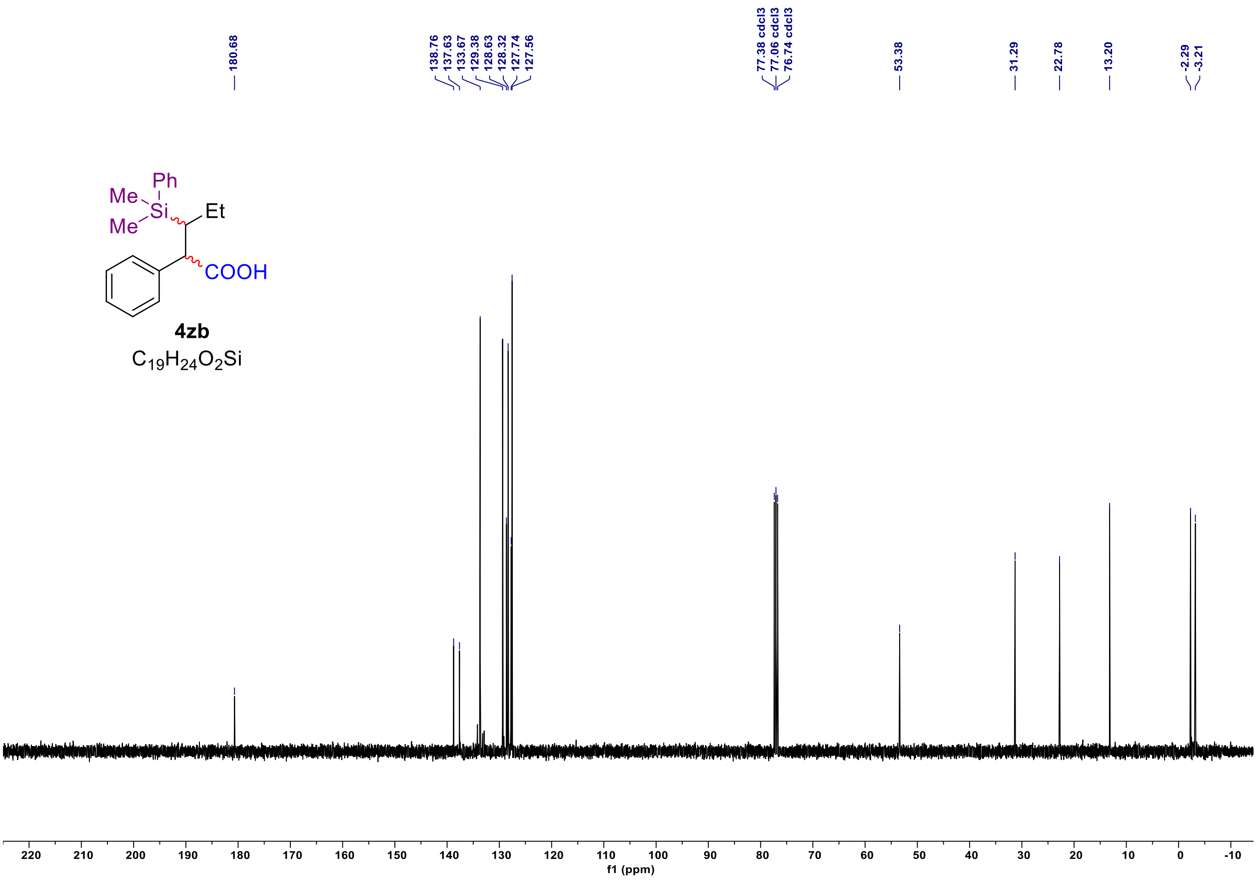
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4za.**



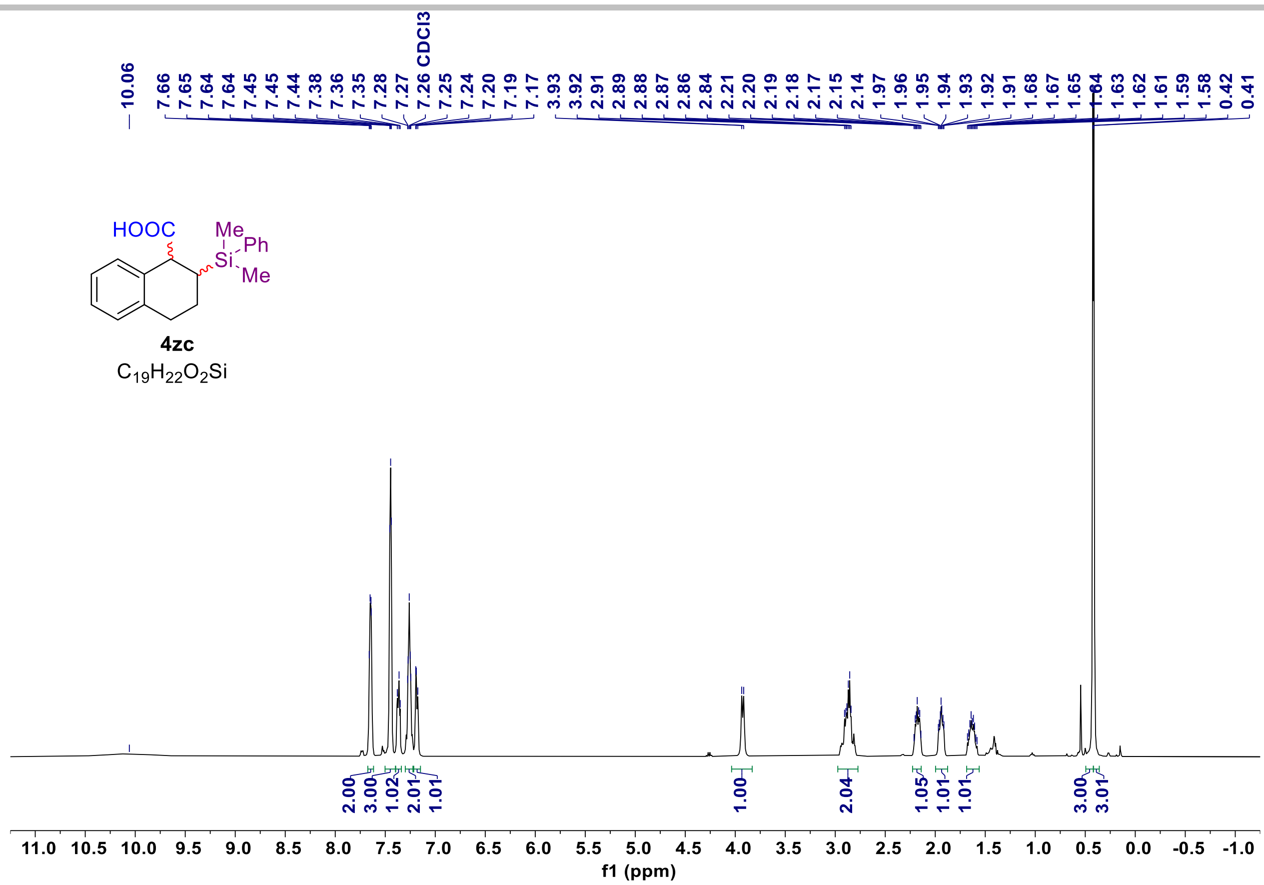
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4za. gao-27-8ch2.**



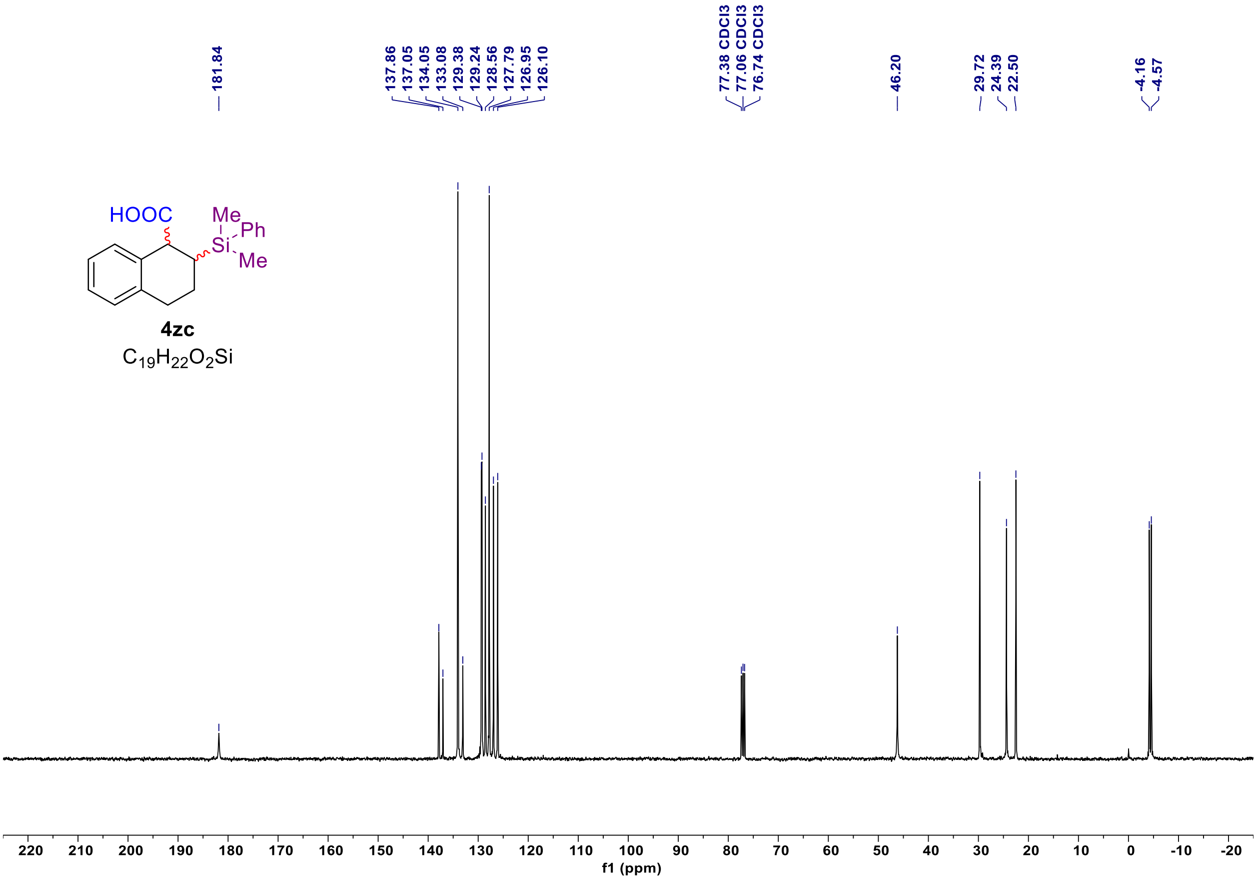
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4zb.**



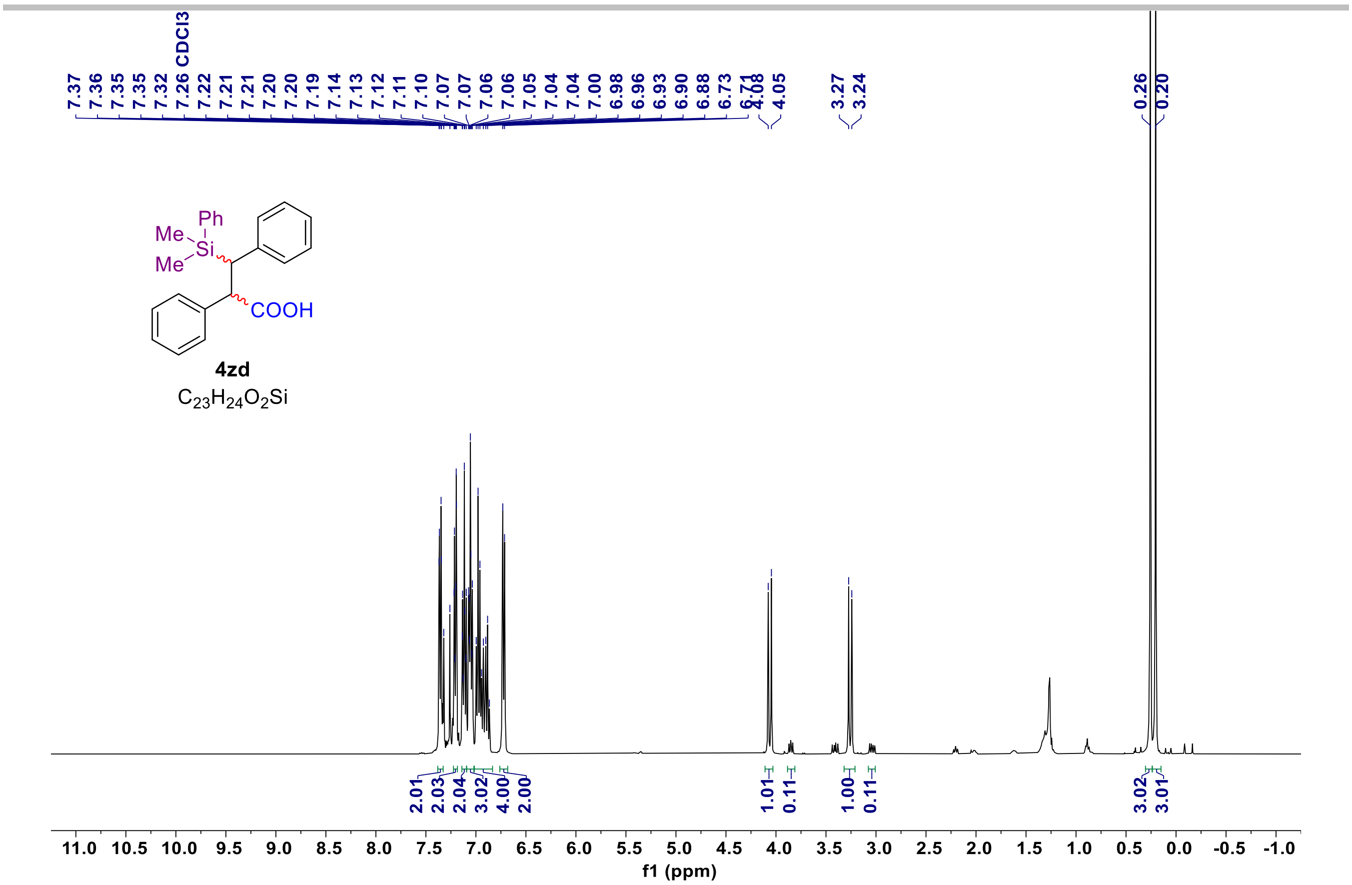
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4zb. gao-27-103ch2.**



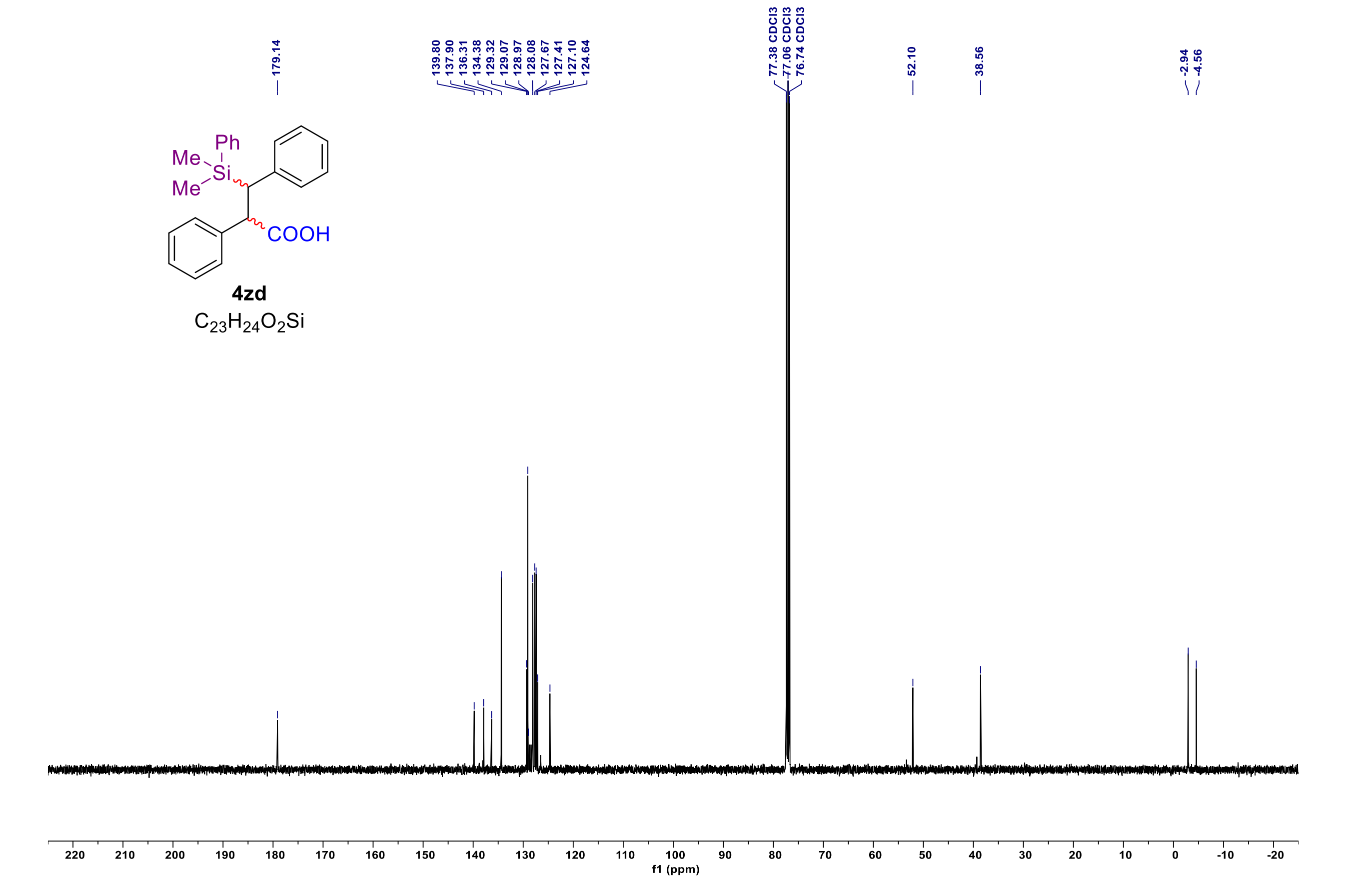
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4zc.**



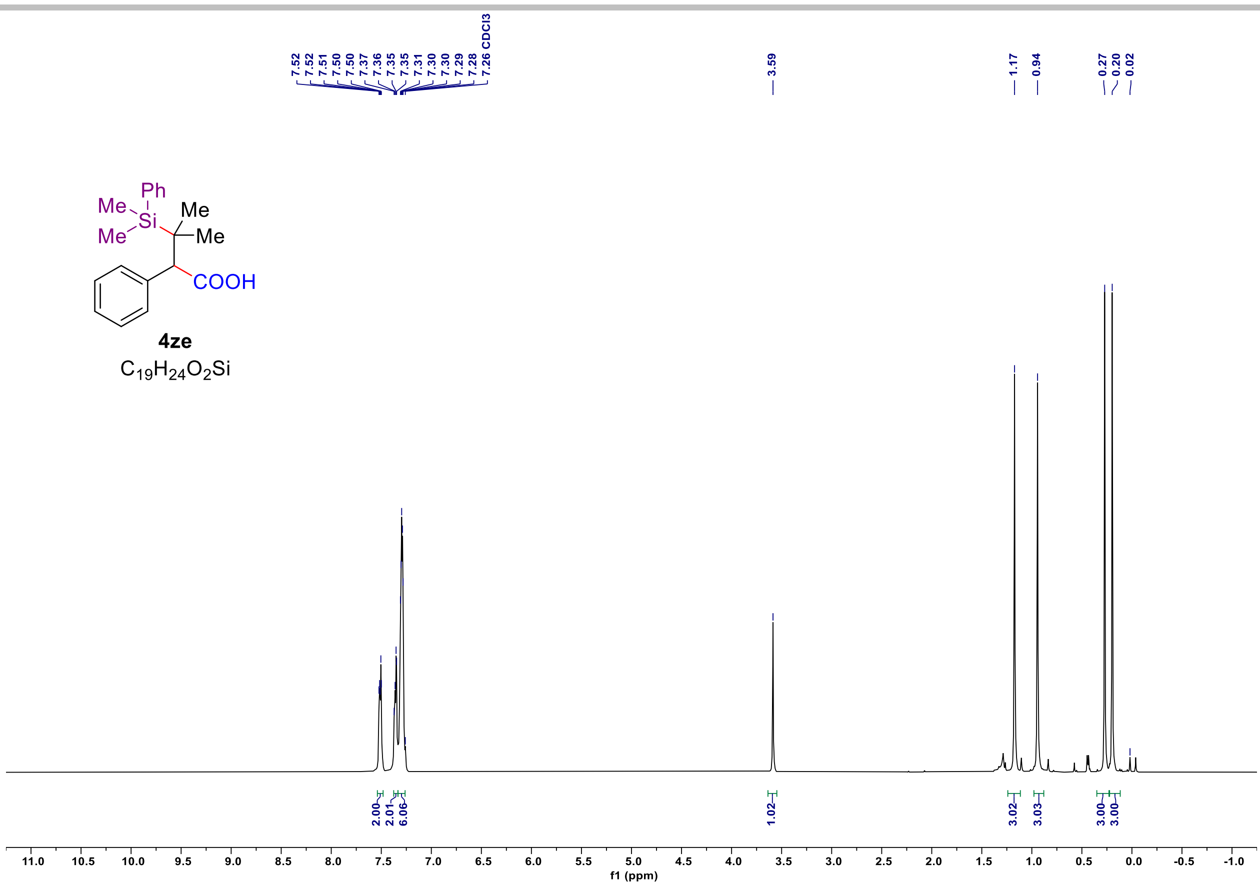
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4zc. gao-23-4ch.**



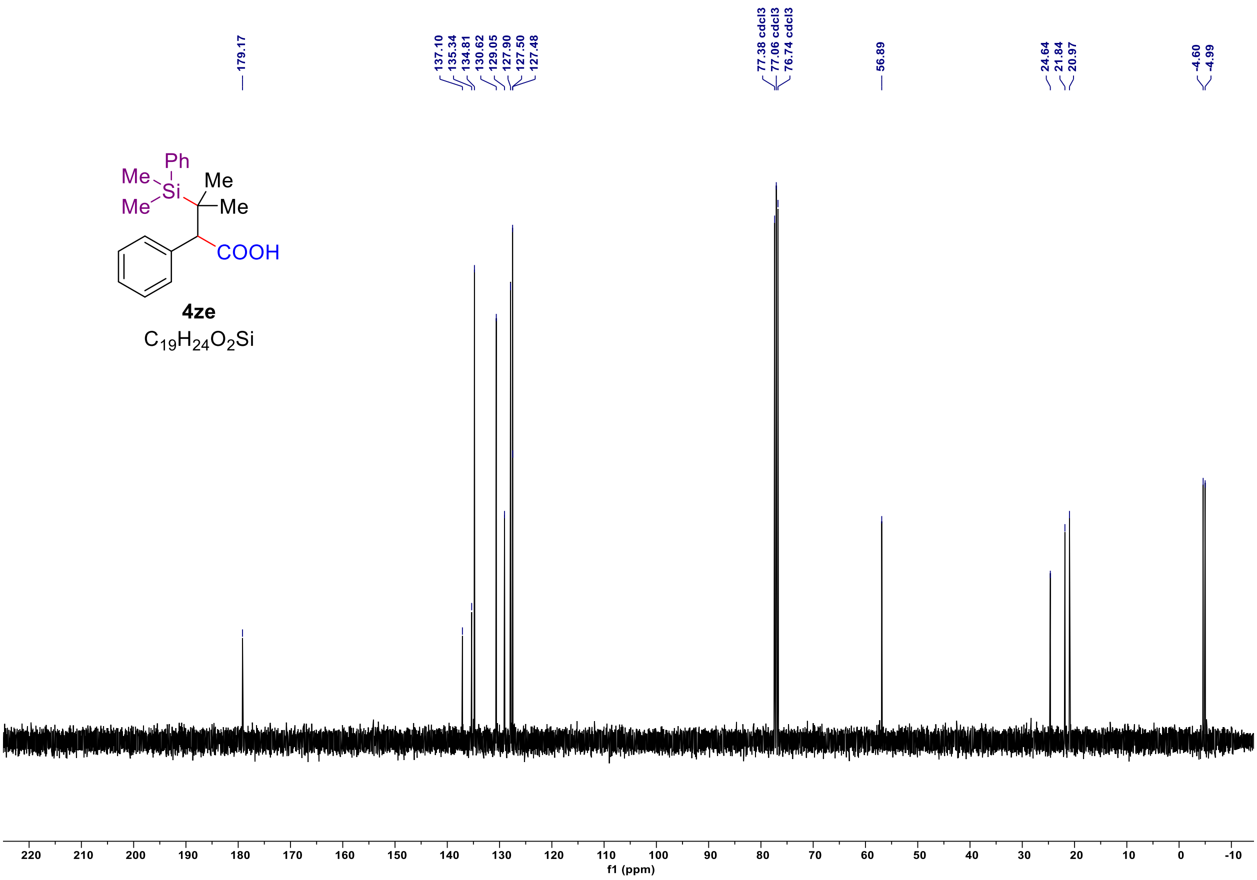
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4zd.**



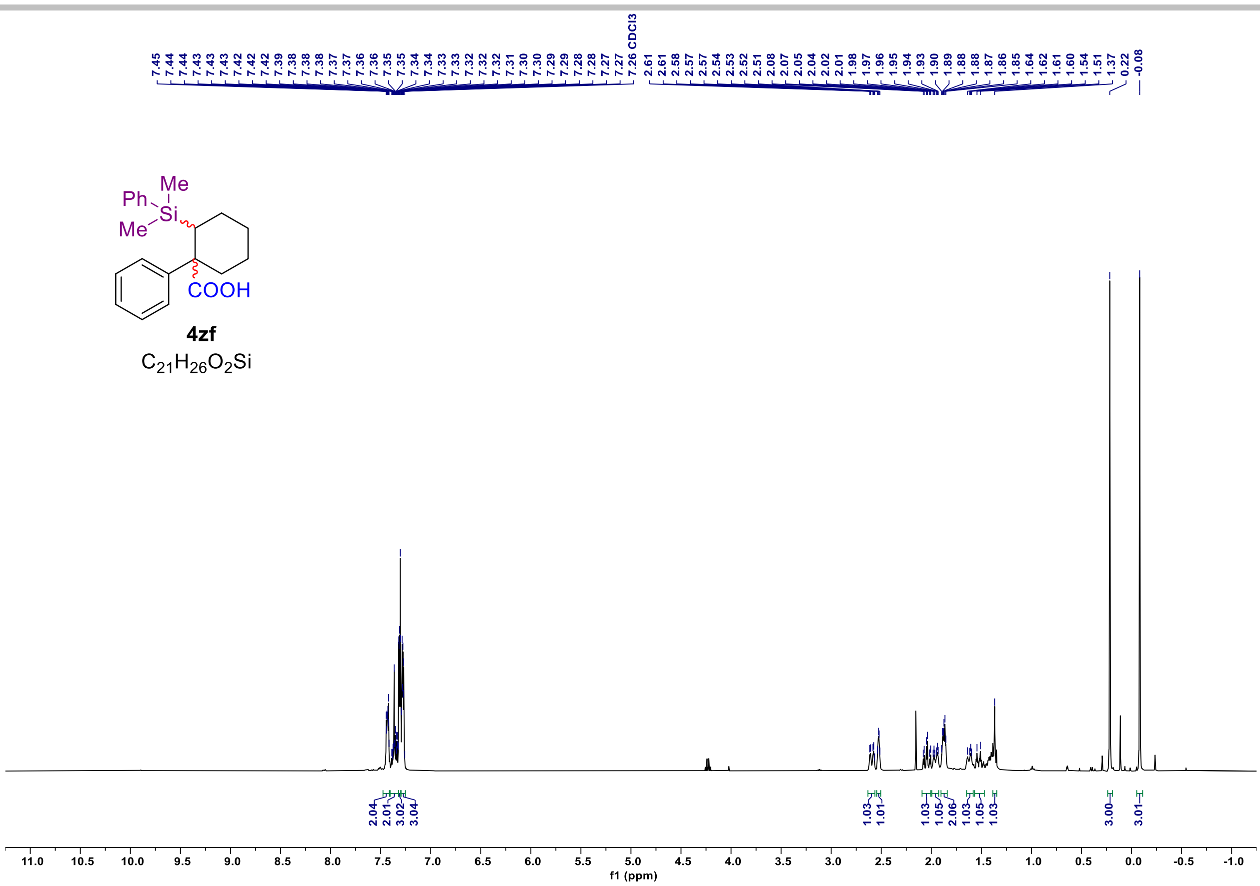
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4zd. gao-27-50chd**



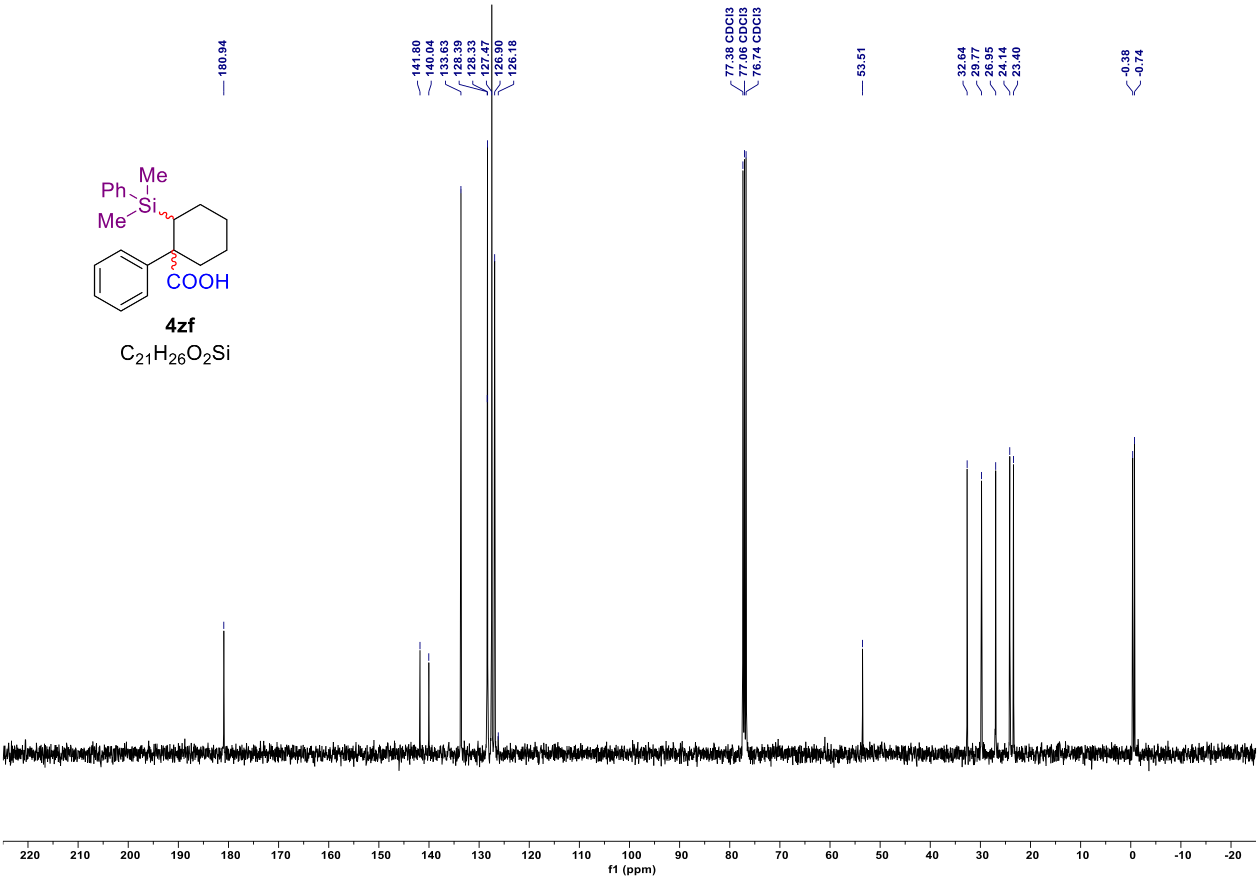
^{1}**H NMR** spectrum (400 MHz, CDCl₃) of compound **4ze.**



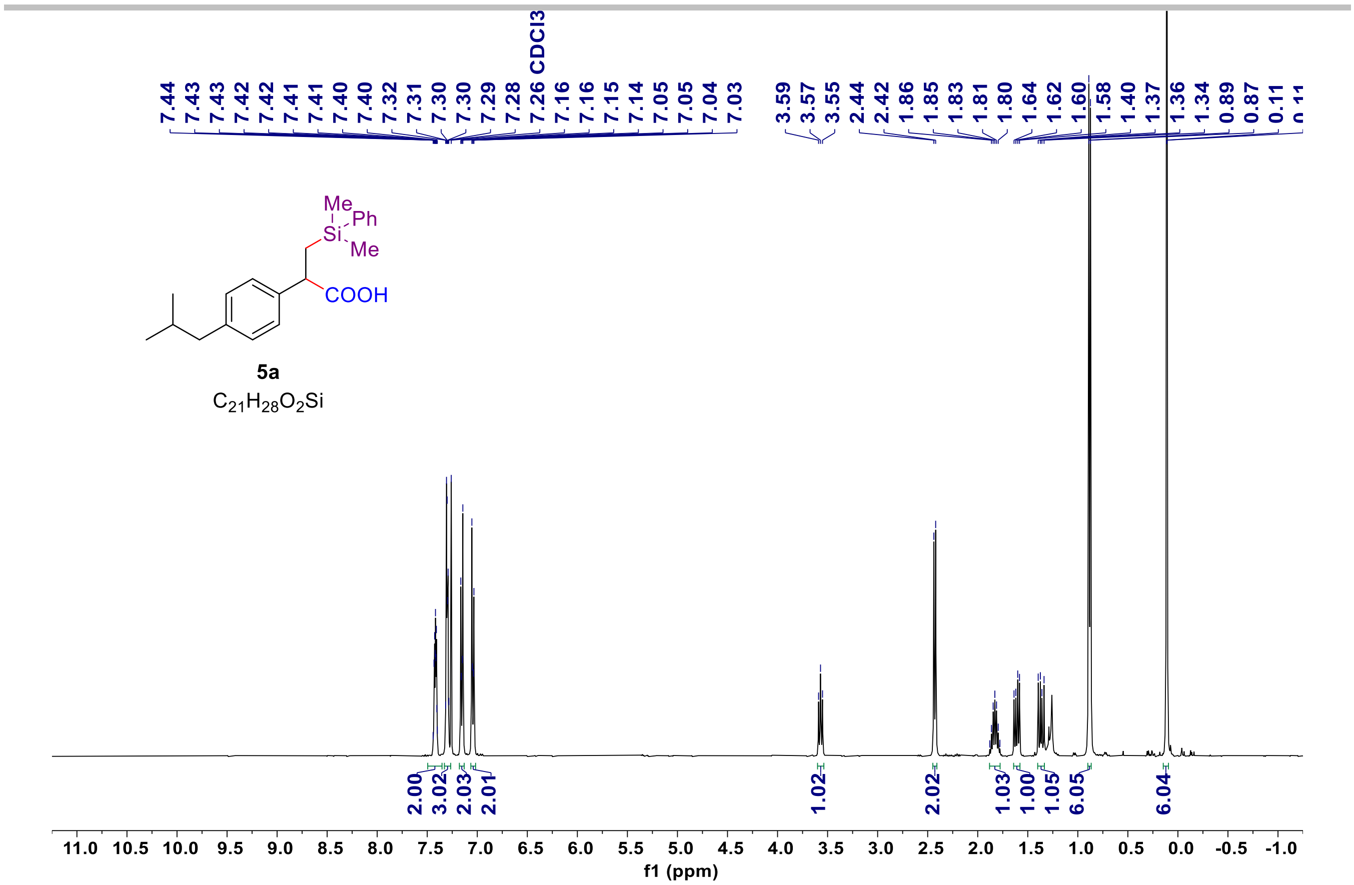
^{13}**C{^{1}H} NMR** spectrum (100 MHz, CDCl₃) of compound **4ze. gao-27-92chu.**



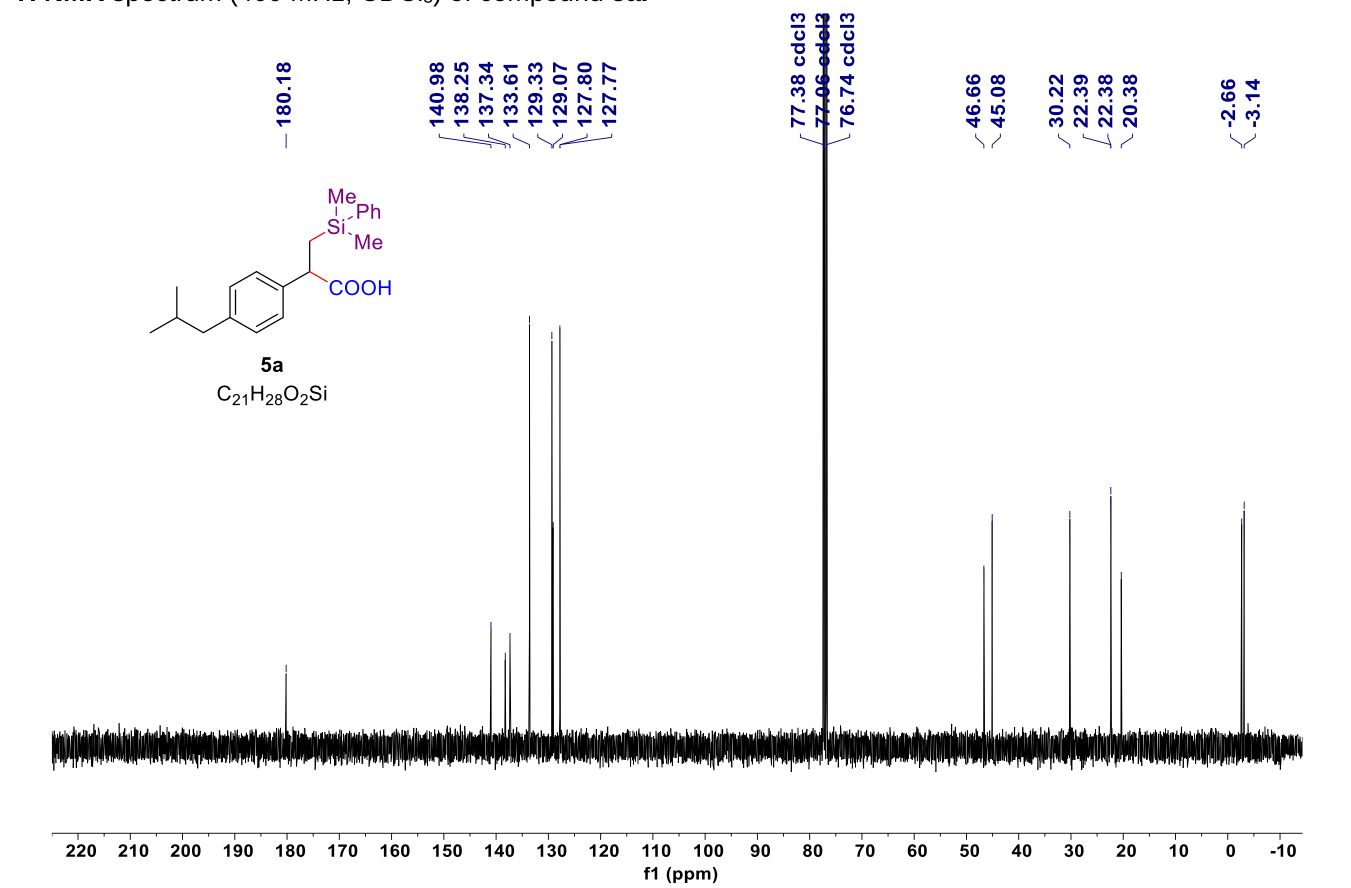
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **4zf.**



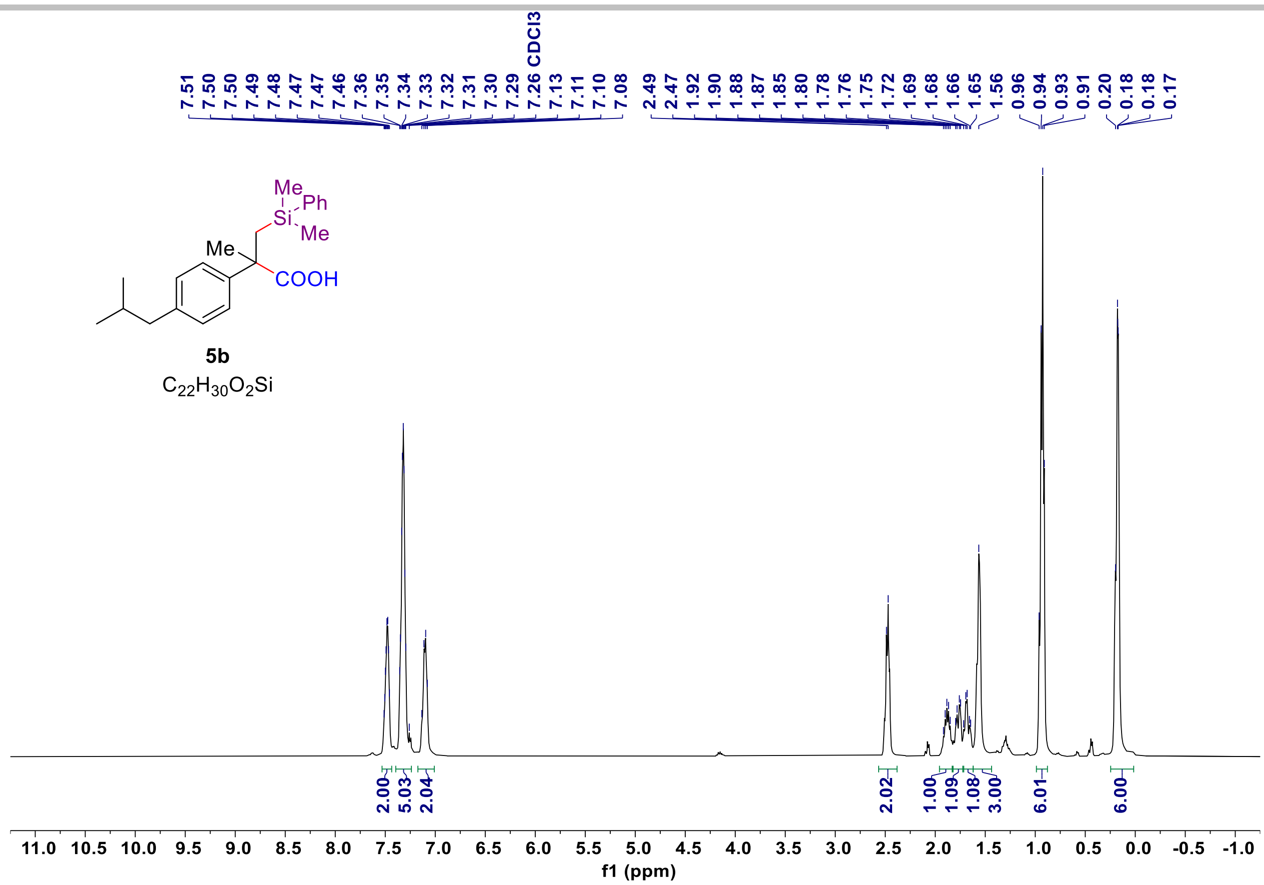
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **4zf. gao-27-16ch**



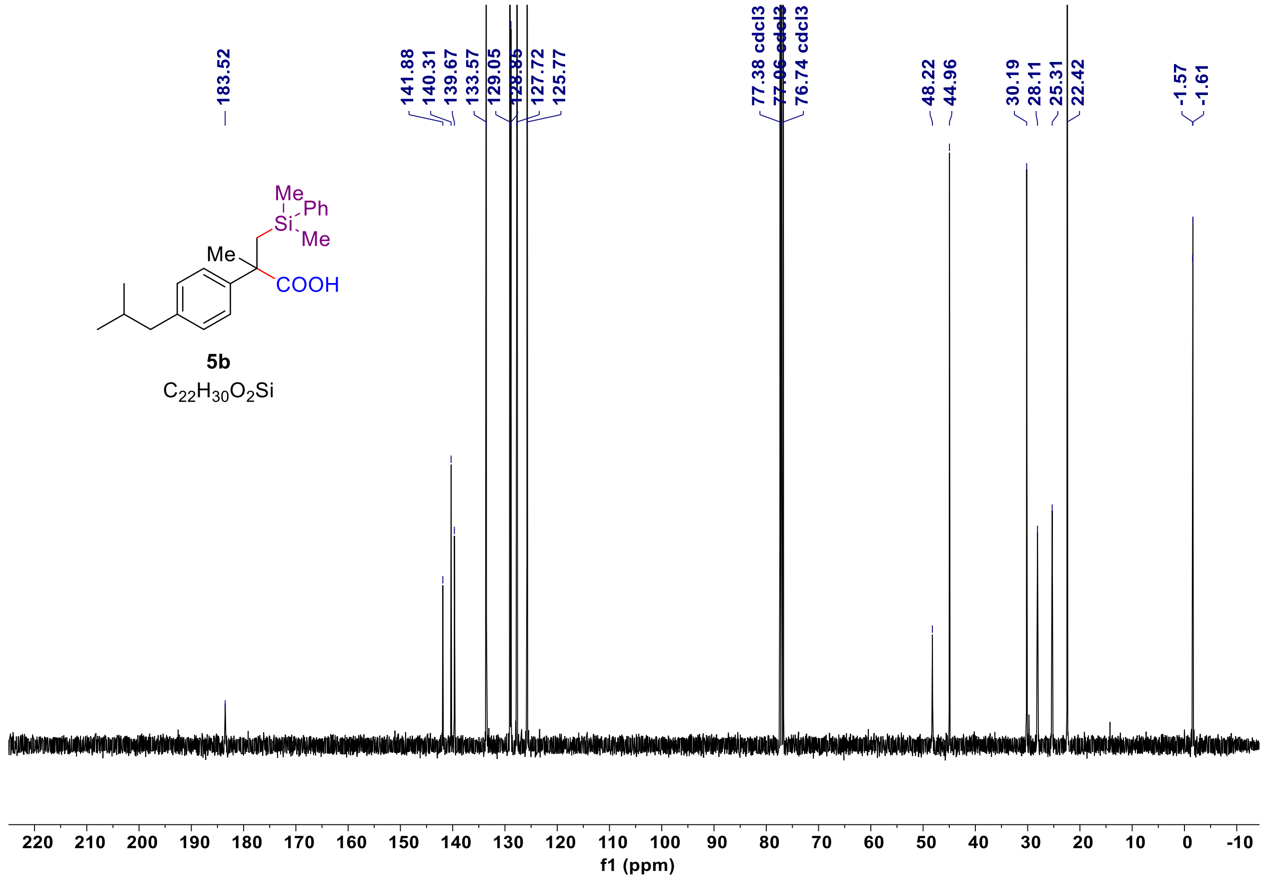
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **5a.**



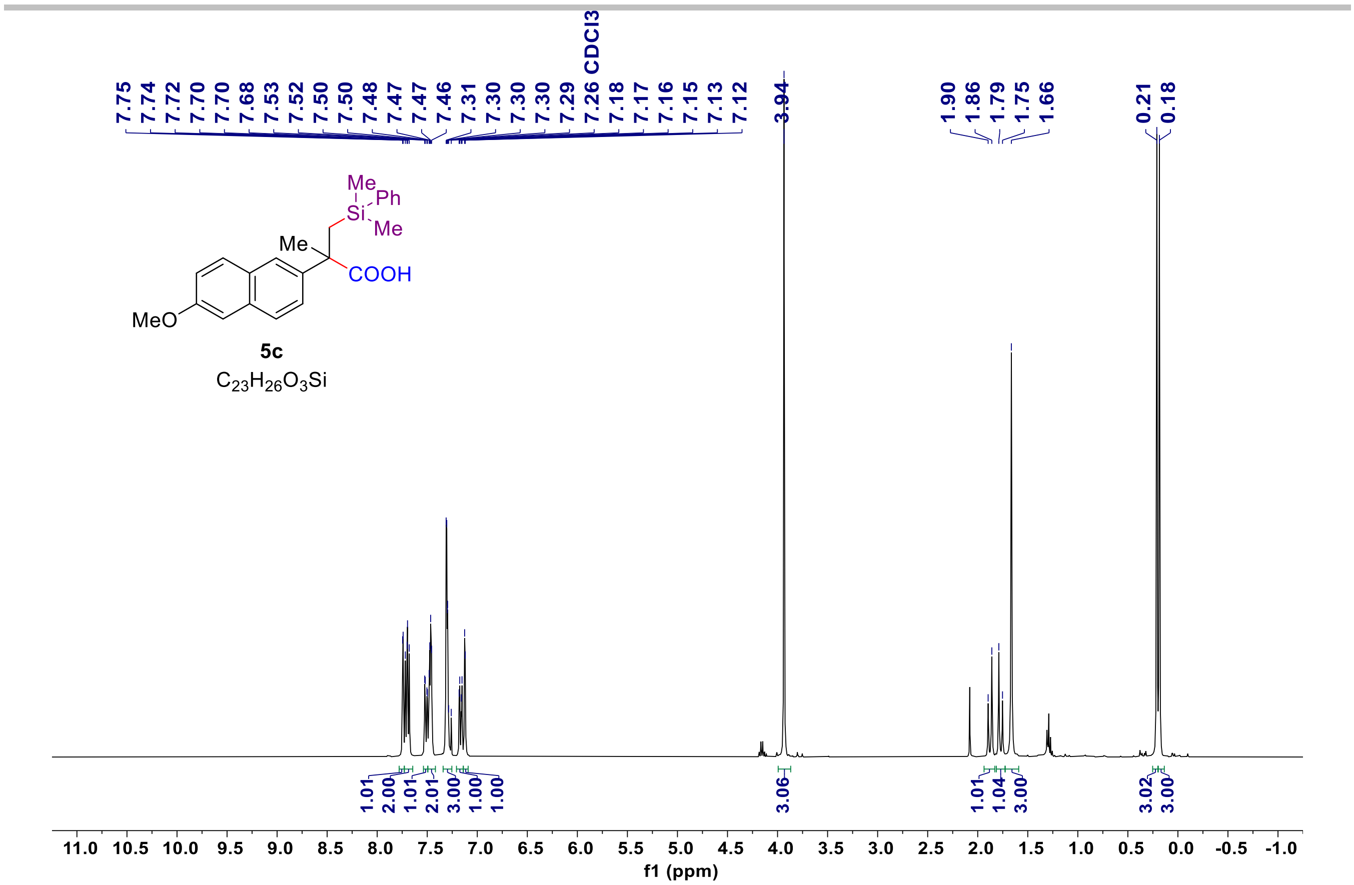
^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **5a. gao-9-2d-ch.**



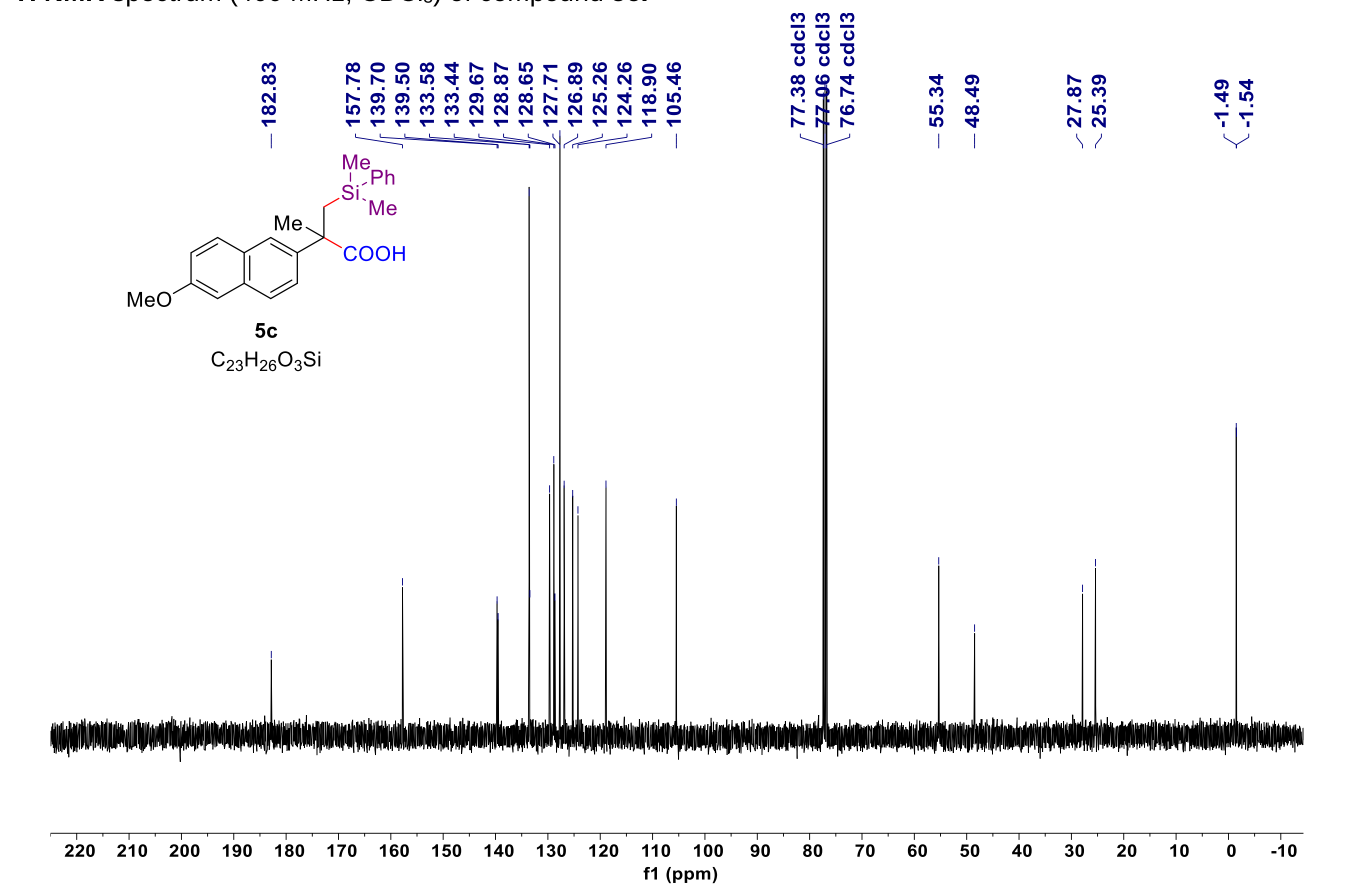
^{1}**H NMR** spectrum (400 MHz, CDCl$_3$) of compound **5b.**



^{13}**C{^{1}H} NMR** spectrum (100 MHz, CDCl$_3$) of compound **5b. gao-9-2B-ch.**



^{1}**H NMR** spectrum (400 MHz, $CDCl_3$) of compound **5c.**



^{13}**C{^{1}H} NMR** spectrum (100 MHz, $CDCl_3$) of compound **5c. gao-27-97ch.**

6. Energies and Cartesian Coordinates of the Optimized Structures

Geometry optimizations and characters of all the stationary points were calculated by using the M06-2X/6-31G(d,p) (using def2-TZVP for K atoms) method. Single point energies (Esol, a.u.) are computed by using the M06-2X/cc-pVTZ (using def2-QZVP for K atom) method in solvent (tetrahydrofuran). The solvent effect was treated with the PCM model.

I—PhMe$_2$SiBpin

M06-2X/6-31G(d,p) Electronic E: -1011.924854 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1011.623459 a.u.

M06-2X/cc-pVTZ Electronic E: -1012.217360 a.u.

B	-0.7127613735	0.0205657299	1.1472679182
O	-1.7942388726	0.4131044384	0.4018661771
O	-0.7130296168	-1.3330943579	1.3964332419
C	-2.6854042195	-0.7215100787	0.2961305100
C	-1.7209148070	-1.9233892658	0.5428299099
C	-3.3461035315	-0.7026258587	-1.0724986491
H	-3.9575932479	-1.5994487677	-1.2150135127
H	-3.9964081387	0.1718226697	-1.1519718721
H	-2.6041330306	-0.6500401235	-1.8703747643
C	-3.7320172549	-0.5640099302	1.3972025465
H	-4.2236278968	0.4041523271	1.2779403755
H	-4.4898298755	-1.3506004402	1.3451408132
H	-3.2635441838	-0.5918542299	2.3850623219
C	-2.3460452124	-3.1092928324	1.2584121631
H	-3.1714878934	-3.5202768332	0.6682748171
H	-1.5962207768	-3.8929668208	1.3907195729
H	-2.7221558210	-2.8267901503	2.2425791248
C	-1.0038835145	-2.3797796862	-0.7265773652
H	-0.2096743043	-3.0775687803	-0.4497086013
H	-1.6873646803	-2.8841971365	-1.4150897344
H	-0.5456170768	-1.5298694948	-1.2411348904
Si	0.8105165493	1.2189250402	1.7119435883
C	1.2849128408	0.8914439923	3.5094134632
H	1.5113587462	-0.1682586360	3.6574711799
H	2.1716993308	1.4694151272	3.7854480367
H	0.4742930351	1.1630738953	4.1920048243
C	0.4144153849	3.0447881716	1.4686868701
H	1.2521312682	3.6805591571	1.7717258182

H	0.1816642910	3.2595593326	0.4220546385
H	-0.4537038177	3.3312510922	2.0690536712
C	2.2531977901	0.7280623462	0.5946784538
C	3.1112660781	1.6730131114	0.0172093299
C	2.4931601370	-0.6286531280	0.3248676772
C	4.1761559260	1.2818975725	-0.7917099420
H	2.9463026067	2.7329964197	0.1968937239
C	3.5569852248	-1.0261078853	-0.4803477689
H	1.8308956271	-1.3824049504	0.7477701778
C	4.4010943786	-0.0694454481	-1.0400755239
H	4.8290190988	2.0307686701	-1.2297591658
H	3.7262659820	-2.0807310755	-0.6758519613
H	5.2296848509	-0.3763461834	-1.6708191935

^{t}BuOK

M06-2X/6-31G(d,p) Electronic E: -832.902319 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -832.810525 a.u.

M06-2X/cc-pVTZ Electronic E: -833.034178 a.u.

C	0.1163704779	0.9514402943	3.1178919267
O	0.1464595237	0.0955884766	2.0458121775
C	-0.6461270245	2.2402065154	2.7547489902
H	-1.6684266072	1.9856823403	2.4553151772
H	-0.6941268259	2.9543814798	3.5856020993
H	-0.1542106019	2.7268323326	1.9057316880
C	-0.5881142234	0.2842474907	4.3151796338
H	-0.6337527408	0.9328746015	5.1982616475
H	-1.6099920730	0.0123896598	4.0297949113
H	-0.0547550934	-0.6336142888	4.5849742643
C	1.5492294432	1.3305884105	3.5399617317
H	2.1021911243	0.4225053255	3.8032935842
H	2.0613073430	1.8088616619	2.6981334740
H	1.5742480810	2.0143671646	4.3969648030
K	0.2285891971	-1.3078604645	0.3202428913

Int2—^{t}BuOK-B-Si

M06-2X/6-31G(d,p) Electronic E: -1844.900554 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1844.478668 a.u.

M06-2X/cc-pVTZ Electronic E: -1845.302959 a.u.

B	-0.6575945042	0.0817110023	-0.3697472715
O	-2.0475565980	0.4692290337	0.0909770929
O	-0.5986155078	-1.3518285310	-0.1670482270

C	-2.7213200321	-0.7025601880	0.5413986142
C	-1.9256996051	-1.8537813765	-0.1577022577
C	-4.1904537689	-0.6180549175	0.1405340602
H	-4.7189316142	-1.5461156764	0.3833150241
H	-4.6770076823	0.1962023849	0.6880811122
H	-4.2965311195	-0.4316671503	-0.9310194213
C	-2.6092128232	-0.7770096274	2.0642128421
H	-2.9752671107	0.1603499674	2.4942950374
H	-3.2003948114	-1.6013048341	2.4749069526
H	-1.5664101624	-0.9075698469	2.3604033744
C	-1.9403928262	-3.1752448048	0.6018640369
H	-2.9636646303	-3.5419257193	0.7389263717
H	-1.3822093228	-3.9244640581	0.0339507377
H	-1.4664143458	-3.0697981338	1.5789998208
C	-2.4033025852	-2.0922360686	-1.5964204183
H	-1.6914706346	-2.7591832918	-2.0917460161
H	-3.3907126163	-2.5649975651	-1.6237065121
H	-2.4324502224	-1.1528101942	-2.1530947461
Si	0.6979437793	1.1169059345	0.8219925030
C	0.3929641331	0.9242883938	2.6878848058
H	0.5448977271	-0.1124975639	3.0041224400
H	1.0928322812	1.5488027482	3.2525816955
H	-0.6266391811	1.2124965851	2.9613732941
C	0.5479500516	3.0189815999	0.5561611950
H	1.2896207145	3.5643264099	1.1487128804
H	0.6830450268	3.3289505552	-0.4886126636
H	-0.4309976236	3.3652919367	0.9191753571
C	2.5339100093	0.6789547818	0.6095216356
C	3.5440765061	1.6147828464	0.3523621551
C	2.9162554481	-0.6667766756	0.7426561780
C	4.8794933359	1.2314282753	0.2334479314
H	3.2883602677	2.6664848120	0.2372677631
C	4.2472105610	-1.0580437955	0.6295816862
H	2.1500756828	-1.4215292465	0.9173292293
C	5.2337375628	-0.1069302166	0.3746566731
H	5.6429439506	1.9771047923	0.0314195294
H	4.5165153339	-2.1048308009	0.7346854056
H	6.2725560512	-0.4090625128	0.2832168476
C	0.3609676002	0.3245725469	-2.7664947629
O	-0.6644503563	0.5350478197	-1.8080840952
K	-2.0020882165	2.5717944701	-1.2328790640

C	-0.3497447346	0.2278337016	-4.1192621673
H	0.3656873970	0.1003926574	-4.9372571551
H	-1.0380254554	-0.6218419195	-4.1178566188
H	-0.9285543175	1.1398596054	-4.3119091612
C	1.3128626076	1.5267007175	-2.7776880934
H	0.7502026620	2.4555156758	-2.9476864476
H	1.8533828640	1.6089590324	-1.8309934367
H	2.0525492981	1.4359573844	-3.5792552669
C	1.1523499634	-0.9600054196	-2.5172694196
H	0.4821953977	-1.8206382540	-2.4822776890
H	1.8827120652	-1.1012910527	-3.3205985934
H	1.6888231301	-0.9148982297	-1.5672137774

TS2-3—^{t}BuOK-B-Si-iso1-Scan-ts

M06-2X/6-31G(d,p) Electronic E: -1844.888550 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1844.467677 a.u.

M06-2X/cc-pVTZ Electronic E: -1845.283773 a.u.

B	-1.8182779437	0.1740027818	-1.0366071488
O	-2.4470526715	1.3852716001	-1.3856863209
O	-2.6011413480	-0.5838346794	-0.1859660134
C	-3.5863439412	1.5339853436	-0.5169708682
C	-3.8925836716	0.0462049589	-0.1218170042
C	-4.7009764200	2.2152923911	-1.2981021034
H	-5.6230805696	2.2375541094	-0.7086305653
H	-4.4160181613	3.2485498396	-1.5155936233
H	-4.8978135172	1.7049697652	-2.2423416207
C	-3.1869159553	2.3943280816	0.6780903998
H	-2.7766696618	3.3404052229	0.3106955058
H	-4.0534380968	2.6149946731	1.3085965646
H	-2.4144252245	1.9055542483	1.2730344783
C	-4.4567285924	-0.1293953204	1.2788564583
H	-5.4056563029	0.4067590010	1.3827655294
H	-4.6401353938	-1.1903058322	1.4661705254
H	-3.7568863860	0.2351337410	2.0317263377
C	-4.7818513717	-0.6606414727	-1.1455727109
H	-4.8083977620	-1.7273660018	-0.9087798553
H	-5.8055998412	-0.2762590602	-1.1291177906
H	-4.3769011650	-0.5445347040	-2.1557014289
Si	0.3585071887	1.2498949325	0.8544279787
C	1.4841573827	-0.0088171641	1.7941098907
H	2.1836696517	-0.5240774616	1.1265199731

H	2.0814141338	0.4917365349	2.5642408649
H	0.8842268010	-0.7838057990	2.2828764700
C	0.0048026120	2.5511990993	2.2393364678
H	0.9249720650	2.9342661698	2.6960355563
H	-0.5782435375	3.4075752364	1.8812438092
H	-0.5870145189	2.0853394179	3.0365006941
C	1.6391282531	2.1853319317	-0.2428708853
C	1.5673166946	3.5811112348	-0.4520360969
C	2.4669412169	1.4765032040	-1.1437510243
C	2.2041572592	4.2112441176	-1.5231624054
H	0.9762123988	4.1856693376	0.2338163847
C	3.1112235830	2.0923886166	-2.2153465157
H	2.5820548362	0.4004015438	-1.0148576178
C	2.9630979003	3.4672308876	-2.4308921545
H	2.1183934659	5.2879874704	-1.6470297638
H	3.7340552595	1.5044050958	-2.8849060054
H	3.4632256958	3.9530573702	-3.2624716608
C	-0.4752896941	-1.6682650810	-2.0459242471
O	-0.9066859829	-0.2980357074	-1.9658927053
K	-0.1589380707	2.1621604162	-2.4787610729
C	0.6070759010	-1.6738985050	-3.1208810193
H	1.0144882768	-2.6794732664	-3.2545608774
H	0.1952117427	-1.3380830247	-4.0781663246
H	1.4245803723	-1.0047812557	-2.8318550941
C	0.0957903797	-2.1344142676	-0.7105107683
H	0.9522858118	-1.5192485211	-0.4269943121
H	-0.6538543117	-2.0568046167	0.0807901983
H	0.4195727225	-3.1766488809	-0.7931550118
C	-1.6580122573	-2.5369913737	-2.4722006431
H	-2.0917807622	-2.1531744692	-3.4007861654
H	-1.3284788905	-3.5662274269	-2.6420372994
H	-2.4255065820	-2.5378974832	-1.6956153624

Int3—^{t}BuOK-B-Si-iso-modSiB-int1

M06-2X/6-31G(d,p) Electronic E: -1844.893370 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1844.475995 a.u.

M06-2X/cc-pVTZ Electronic E: -1845.289937 a.u.

B	-1.8794677410	-0.1877349522	-1.1299788970
O	-2.0992887144	1.1550436559	-1.4020769483
O	-2.8096968117	-0.7273700695	-0.2853918750
C	-3.0761566208	1.6043371049	-0.4284889796

C	-3.8367346596	0.2747264325	-0.1016429055
C	-3.9372430927	2.6859604550	-1.0574645140
H	-4.7493183054	2.9657096066	-0.3792979233
H	-3.3304615297	3.5760543930	-1.2429463133
H	-4.3662075088	2.3560025904	-2.0048888973
C	-2.2996553572	2.1508255804	0.7653136406
H	-1.6479698315	2.9614090277	0.4234006362
H	-2.9720117014	2.5497586362	1.5299555044
H	-1.6562394372	1.3838446144	1.2086475166
C	-4.3587595854	0.1815412026	1.3216503368
H	-5.0681781698	0.9905387906	1.5218267514
H	-4.8770947536	-0.7704810625	1.4590547132
H	-3.5434712539	0.2376609999	2.0438698023
C	-4.9429911402	-0.0367666453	-1.1064227782
H	-5.2850304918	-1.0617048435	-0.9454496569
H	-5.7943608272	0.6381824574	-0.9856674685
H	-4.5730911294	0.0457280262	-2.1327276362
Si	1.5968292193	1.3924429786	1.1645697901
C	3.2625888399	0.7308575173	1.8808661136
H	3.8615670879	0.2159780249	1.1219536479
H	3.8776651603	1.5246851676	2.3200487411
H	3.0570813335	-0.0057009481	2.6652503853
C	0.9256216926	2.4389299664	2.6447288654
H	1.6632338743	3.1616276222	3.0131620459
H	0.0105241928	2.9890578186	2.3966979474
H	0.6708425545	1.7714921061	3.4756353562
C	2.1948372521	2.7672487025	-0.0529744138
C	1.4185609883	3.9216452632	-0.3004379815
C	3.2136714281	2.5074134097	-0.9978305620
C	1.5822880996	4.7052691202	-1.4433457415
H	0.6456348155	4.1982229387	0.4156560137
C	3.3924090501	3.2840450968	-2.1417387402
H	3.8649148813	1.6475910409	-0.8435858702
C	2.5558740293	4.3770728762	-2.3905927769
H	0.9551236786	5.5803258434	-1.5951372067
H	4.1876663874	3.0423605005	-2.8425766708
H	2.6880475453	4.9832395065	-3.2809230091
C	-0.4088270757	-2.1597302634	-1.4494117646
O	-0.8259125700	-0.7971754642	-1.7271890833
K	0.5085017121	1.5316291925	-1.9936611447
C	0.9512868623	-2.2858293009	-2.1248123555

H	1.3379149696	-3.3023524700	-2.0175371629
H	0.8714191265	-2.0568027519	-3.1923039958
H	1.6633972249	-1.5979801707	-1.6553718009
C	-0.2743412844	-2.3707602694	0.0556978176
H	0.3489824525	-1.5784033651	0.4843304266
H	-1.2509401917	-2.3556576349	0.5435628088
H	0.1949162468	-3.3405438154	0.2452296162
C	-1.4320058529	-3.1043991710	-2.0702520869
H	-1.5130399365	-2.9273834603	-3.1467106818
H	-1.1310629771	-4.1432238404	-1.9096173710
H	-2.4117471547	-2.9528847676	-1.6091872637

Int4′—^{t}BuOBpin

M06-2X/6-31G(d,p) Electronic E: -644.138280 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -643.867313 a.u.

M06-2X/cc-pVTZ Electronic E: -644.375645 a.u.

B	0.0160731023	3.1641124245	-1.3051748019
O	0.6093882360	2.7976106775	-2.5011278281
O	-1.2812244529	2.7161284532	-1.1985621167
C	-0.2695757976	1.8327970677	-3.1120380713
C	-1.6536358185	2.2174612222	-2.4940746655
C	0.2059089083	0.4502160548	-2.6693842274
H	-0.3749113872	-0.3457269072	-3.1432662775
H	1.2552106897	0.3318940647	-2.9509360896
H	0.1261153577	0.3431257962	-1.5834494124
C	-0.1823161088	1.9688675173	-4.6229456908
H	0.8155015688	1.6776793019	-4.9605971484
H	-0.9129294554	1.3147348096	-5.1091995018
H	-0.3635920585	2.9972053144	-4.9388021079
C	-2.3293894028	3.3638992289	-3.2446209242
H	-2.7079842250	3.0407979998	-4.2182695891
H	-3.1667279428	3.7284362906	-2.6453825745
H	-1.6305912439	4.1917731662	-3.3969379608
C	-2.6170571319	1.0547093717	-2.3197114644
H	-3.5535545468	1.4183466865	-1.8899489285
H	-2.8396025552	0.5908432275	-3.2859858137
H	-2.2059836794	0.2984210466	-1.6495031679
C	1.9726164266	4.2881464980	-0.3203551015
O	0.5948096738	3.8781082022	-0.3163039102
C	2.2277597135	5.2244733403	-1.5001375735
H	1.5372747300	6.0716556909	-1.4572374696

H	3.2505003310	5.6102046080	-1.4603772759
H	2.0878688416	4.6997127421	-2.4475741969
C	2.1621874756	5.0266613132	1.0001227851
H	1.4841946636	5.8823857858	1.0515567325
H	1.9403832726	4.3603621406	1.8376486400
H	3.1908775105	5.3844298144	1.0956471130
C	2.8763136857	3.0575021243	-0.3804637435
H	2.6409792754	2.3830823752	0.4480123125
H	2.7387592429	2.5242377738	-1.3236771352
H	3.9253131011	3.3554007765	-0.2962088143

Int4—$K^+[^tBu_2Obpin]^-$

M06-2X/6-31G(d,p) Electronic E: -1477.104563 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1476.715338 a.u.

M06-2X/cc-pVTZ Electronic E: -1477.454668 a.u.

B	-0.1538988672	3.6811063256	-1.5510228844
O	0.5232486550	3.0977289699	-2.7070499439
O	-1.2833404841	2.7048970931	-1.2795135703
C	-0.1358278976	1.9263290673	-3.1359407362
C	-1.5639474630	2.0667193444	-2.5148572645
C	0.6023354815	0.6991168728	-2.5848890640
H	0.1620070090	-0.2413984897	-2.9310587224
H	1.6435697252	0.7326633700	-2.9160866491
H	0.6027966932	0.7084013522	-1.4883395345
C	-0.1230362848	1.8724512333	-4.6606729151
H	0.9062180182	1.7585726285	-5.0120892463
H	-0.7097202150	1.0262886642	-5.0360118574
H	-0.5215408851	2.7974446474	-5.0794594557
C	-2.4714961567	2.9689082226	-3.3575470147
H	-2.7882484367	2.4724286278	-4.2800916494
H	-3.3641209965	3.2102795730	-2.7705805590
H	-1.9575738031	3.9015796443	-3.5986844753
C	-2.2755593623	0.7460450308	-2.2410272950
H	-3.2670827416	0.9427409873	-1.8204136280
H	-2.4089032732	0.1691012832	-3.1619652695
H	-1.7135301184	0.1272569277	-1.5338981542
C	2.0530311953	3.9322028482	-0.2809210262
O	0.6554219461	3.6696969511	-0.2891432312
C	2.4565881594	5.0111333606	-1.2902622442
H	1.9649959314	5.9587362690	-1.0675662350
H	3.5405755299	5.1610584842	-1.2492779739

H	2.1765030794	4.7071175818	-2.3004275978
C	2.3896699024	4.3925265483	1.1390839842
H	1.8315087407	5.2991126540	1.3896205280
H	2.1254222371	3.6122979552	1.8660686777
H	3.4583761112	4.5993294081	1.2474128043
C	2.8156966273	2.6407751681	-0.5945575110
H	2.5082585645	1.8397670966	0.0918823552
H	2.5947644989	2.3301663841	-1.6159868144
H	3.8956179183	2.7830915127	-0.4843579233
C	-1.3659782524	5.8747494914	-1.0918462812
O	-0.6122695250	5.0055668028	-1.9037856766
C	-2.3462606285	6.5859950540	-2.0302421705
H	-3.0386751720	5.8599659270	-2.4664588718
H	-2.9239719665	7.3536606220	-1.5051438216
H	-1.7884259888	7.0565068037	-2.8441939258
C	-2.1657013697	5.1722205667	0.0174885640
H	-2.7780972333	5.9045327382	0.5532199484
H	-2.8092854886	4.3956452459	-0.4003138000
H	-1.4722779363	4.7247012564	0.7402497665
C	-0.4397275040	6.9085482542	-0.4428575020
H	0.2484746555	6.4080800871	0.2443705928
H	0.1460841664	7.4156935148	-1.2148015962
H	-1.0092076315	7.6591349068	0.1157789369
K	-0.7338271636	2.0996091312	1.0431009334

1a—styrene

M06-2X/6-31G(d,p) Electronic E: -309.505959 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -309.402619 a.u.

M06-2X/cc-pVTZ Electronic E: -309.616905 a.u.

C	-0.3234079035	0.1663991970	0.6833949312
H	0.1318371020	0.1308067083	-0.2996875977
C	-0.2591434771	-0.8800550639	1.5068190829
H	0.2465913139	-1.7820327130	1.1652489781
C	-0.8306874072	-0.9638605711	2.8631710483
C	-1.2821097963	0.1630997952	3.5628476455
C	-0.9262967852	-2.2138051708	3.4847616866
C	-1.8274851010	0.0374958759	4.8337390680
H	-1.1906280098	1.1473766544	3.1143168612
C	-1.4726018184	-2.3423061592	4.7577781035
H	-0.5717659864	-3.0948956883	2.9564397748
C	-1.9277399384	-1.2160984655	5.4362753357

H	-2.1694776837	0.9219187735	5.3618441744
H	-1.5407070960	-3.3219286943	5.2198882545
H	-2.3514064200	-1.3109814805	6.4307152979
H	-0.8362049931	1.0852220022	0.9504323552

Int5—Si-K-ion

M06-2X/6-31G(d,p) Electronic E: -1200.719248 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1200.592954 a.u.

M06-2X/cc-pVTZ Electronic E: -1200.899095 a.u.

Si	2.4881224403	-0.6641257656	0.8004877396
C	3.6641511771	-2.0095697861	1.5133136495
H	3.1233919142	-2.7850276442	2.0656187257
H	4.2603973626	-2.4959152040	0.7329195828
H	4.3571320301	-1.5476634358	2.2242443499
C	3.6680572216	0.3942319444	-0.2902349459
H	4.3648055717	0.9418180030	0.3529303905
H	4.2603002066	-0.2196273868	-0.9783937091
H	3.1306180497	1.1464432308	-0.8768875054
C	1.4395609432	-1.6357089451	-0.4990938088
C	0.8745743901	-0.9738310774	-1.6131651940
C	0.8599850224	-2.8840604990	-0.1763555926
C	-0.2450217153	-1.4617225138	-2.2863207009
H	1.3035285929	-0.0249273138	-1.9326474280
C	-0.2594514003	-3.3846550943	-0.8404398853
H	1.2769805783	-3.4582113406	0.6501357822
C	-0.8456965524	-2.6586246816	-1.8824622717
H	-0.6522991224	-0.9116572289	-3.1309682652
H	-0.6780382579	-4.3448712416	-0.5495009755
H	-1.7195674892	-3.0410827282	-2.3996620477
K	-0.7391046031	-0.5509899314	0.9229007201

Int5′—SiB-Si-K-new

M06-2X/6-31G(d,p) Electronic E: -2212.713260 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2212.256014 a.u.

M06-2X/cc-pVTZ Electronic E: -2213.158858 a.u.

B	-1.0962939907	-0.0476055343	-0.1513820634
O	-1.6180116597	0.9762736852	-1.1388633359
O	-2.2467586041	-0.3115664536	0.7218624683
C	-2.8694306961	1.4595842243	-0.6679643448
C	-3.4152649823	0.2483445254	0.1566307645
C	-3.7228845563	1.8496775399	-1.8710724590

H	-4.7416395621	2.1121846980	-1.5673169427
H	-3.2906657020	2.7296200231	-2.3638794534
H	-3.7726261655	1.0370723289	-2.5993108818
C	-2.6390608744	2.6893292716	0.2113878429
H	-2.0380648547	3.4198438473	-0.3428308562
H	-3.5805388504	3.1676431135	0.4987680273
H	-2.1000194799	2.4115047704	1.1178055061
C	-4.3640839989	0.6363717004	1.2860587155
H	-5.2359857995	1.1797245097	0.9050180252
H	-4.7173463948	-0.2687992599	1.7870917020
H	-3.8545753787	1.2544206027	2.0276500406
C	-4.1002605485	-0.7788823353	-0.7490605012
H	-4.2485042761	-1.7028718575	-0.1848696267
H	-5.0721361620	-0.4258590720	-1.1088653257
H	-3.4704930816	-1.0067238080	-1.6124664076
Si	0.4737342636	0.7301362091	0.9916164065
C	1.6779546929	-0.5066896739	1.7894913489
H	2.2751464262	-1.0706523184	1.0703771374
H	2.3650691574	0.0123233050	2.4651910527
H	1.1160200386	-1.2363776042	2.3824832544
C	-0.0223008565	1.8622974120	2.4438189859
H	0.7951257524	1.9396172719	3.1672527048
H	-0.2995899034	2.8777546604	2.1486487957
H	-0.8868308925	1.4251958808	2.9556452638
C	1.5188802360	1.7962039882	-0.2146301179
C	1.2618401656	3.1653085379	-0.4166167460
C	2.4519675250	1.1984276685	-1.0814736068
C	1.8893738013	3.8953227842	-1.4286711991
H	0.5544537310	3.6751312923	0.2332524639
C	3.0820470277	1.9128993318	-2.1027849570
H	2.6919858885	0.1442239426	-0.9578202610
C	2.7985158638	3.2679931820	-2.2848549986
H	1.6801443690	4.9553629602	-1.5434204372
H	3.7988996799	1.4160902173	-2.7507168297
H	3.2965008617	3.8330774328	-3.0667055239
K	-0.0061307872	1.8046477261	-2.9035232354
Si	-0.4942719490	-1.7441360861	-1.2723946934
C	-1.7734996214	-3.1550968116	-1.3324828058
H	-2.5782870945	-2.9711085465	-2.0492175299
H	-1.2904746379	-4.0975273330	-1.6088468679
H	-2.2351674729	-3.2794048462	-0.3481841240

C	1.1292081939	-2.6350752122	-0.8249151387
H	1.0782869838	-3.0287984844	0.1950612127
H	1.2904526625	-3.4808093486	-1.5023312604
H	2.0150567043	-1.9949065590	-0.8753613876
C	-0.2272741810	-1.1934510067	-3.0928739930
C	1.0513018948	-0.9953934482	-3.6434813137
C	-1.3214306920	-0.7957299939	-3.8857403642
C	1.2362741242	-0.4045542671	-4.8966322916
H	1.9282461236	-1.3025612261	-3.0779014079
C	-1.1535588045	-0.2082111632	-5.1398444725
H	-2.3314115777	-0.9385762222	-3.5071916625
C	0.1321471755	0.0022775493	-5.6471464700
H	2.2396940107	-0.2708119882	-5.2911556057
H	-2.0217824164	0.0799270858	-5.7258903517
H	0.2690476410	0.4529083017	-6.6253000272

TS5-6—Styrene-Si-K-ion-Scan-ts

M06-2X/6-31G(d,p) Electronic E: -1510.245317 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1509.993206 a.u.

M06-2X/cc-pVTZ Electronic E: -1510.516031 a.u.

Si	2.8190839371	-0.6957895686	0.4567545940
C	3.8656488685	-1.9755070743	1.4281943058
H	3.2315896533	-2.7227804367	1.9178138836
H	4.5595157435	-2.5087961045	0.7702981230
H	4.4547210752	-1.4881877033	2.2126715898
C	4.0473172510	0.0038503549	-0.8453592782
H	4.8673449408	0.5143883213	-0.3302547749
H	4.4863842266	-0.7863223673	-1.4665817424
H	3.5829140171	0.7435409573	-1.5053115319
C	1.5893900038	-1.7395760161	-0.5552983899
C	1.3062300887	-1.4573812848	-1.9120666945
C	0.6769848816	-2.5973045933	0.1028065730
C	0.1595757318	-1.9338309869	-2.5462064313
H	1.9970843989	-0.8337694157	-2.4765429762
C	-0.4736098610	-3.0774260292	-0.5222836237
H	0.8628050839	-2.8699965853	1.1395804520
C	-0.7563614632	-2.7268265033	-1.8457703546
H	-0.0198970724	-1.6973218495	-3.5917684349
H	-1.1540583365	-3.7274683295	0.0211864514
H	-1.6504917919	-3.0988491263	-2.3352039347
C	-1.5296476795	2.8612418274	1.8586272902

C	-0.5782246508	1.9388361171	2.2877624655
C	-0.9340206927	0.5960497192	2.5669599910
C	-2.2980944245	0.2511328900	2.4113191553
C	-3.2403861048	1.1765826973	1.9808271180
C	-2.8644871843	2.4920979268	1.6886216326
H	-1.2218793144	3.8830797712	1.6559194686
H	0.4527498864	2.2564887846	2.4042261549
H	-2.6031754726	-0.7704939144	2.6262486688
H	-4.2774868521	0.8726125979	1.8734903797
H	-3.5997896561	3.2152225690	1.3537928526
C	0.0488089519	-0.4304399020	2.8383795809
H	-0.3373306449	-1.4392876643	2.9683458333
C	1.4035957711	-0.2318240511	2.8269200406
H	1.8359011529	0.7587944702	2.8717351974
H	2.0662972055	-1.0352607901	3.1278032707
K	-0.4997986677	0.1692142923	-0.1604599053

Int6—Styrene-Si-K-ion-Int

M06-2X/6-31G(d,p) Electronic E: -1510.278684 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1510.026525 a.u.

M06-2X/cc-pVTZ Electronic E: -1510.563598 a.u.

Si	-1.9235559222	2.1098169889	1.6852391651
C	-3.2973452517	1.6153990189	0.4963548868
H	-3.4405425860	0.5304041941	0.4717187062
H	-4.2510539952	2.0792254175	0.7655562534
H	-3.0362700259	1.9397846207	-0.5151637448
C	-1.6857126256	3.9758786324	1.6337294330
H	-2.6445798931	4.4866166016	1.7644835138
H	-1.0128473366	4.3235357253	2.4235213377
H	-1.2567420147	4.2781545413	0.6735155890
C	-2.4105808287	1.6019778239	3.4405133384
C	-1.6072817489	1.9740744611	4.5295905580
C	-3.5451502188	0.8249825389	3.7101491694
C	-1.9196149519	1.5894268898	5.8299602579
H	-0.7186766159	2.5805837859	4.3598673112
C	-3.8672665916	0.4348463571	5.0088181138
H	-4.1939875304	0.5194363288	2.8924621170
C	-3.0539421061	0.8168317587	6.0715827600
H	-1.2826649948	1.8925361898	6.6555859734
H	-4.7536857111	-0.1652495508	5.1915403776
H	-3.3026767325	0.5158666724	7.0846327680

C	2.5658865276	4.3331537921	-0.0047272411
C	1.5191648154	3.5120045642	0.3784220337
C	0.8172986322	2.6729217127	-0.5842618223
C	1.1086309569	3.0104889359	-1.9712009022
C	2.1575365169	3.8324863453	-2.3183253699
C	2.9834797274	4.4478901856	-1.3450686383
H	3.0764082683	4.9148466764	0.7606395219
H	1.2258522117	3.4772861567	1.4229454766
H	0.4986293867	2.5521938085	-2.7463710410
H	2.3488555987	4.0205897886	-3.3729482345
H	3.7692738426	5.1357258775	-1.6313407615
C	0.0636553298	1.5680311951	-0.2398585076
H	-0.4576728225	1.0440216612	-1.0396509384
C	-0.3316245324	1.2159618495	1.1732002810
H	-0.5135129539	0.1379692573	1.2696330468
H	0.4651679501	1.4528772987	1.8939748227
K	3.2461602263	1.5109118983	-0.7565876109

Int6′—Styrene-Si-K-ion

M06-2X/6-31G(d,p) Electronic E: -1510.294284 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1510.039178 a.u.

M06-2X/cc-pVTZ Electronic E: -1510.567397 a.u.

Si	2.4469074204	-0.8393525925	1.0512749207
C	3.7856358761	-2.1537994973	1.2668072212
H	3.3670641482	-3.0704100108	1.6944616182
H	4.2613044310	-2.4112824665	0.3161264724
H	4.5642747764	-1.7971674875	1.9489906226
C	3.2279006439	0.6460847691	0.1880921840
H	3.8872128477	1.1761963541	0.8826855297
H	3.8365822505	0.3301943687	-0.6653267911
H	2.4818757819	1.3617056336	-0.1687788892
C	1.1521865079	-1.5897175703	-0.1143561680
C	0.9615205540	-1.1374028094	-1.4287791669
C	0.3604972371	-2.6671957425	0.3238515923
C	0.0246997505	-1.7330590432	-2.2795904726
H	1.5565898731	-0.3065277713	-1.8006615885
C	-0.5766706520	-3.2714447702	-0.5173730331
H	0.4752894477	-3.0331984823	1.3410257818
C	-0.7469756251	-2.8032578147	-1.8228334942
H	-0.0915981825	-1.3741911394	-3.2978132006
H	-1.1663162973	-4.1107188564	-0.1606722731

H	-1.4635849855	-3.2806908498	-2.4843241507
C	-1.0396038909	2.4169420998	0.9059144907
C	-0.1547777076	1.5695986583	1.5554952602
C	-0.6155117469	0.5207144608	2.4531433639
C	-2.0429328723	0.5750506644	2.7397891513
C	-2.8932929118	1.4293534745	2.0746766750
C	-2.4312581592	2.3294137361	1.0816107504
H	-0.6356393065	3.1805840072	0.2433587974
H	0.9126433182	1.7144978141	1.4214363505
H	-2.4345062102	-0.0911063066	3.5053096825
H	-3.9511048532	1.4188286072	2.3306123356
H	-3.1044449298	3.0298951919	0.6030912752
C	0.2089210883	-0.4634693487	2.9468297871
H	-0.2028445056	-1.1744029485	3.6581799529
C	1.7042863646	-0.4486111391	2.7631132006
H	2.1387144124	0.5236104627	3.0572778304
H	2.1575053398	-1.1787093917	3.4446980002
K	-1.6860972331	-0.3822802636	0.0295743812

CO_2

M06-2X/6-31G(d,p) Electronic E: -188.507408 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -188.516816 a.u.

M06-2X/cc-pVTZ Electronic E: -188.593396 a.u.

C	1.6671591344	-0.9283795404	-0.7051757652
O	0.7447147627	-1.3257927083	-0.1191578010
O	2.5896035329	-0.5309664113	-1.2911937437

TS6-7—Styrene-Si-K-ion-CO2-Scan-new-1-ts

M06-2X/6-31G(d,p) Electronic E: -1698.807210 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1698.543617 a.u.

M06-2X/cc-pVTZ Electronic E: -1699.168789 a.u.

Si	2.4553198933	-0.7545395407	1.0730823891
C	3.7688140655	-2.0910211479	1.2922113599
H	3.3489690802	-2.9691859431	1.7927457718
H	4.1844406417	-2.4142938914	0.3333989167
H	4.5916506238	-1.7191427549	1.9110471473
C	3.2187878435	0.6758571762	0.1061349097
H	3.9023937889	1.2343066638	0.7532274829
H	3.7983735435	0.3202353855	-0.7519311146
H	2.4632164251	1.3792181444	-0.2571395558
C	1.1120219458	-1.5339081496	-0.0288422803

C	1.0385221499	-1.2681705011	-1.4062515277
C	0.1991235201	-2.4659496965	0.4986089582
C	0.1003210335	-1.9017667228	-2.2274749352
H	1.7327205249	-0.5596339577	-1.8525869160
C	-0.7445833759	-3.1021136483	-0.3109272074
H	0.2219462109	-2.6888991169	1.5620776811
C	-0.7963296094	-2.8208300870	-1.6790283764
H	0.0803228818	-1.6921804496	-3.2929792272
H	-1.4294901363	-3.8258592719	0.1206218729
H	-1.5153347696	-3.3289090034	-2.3144660197
C	-1.0821756602	2.5470294800	0.9850881949
C	-0.1683037235	1.6744342749	1.5675470374
C	-0.5922477274	0.5727984496	2.3912132828
C	-2.0197608215	0.4422675495	2.5527153035
C	-2.9072347073	1.3224359115	1.9624974749
C	-2.4653322443	2.3784495268	1.1365467025
H	-0.7063156016	3.3850087685	0.4018783630
H	0.8936001832	1.8713368400	1.4578112146
H	-2.3856043961	-0.3380822751	3.2141875314
H	-3.9716573101	1.1996182423	2.1492692350
H	-3.1669242485	3.0843833598	0.7076785779
C	0.3061163856	-0.2811931059	3.0465039924
H	-0.1042880759	-1.1810098769	3.4964082958
C	1.7869887992	-0.2489501571	2.7789785374
H	2.1762441346	0.7579351176	2.9967472579
H	2.2922728342	-0.8972852438	3.5055447474
K	-1.6124856354	-0.0866259996	-0.3278654779
C	0.1086995590	0.8344052747	4.9928049152
O	-0.9100200006	0.4124720527	5.4299723402
O	1.0902109754	1.4999033232	5.0029311442

Int7—Styrene-Si-K-ion-CO2-Scan-P-new

M06-2X/6-31G(d,p) Electronic E: -1698.816038 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1698.549164 a.u.

M06-2X/cc-pVTZ Electronic E: -1699.202312 a.u.

Si	2.4469102467	-0.7351266856	1.0548118609
C	3.6839298452	-2.1240932963	1.3508940525
H	3.2226549228	-2.9444101765	1.9096692079
H	4.0767457542	-2.5285044114	0.4136798312
H	4.5261320268	-1.7573433256	1.9457241291
C	3.2811785859	0.6114619522	0.0295662414

H	4.0464818233	1.1041467215	0.6372103642
H	3.7795402826	0.1981879306	-0.8531106056
H	2.5838188701	1.3862497448	-0.3052426473
C	1.0979891000	-1.5165875706	-0.0537707149
C	0.9408437680	-1.1455171102	-1.4005544887
C	0.2986784348	-2.5759825656	0.4164897354
C	0.0354389810	-1.7984502642	-2.2437364249
H	1.5508454678	-0.3430883046	-1.8085018524
C	-0.6132208368	-3.2320764244	-0.4136932903
H	0.3995348702	-2.9069415604	1.4475917499
C	-0.7465499289	-2.8448116299	-1.7504367946
H	-0.0433888662	-1.5063362997	-3.2869351969
H	-1.2023858363	-4.0577552113	-0.0259351992
H	-1.4341639125	-3.3705526204	-2.4058301268
C	-1.1127627851	2.4959209627	0.7925716260
C	-0.1947436311	1.6600589230	1.4391784822
C	-0.6109476152	0.6799537525	2.3582623469
C	-2.0008356761	0.5819691637	2.6147102755
C	-2.9110860373	1.4225342785	1.9798316320
C	-2.4787439781	2.3794049082	1.0497071398
H	-0.7524120922	3.2545719850	0.1034263279
H	0.8641956922	1.7937735597	1.2424721402
H	-2.3117631247	-0.1171100417	3.3846425607
H	-3.9666859527	1.3488145698	2.2264872466
H	-3.1892196052	3.0461135383	0.5713848343
C	0.3370042090	-0.2006685094	3.1025196240
H	-0.0209937156	-1.2354370390	3.0292049087
C	1.8073750972	-0.0923297801	2.7074630955
H	2.1264146945	0.9496717994	2.8373926716
H	2.3657121416	-0.6152624303	3.4917019834
K	-1.7746885429	-0.3384944753	-0.1983422770
C	0.1538249054	0.0927648029	4.7171330732
O	-0.9960125530	-0.1430316196	5.1179943075
O	1.1856179705	0.4701397593	5.2729021703

THF

M06-2X/6-31G(d,p) Electronic E: -232.336851 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -232.245353 a.u.

M06-2X/cc-pVTZ Electronic E: -232.425304 a.u.

C	-0.2986478739	-2.0349425240	-3.4134042446

O	1.1158075460	-2.0107092415	-3.4134039620
C	1.6347799365	-0.6947817318	-3.4134040756
C	0.4551117373	0.2958342518	-3.4134050774
C	-0.8122749426	-0.5826398887	-3.4134049078
H	-0.6437348218	-2.5827131879	-4.2984224644
H	-0.6437352275	-2.5827124967	-2.5283857478
H	2.2688303952	-0.5638003996	-2.5283998308
H	2.2688314253	-0.5638010120	-4.2984076653
H	0.4874536314	0.9426851763	-2.5346915113
H	0.4874541264	0.9426840614	-4.2921194458
H	-1.4293562863	-0.3859259243	-2.5347037558
H	-1.4293560159	-0.3859266131	-4.2921064013

II

M06-2X/6-31G(d,p) Electronic E: -2774.365962 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2773.497638 a.u.

M06-2X/cc-pVTZ Electronic E: -2775.081690 a.u.

B	-0.7398013196	0.5024509966	0.2415979981
O	-1.9821826435	0.8101807226	1.0314236382
O	-0.8616170252	-0.9131780927	-0.0972646126
C	-2.7751530152	-0.3688459036	1.1190430148
C	-2.2318466022	-1.2641677664	-0.0467438246
C	-4.2497708241	-0.0034844822	0.9825575854
H	-4.8790701506	-0.9003244632	1.0027514103
H	-4.5500127271	0.6390267023	1.8170591159
H	-4.4405724490	0.5325315386	0.0516609945
C	-2.5483123510	-1.0264613520	2.4834980440
H	-2.8041022589	-0.3161904504	3.2762122016
H	-3.1734519512	-1.9148678304	2.6156923854
H	-1.5003387658	-1.3121554834	2.5970475268
C	-2.3371377712	-2.7643911378	0.2102345437
H	-3.3772896122	-3.0702558507	0.3694762401
H	-1.9505211465	-3.3056920664	-0.6576756858
H	-1.7438306233	-3.0536679287	1.0793013051
C	-2.9047377033	-0.9445869738	-1.3898383395
H	-2.3762958967	-1.4868148117	-2.1791206378
H	-3.9540430793	-1.2578902335	-1.4053306897
H	-2.8391586157	0.1241021377	-1.6104674447
Si	0.9692913355	0.7344646609	1.4291747679
C	0.8906831592	-0.2100071164	3.0847090398
H	0.8063937659	-1.2859140524	2.8985897719

H	1.8141164673	-0.0458493837	3.6504177462
H	0.0471115050	0.0869796688	3.7144935380
C	1.3937970928	2.5361428557	1.9470692983
H	2.3209105758	2.5673141258	2.5305761590
H	1.5236304723	3.2111238151	1.0895162984
H	0.6038117706	2.9438772553	2.5922095320
C	2.5495983622	0.0156128618	0.6455956400
C	3.7652600909	0.7056323308	0.5518297887
C	2.5144111006	-1.3019374721	0.1569751420
C	4.9002682989	0.1134049053	-0.0013633003
H	3.8314011501	1.7303098427	0.9131578228
C	3.6437024998	-1.9021088387	-0.3933559568
H	1.5736202535	-1.8504242064	0.1875879423
C	4.8421155353	-1.1945634025	-0.4729887017
H	5.8297196516	0.6724956372	-0.0637454325
H	3.5895058540	-2.9207148932	-0.7666990661
H	5.7236683497	-1.6595228131	-0.9041712565
C	-0.0165974516	1.5056482837	-2.0552495428
O	-0.8448411437	1.4446510374	-0.9099886750
K	-1.2993943345	3.5003226071	0.7085097111
C	-0.8887424021	2.1612054726	-3.1319145169
H	-0.3197387244	2.3732568032	-4.0433551919
H	-1.7186932329	1.4935037101	-3.3871151483
H	-1.3081357490	3.0987919934	-2.7454753240
C	1.2064939129	2.3907174540	-1.7808055546
H	0.8783371689	3.3562347577	-1.3814650670
H	1.8801861324	1.9161655658	-1.0621722369
H	1.7751128590	2.5670821634	-2.7010630012
C	0.4454286556	0.1315047734	-2.5427057677
H	-0.4118679986	-0.5195647773	-2.7230288097
H	1.0109619642	0.2459868219	-3.4740650447
H	1.0865075068	-0.3540581189	-1.8045322478
C	-0.3570252126	5.6871853606	-2.2460662881
O	-0.1238153427	5.3914810435	-0.8766579498
C	1.1319362272	5.9892815737	-0.5757755955
C	1.1374720920	7.3363610924	-1.3271942735
C	0.0145085122	7.1671186883	-2.3788833798
H	0.2887762316	5.0561291990	-2.8759547190
H	-1.3997022572	5.4507338410	-2.4645585115
H	1.2012938959	6.0745559692	0.5100773785
H	1.9397461997	5.3356494244	-0.9363737144

H	0.9208311327	8.1692155726	-0.6531481972
H	2.1089137314	7.5277344562	-1.7869739899
H	-0.8462355049	7.7927816237	-2.1268580273
H	0.3345775958	7.4258762294	-3.3897146484
C	-1.0546385221	7.1169595116	1.6868666222
O	-0.6310641174	5.8019684165	2.0459926339
C	0.2759127089	5.8547511848	3.1541199263
C	0.2039233627	7.2874080409	3.6788930722
C	-0.0938490493	8.0678597989	2.3961111045
H	-1.0362983477	7.1927131193	0.5950096968
H	-2.0862629593	7.2716931353	2.0338476137
H	-0.0267393362	5.0918705352	3.8757742037
H	1.2864175035	5.6111129905	2.7975608964
H	-0.6261242057	7.3959305794	4.3854770590
H	1.1228663894	7.5986570629	4.1789064147
H	-0.5252137139	9.0554160980	2.5704440929
H	0.8237008811	8.1901678959	1.8087916426
C	-1.8530609225	2.2644258015	4.0057518533
O	-1.7491418185	3.5338757131	3.3510798312
C	-2.7707245363	4.4192904468	3.8102545126
C	-3.5245327128	3.6670951750	4.9112877793
C	-3.2861966021	2.2061619602	4.5179891305
H	-1.6182299319	1.4977444357	3.2637395180
H	-1.1301003323	2.2195023511	4.8329235692
H	-2.3097314705	5.3502526402	4.1613447252
H	-3.4280655038	4.6647413069	2.9651552798
H	-3.0732630388	3.8700493982	5.8876373525
H	-4.5797087227	3.9429836213	4.9586756002
H	-3.4169398033	1.5043320335	5.3440199289
H	-3.9568114416	1.9135606136	3.7026593047
C	-3.8439670067	2.9895842749	-1.1798450776
O	-3.2537782431	4.2740132358	-0.9303874403
C	-3.9801262089	5.2107916026	-1.7077934073
C	-4.1669977528	4.5063072918	-3.0490027705
C	-4.4066909046	3.0456320732	-2.6173166229
H	-3.0617028692	2.2360246249	-1.0374103090
H	-4.6462058975	2.8217924631	-0.4489702714
H	-4.9524653200	5.4225722854	-1.2367079769
H	-3.4016189567	6.1375780386	-1.7521380358
H	-4.9869647906	4.9214134728	-3.6383295494
H	-3.2468139173	4.5833633600	-3.6367562972

H	-5.4718903821	2.8032809264	-2.6236689022
H	-3.8991107013	2.3407058111	-3.2775726038

TS1

M06-2X/6-31G(d,p) Electronic E: -2774.346697 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2773.480376 a.u.

M06-2X/cc-pVTZ Electronic E: -2775.064086 a.u.

B	-1.7582209720	0.4769621305	-0.8220021031
O	-2.5884721545	1.4550014254	-1.3847964304
O	-2.2846840002	-0.0336422586	0.3534542948
C	-3.5908991521	1.7885787833	-0.4170080022
C	-3.5948421938	0.5257789726	0.5256025234
C	-4.9092065836	2.0120809512	-1.1500525721
H	-5.7290858092	2.1539348969	-0.4385209509
H	-4.8358708074	2.9153594231	-1.7642168359
H	-5.1509654858	1.1706485250	-1.8039671297
C	-3.1771492430	3.0816215444	0.2793156656
H	-3.0138315619	3.8340951272	-0.4993970138
H	-3.9561397219	3.4369379121	0.9611610625
H	-2.2409277942	2.9544366288	0.8234636656
C	-3.7998360990	0.8478771424	1.9979223832
H	-4.7675396287	1.3345707743	2.1581078348
H	-3.7796739243	-0.0776182641	2.5788453115
H	-3.0064379728	1.5002786371	2.3666325473
C	-4.5857799205	-0.5485732395	0.0738945482
H	-4.4158286338	-1.4499892631	0.6684617148
H	-5.6245911205	-0.2337536031	0.2078122831
H	-4.4262712699	-0.8027752165	-0.9792804155
Si	0.4654699682	2.1206284716	0.4903497941
C	1.4239040410	1.0293986289	1.7735395477
H	2.1143189432	0.3272562180	1.2946886775
H	2.0151671396	1.6506987822	2.4562015858
H	0.7264168262	0.4351072928	2.3752568180
C	0.0926225879	3.6361899825	1.6514909784
H	1.0120550078	4.0466175945	2.0875090679
H	-0.4502899881	4.4649696277	1.1786911035
H	-0.5335169972	3.2933704274	2.4858222512
C	1.9785548486	2.8100870591	-0.5160604320
C	2.2785422196	4.1781456883	-0.6548148255
C	2.8435549983	1.9232981814	-1.1891570425
C	3.3763943952	4.6320397436	-1.3868002652

H	1.6539118935	4.9109986777	-0.1454859527
C	3.9565257112	2.3603091867	-1.9062015536
H	2.6573454293	0.8494054041	-1.1146318291
C	4.2318527040	3.7239750717	-2.0065749602
H	3.5784725037	5.6982585101	-1.4544534435
H	4.6199019834	1.6376899016	-2.3768876604
H	5.0988919006	4.0720976817	-2.5602925360
C	-0.4314510227	-1.5077853854	-1.5179496585
O	-0.9363891255	-0.1822068380	-1.7138381410
C	0.4886272012	-1.7480089692	-2.7108354634
H	0.9377167247	-2.7446100069	-2.6660770371
H	-0.0731763886	-1.6540254744	-3.6467876348
H	1.2865660379	-0.9982287557	-2.7109257589
C	0.3545271523	-1.6092133683	-0.2147981754
H	1.2050760830	-0.9248128610	-0.2343650953
H	-0.2727005870	-1.3438923490	0.6394330885
H	0.7252187564	-2.6308050810	-0.0828441276
C	-1.5999375348	-2.4938312438	-1.5333270574
H	-2.1847413288	-2.3681687208	-2.4507032006
H	-1.2320553069	-3.5235481539	-1.4939799263
H	-2.2496428966	-2.3212002834	-0.6722297651
K	-0.2812060267	2.2210024547	-2.8242469485
C	0.5238354642	0.4777455869	-5.9369661877
O	1.1763722393	1.0850789712	-4.8149275683
C	2.5172985636	0.5970641917	-4.7034259764
C	2.5697743069	-0.6591197967	-5.5651828523
C	1.6115272689	-0.2801159041	-6.6964364778
H	-0.2557702513	-0.1971122164	-5.5662009217
H	0.0402355483	1.2614842272	-6.5289916891
H	3.2139568920	1.3614496535	-5.0789332876
H	2.7345241379	0.4287586093	-3.6458356406
H	3.5798567201	-0.8929839046	-5.9065339614
H	2.1805281611	-1.5171279601	-5.0076400013
H	2.1144633246	0.3822318846	-7.4094705801
H	1.2176755040	-1.1380055215	-7.2445638810
C	2.0892021230	4.1292289022	-4.7110745590
O	0.7249871619	4.2411886502	-4.2908318695
C	-0.1449581910	4.2169909661	-5.4183742892
C	0.7346737675	4.5407803425	-6.6225168160
C	2.0515525939	3.8717165920	-6.2179691513
H	2.6027947377	5.0687298231	-4.4720095505

H	2.5675207200	3.3284390895	-4.1393572327
H	-0.5913233608	3.2143058940	-5.5172892345
H	-0.9487830920	4.9387038713	-5.2442559414
H	0.3227495600	4.1625810968	-7.5608271193
H	0.8682384195	5.6234250264	-6.7132441040
H	1.9964463890	2.7957681322	-6.4117171135
H	2.9230237454	4.2776528784	-6.7355433393
C	-2.8584926525	5.4266226224	-2.9552163010
O	-1.7803671053	4.5314775805	-2.7035777730
C	-0.8732999958	5.1047572129	-1.7433771980
C	-1.5800762663	6.3376306755	-1.1882273880
C	-2.4198024634	6.7759952724	-2.3911613798
H	-3.0559534593	5.4480112924	-4.0326592709
H	-3.7641272603	5.0644276004	-2.4453549788
H	-0.6643884185	4.3491870977	-0.9770805780
H	0.0580485377	5.3590756431	-2.2609476260
H	-2.2295104443	6.0641493267	-0.3496141328
H	-0.8779045440	7.0991436986	-0.8437350772
H	-3.2630017810	7.4186762708	-2.1306190144
H	-1.7919339133	7.3010733314	-3.1184892902
C	-2.8605198418	0.0923335872	-4.3149084533
O	-2.2061990855	1.3349825457	-4.5535167169
C	-3.2259502985	2.3350849588	-4.4953926038
C	-4.5293884060	1.6618946140	-4.9820690022
C	-4.1321675229	0.1823920700	-5.1538488236
H	-2.1794991546	-0.7111150834	-4.6079791026
H	-3.0865602926	-0.0049407891	-3.2455488929
H	-3.3173563047	2.6878235470	-3.4617662743
H	-2.9032195041	3.1685251163	-5.1255333144
H	-5.3177873127	1.7761732007	-4.2339820399
H	-4.8936083589	2.0941555897	-5.9160356887
H	-4.9076863974	-0.5099585318	-4.8197333591
H	-3.9038340124	-0.0349246607	-6.2007811781

III

M06-2X/6-31G(d,p) Electronic E: -2774.358519 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2773.493402 a.u.

M06-2X/cc-pVTZ Electronic E: -2775.077529 a.u.

B	-2.0260608189	-1.8133569743	1.2902219190
O	-2.5666405066	-0.5631541312	1.0746149382
O	-2.3491472026	-2.3418651172	2.5137960941

C	-3.1261221466	-0.1262266958	2.3353124594
C	-3.3797999804	-1.4896990492	3.0661335694
C	-4.3744539558	0.6888521580	2.0389672366
H	-4.8858130415	0.9627654125	2.9671628541
H	-4.0776545136	1.6076651634	1.5246543946
H	-5.0699649748	0.1396942268	1.4002306430
C	-2.0797028684	0.7349009092	3.0302052546
H	-1.8472576219	1.5763192573	2.3732766716
H	-2.4529538330	1.1206554934	3.9835451888
H	-1.1542388272	0.1770375605	3.1988310691
C	-3.2127614342	-1.4394527174	4.5746373243
H	-3.9232541300	-0.7323991334	5.0141904074
H	-3.4058878485	-2.4284380603	4.9976625333
H	-2.1998235120	-1.1387629699	4.8458831270
C	-4.7173965787	-2.1223822160	2.6880210202
H	-4.7446423518	-3.1464129903	3.0682629233
H	-5.5577473853	-1.5678429502	3.1140666705
H	-4.8373916214	-2.1565693747	1.6001445016
Si	1.7789260018	0.0595952200	2.2777246357
C	2.9524163960	-1.4027621544	2.7788044967
H	3.3165920321	-1.9734896075	1.9138793425
H	3.8294161939	-1.0654436113	3.3444663015
H	2.4017917042	-2.1142074291	3.4064201130
C	1.4148844641	0.8401443826	4.0141160829
H	2.3281656038	1.1006554794	4.5616991077
H	0.7991769928	1.7453421945	3.9368605164
H	0.8472400036	0.1306951755	4.6297932531
C	3.0727131685	1.3177697824	1.5826485954
C	2.8716204655	2.7108317477	1.6606989394
C	4.1926567752	0.9063661304	0.8342315342
C	3.6877251550	3.6244445226	0.9980207901
H	2.0482885603	3.0908025505	2.2649992747
C	5.0117807825	1.8072075790	0.1540545243
H	4.4308563634	-0.1557308954	0.7809788139
C	4.7552368531	3.1761899550	0.2192633647
H	3.4955380446	4.6910027430	1.0905827565
H	5.8619036523	1.4425360592	-0.4179818344
H	5.3918893592	3.8828934967	-0.3046145269
C	-0.7163465450	-3.7027139489	0.3827750167
O	-1.3227373473	-2.3944294609	0.2840060511
C	-0.0605131601	-3.9211646895	-0.9751561658

H	0.5135311518	-4.8520729515	-0.9808602853
H	-0.8200056367	-3.9754890832	-1.7630349347
H	0.6072068598	-3.0818567292	-1.1938301735
C	0.3300615416	-3.6895298416	1.4920052472
H	1.0680365972	-2.9030529729	1.3063557034
H	-0.1360248420	-3.4898427928	2.4605693037
H	0.8381312301	-4.6573595283	1.5407143307
C	-1.8025169326	-4.7466929065	0.6317255466
H	-2.5755842587	-4.6719282291	-0.1402524294
H	-1.3707708185	-5.7507236159	0.5915926470
H	-2.2629883011	-4.6024524302	1.6110351705
K	-0.3233733841	0.2068646960	-0.3961967111
C	1.6612657949	-1.6858400654	-3.3868941274
O	1.4733762419	-1.0139694060	-2.1391407378
C	2.6358086630	-1.1894092372	-1.3089855320
C	3.3664658877	-2.3941355796	-1.8859936904
C	3.0988304079	-2.2126716130	-3.3827728265
H	0.9343730998	-2.5069334003	-3.4561655166
H	1.4672937664	-0.9822989236	-4.2052823510
H	3.2587296934	-0.2879513327	-1.3625048369
H	2.2998870449	-1.3093236831	-0.2721994079
H	4.4280462804	-2.3968973661	-1.6314050407
H	2.9202414855	-3.3258957207	-1.5234547211
H	3.7803947515	-1.4618017307	-3.7958612396
H	3.2072048795	-3.1299210773	-3.9647387933
C	2.0144224761	2.3502596335	-1.8261310988
O	0.6236244697	2.0700429384	-2.0504560139
C	0.3787222130	1.8458295906	-3.4379885766
C	1.6387812171	2.3156540488	-4.1629060389
C	2.7203242235	1.9924187409	-3.1288255865
H	2.1279169886	3.4175765293	-1.5894993439
H	2.3617531913	1.7769467106	-0.9595642458
H	0.1996123927	0.7748113277	-3.5967589674
H	-0.5257310186	2.3923104262	-3.7256915406
H	1.7829599924	1.8140371244	-5.1226701773
H	1.5952588739	3.3952658193	-4.3416273430
H	2.9469840597	0.9210235776	-3.1505760387
H	3.6489434354	2.5498707342	-3.2642166414
C	-2.0052155460	3.2834420457	-0.9748002645
O	-1.5275329992	2.5748371387	0.1749671787
C	-0.3957116381	3.2532673135	0.7267778018

C	-0.5324874255	4.6997401061	0.2699711624
C	-1.1113195061	4.5193902129	-1.1377543107
H	-1.9597233246	2.6199031233	-1.8454979950
H	-3.0518762241	3.5570158612	-0.7901576975
H	-0.4153585807	3.1218664064	1.8129495531
H	0.5352438881	2.8114578442	0.3479877989
H	-1.2374515990	5.2361502236	0.9130071040
H	0.4234039908	5.2284296479	0.2812512929
H	-1.6673851995	5.3909229497	-1.4896604600
H	-0.3072693063	4.3008762776	-1.8453043536
C	-1.8749550447	-1.1535078976	-2.9783429720
O	-2.1399701003	0.1170538786	-2.3739808804
C	-3.4917404471	0.1720239907	-1.9057148260
C	-3.9555871316	-1.2782761886	-1.8364779361
C	-3.2112189766	-1.8976670910	-3.0221414734
H	-1.4415620611	-0.9896301639	-3.9716589614
H	-1.1415023764	-1.6900202957	-2.3610391521
H	-3.4928987789	0.6697344552	-0.9317486362
H	-4.0961647708	0.7533984158	-2.6161920739
H	-3.6106567397	-1.7257213215	-0.9004564882
H	-5.0410416544	-1.3789813256	-1.9034057099
H	-3.0852160283	-2.9794147977	-2.9358616614
H	-3.7385315045	-1.6857905123	-3.9576058042

IV

M06-2X/6-31G(d,p) Electronic E: -2174.211575 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2173.492466 a.u.

M06-2X/cc-pVTZ Electronic E: -2174.789762 a.u.

B	-0.5527444282	-0.0233054668	-0.9219112790
O	-1.0545638522	0.5056323189	-2.1756780029
O	-1.7839534193	-0.3657545147	-0.1493090059
C	-2.2707619475	-0.1470977702	-2.4711674386
C	-2.8682686687	-0.5261841823	-1.0426320296
C	-1.9659228036	-1.3723687365	-3.3464596403
H	-2.8717799892	-1.9117733195	-3.6410123823
H	-1.4660720158	-1.0222237754	-4.2547937195
H	-1.2890583625	-2.0520484029	-2.8258037849
C	-3.1466953157	0.8119477641	-3.2751582723
H	-2.6370095852	1.0539308256	-4.2117603151
H	-4.1151476987	0.3613659856	-3.5173734766
H	-3.3188195819	1.7453829112	-2.7352302938

C	-3.9990387401	0.3990666315	-0.5807477665
H	-4.8968364492	0.2912160117	-1.1975507916
H	-4.2581674908	0.1389097511	0.4511536906
H	-3.6890800911	1.4446255868	-0.5895072855
C	-3.3762594111	-1.9691258795	-0.9715828934
H	-3.7808079712	-2.1551291993	0.0290213246
H	-4.1770362265	-2.1546008605	-1.6954763205
H	-2.5616274905	-2.6744065350	-1.1523513806
C	1.4728977964	-1.4454869446	-1.5715770562
O	0.1855951499	-1.3150777566	-0.9968000112
C	1.6966172120	-0.4896691582	-2.7461942523
H	1.6408919397	0.5477833201	-2.4119574128
H	2.6818005034	-0.6687345512	-3.1903663922
H	0.9274633847	-0.6368994066	-3.5076420943
C	2.5411097006	-1.2076000022	-0.4929989154
H	2.4572380021	-0.1859237370	-0.1108143198
H	2.3884572731	-1.9128277996	0.3351917898
H	3.5518553684	-1.3632440524	-0.8866256564
C	1.5735735267	-2.8901778646	-2.0674637649
H	1.3671122745	-3.5808757074	-1.2433359940
H	0.8362121927	-3.0691036653	-2.8553047228
H	2.5700932148	-3.1069045989	-2.4664336088
C	0.1678860833	2.3048924533	-0.1337945910
O	0.3164956705	0.8990385334	-0.1837124506
C	0.9586944662	2.7497920907	1.0997718877
H	1.9853125773	2.3738534876	1.0309973836
H	0.9857802128	3.8401988827	1.1900571442
H	0.5017858415	2.3402426383	2.0094369420
C	0.7730682147	2.9321551523	-1.3930511785
H	0.6811407516	4.0234485952	-1.3723631180
H	1.8355890895	2.6761544399	-1.4639545196
H	0.2555109395	2.5432491820	-2.2732322801
C	-1.2936135110	2.7343639458	0.0070661251
H	-1.8357950730	2.4855821115	-0.9070610104
H	-1.7680674425	2.2115616973	0.8433268805
H	-1.3572706050	3.8143278906	0.1770524609
K	0.0588177891	-0.9206440836	1.6881269939
C	3.4556657485	-0.9140484931	2.9037637540
O	2.2088297049	-0.2792996485	3.1727463575
C	2.5214168371	0.8242296890	4.0122600579
C	3.5354589854	0.2697266471	5.0210130834

C	4.2249699214	-0.8734211951	4.2365876912
H	3.2390964476	-1.9191673994	2.5355204540
H	3.9850639172	-0.3548996201	2.1198285821
H	2.9603830553	1.6319111129	3.4095379498
H	1.5934636463	1.1842174357	4.4606490617
H	4.2360149727	1.0357279547	5.3580726425
H	3.0190363322	-0.1234246157	5.8995979242
H	5.2885892276	-0.6875250525	4.0762532625
H	4.1313413746	-1.8222290895	4.7711682004
C	-2.8288043490	-2.0715415077	3.8631428749
O	-1.6293119673	-2.3972910095	3.1609932240
C	-1.8981940067	-3.4089482861	2.1755409258
C	-3.3766239916	-3.7750576890	2.3291497269
C	-3.9625653640	-2.4999753682	2.9410879455
H	-2.8617761431	-2.6232313178	4.8132953227
H	-2.8176158979	-1.0002722630	4.0792724616
H	-1.6922867433	-2.9902510534	1.1809400449
H	-1.2252475047	-4.2561145262	2.3490285802
H	-3.8323956502	-4.0495642867	1.3758416094
H	-3.4962519818	-4.6133489342	3.0228472078
H	-4.1178379501	-1.7402285646	2.1685091318
H	-4.9036142630	-2.6630958136	3.4698143693
C	1.6110207223	-4.3930324652	1.6260197347
O	1.2120852084	-3.2227060992	2.3499501528
C	1.3050823249	-3.4565696538	3.7583745258
C	2.2722757241	-4.6253477406	3.8977185776
C	1.8851844651	-5.4687565954	2.6797967341
H	0.8151794296	-4.6639102164	0.9249302129
H	2.5119987468	-4.1526161421	1.0476255022
H	1.6440950577	-2.5271719742	4.2267163141
H	0.3098288625	-3.7039175159	4.1506815757
H	3.3068906506	-4.2752786006	3.8054218780
H	2.1676344404	-5.1545674579	4.8466801109
H	2.6585603877	-6.1723086353	2.3670003640
H	0.9729520070	-6.0350617954	2.8946905163

V-1

M06-2X/6-31G(d,p) Electronic E: -2130.191742 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2129.621596 a.u.

M06-2X/cc-pVTZ Electronic E: -2130.681220 a.u.

Si	3.3976920642	-0.9820236909	-0.1840142846

C	4.5013228908	-2.0198018050	1.0184768267
H	4.0318072207	-2.1405817883	2.0013093556
H	4.7353046936	-3.0174528577	0.6289416927
H	5.4486732807	-1.4966744877	1.1904652156
C	4.3841378480	-1.1780133023	-1.8427756098
H	5.3711310773	-0.7154269430	-1.7255993442
H	4.5406905687	-2.2281444898	-2.1181332340
H	3.9109902476	-0.6767486221	-2.6965101905
C	1.9252113572	-2.1986332090	-0.4833156091
C	1.2757965809	-2.3079003775	-1.7321460212
C	1.2568861464	-2.8055629837	0.6027459657
C	0.0233227981	-2.9065589484	-1.8771490872
H	1.7658031231	-1.9055574664	-2.6187991117
C	0.0176534328	-3.4270993941	0.4675160635
H	1.7230123822	-2.7755776770	1.5880895999
C	-0.6264254938	-3.4581801365	-0.7721888503
H	-0.4438444259	-2.9559779437	-2.8580188488
H	-0.4482133679	-3.8972232961	1.3318723054
H	-1.5969835314	-3.9328906669	-0.8822115420
K	0.1261044056	0.0456626863	-0.0117478009
C	0.9316583786	3.3587412241	-1.6782463519
O	0.7809003787	1.9440201165	-1.7648807784
C	1.7593632836	1.4716960665	-2.6867668549
C	3.0051545429	2.2980218516	-2.3865231011
C	2.4230721206	3.6578030720	-1.9435939570
H	0.2944262989	3.8381607888	-2.4373565715
H	0.5864814790	3.6598870641	-0.6860994353
H	1.9010799453	0.4026117807	-2.5027344300
H	1.4013298147	1.6253292983	-3.7183315342
H	3.5486182158	1.8144569726	-1.5687665351
H	3.6693039493	2.3788857715	-3.2492341653
H	2.9225923863	4.0293376377	-1.0464437781
H	2.5303159814	4.4174444746	-2.7212736337
C	-1.5942566125	0.2600930762	-3.0217100396
O	-1.9592671945	0.3675863635	-1.6395060592
C	-2.4206830620	1.6894236730	-1.3528771497
C	-2.8447370992	2.2667928736	-2.6989033141
C	-1.8024461285	1.6470788949	-3.6348372323
H	-0.5547182701	-0.0801361610	-3.0928777162
H	-2.2398012706	-0.4954245197	-3.4843735649
H	-3.2366976406	1.6115064200	-0.6286778450

H	-1.6050886317	2.2789382846	-0.9101319904
H	-3.8498762489	1.9200819139	-2.9583110392
H	-2.8398604410	3.3586183952	-2.7088446201
H	-2.1304306151	1.5971073965	-4.6748067112
H	-0.8714401308	2.2176576924	-3.5851536570
C	-1.4470997110	-1.3417013107	3.0186386225
O	-1.7069492878	-0.6112782560	1.8137706807
C	-2.9459053392	-1.0347224217	1.2313676402
C	-3.2452792555	-2.3901132790	1.8593854952
C	-2.6867853106	-2.2025059971	3.2729708942
H	-0.5521271939	-1.9558302058	2.8624770499
H	-1.2462931223	-0.6309412133	3.8277069727
H	-3.7282112500	-0.3039007953	1.4806051227
H	-2.8165188001	-1.0636420175	0.1456629107
H	-4.3089592477	-2.6354730127	1.8439636974
H	-2.6963829381	-3.1733413232	1.3293420401
H	-3.4071635106	-1.6614037498	3.8941928734
H	-2.4425014488	-3.1420648484	3.7722731821
C	0.1224611343	1.9678765418	2.7441170606
O	0.5002135262	2.3095848884	1.4144956672
C	1.9226052684	2.5199310506	1.4091941714
C	2.4876712238	1.7946597893	2.6456661490
C	1.2601786671	1.0734113922	3.2234767436
H	0.0506803338	2.8746279233	3.3641889364
H	-0.8554867390	1.4820843394	2.6963437096
H	2.3150229958	2.0857716732	0.4829679340
H	2.1259391884	3.5990520177	1.4354973167
H	3.2736246437	1.0943627685	2.3524721880
H	2.8895467067	2.5087699931	3.3695268128
H	1.1662357195	0.0750034452	2.7750769162
H	1.2946708585	0.9591846754	4.3094218469

V

M06-2X/6-31G(d,p) Electronic E: -1897.823682 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -1897.366516 a.u.

M06-2X/cc-pVTZ Electronic E: -1898.234927 a.u.

Si	2.2968534843	-0.8683367336	0.9367538042
C	2.5982179134	-2.5413822032	1.8623984850
H	1.7141682834	-2.9088799203	2.3973900209
H	2.9340673652	-3.3369544546	1.1859231471
H	3.3761929290	-2.3953772423	2.6201948139

C	4.0203178822	-0.6400595637	0.0784125294
H	4.7910695498	-0.4599958778	0.8374081278
H	4.3171114711	-1.5259159692	-0.4951650439
H	4.0456755455	0.2204023486	-0.6019131422
C	1.2782149372	-1.5179181102	-0.5902720208
C	1.3571653477	-0.8983158587	-1.8558548987
C	0.3993234374	-2.6164005894	-0.5049800381
C	0.6486143867	-1.3621943868	-2.9635407046
H	2.0358396104	-0.0554264358	-1.9904839914
C	-0.3256544025	-3.0843196463	-1.6020118812
H	0.3154210446	-3.1511414038	0.4404161416
C	-0.2014784618	-2.4621184720	-2.8436218268
H	0.7695092175	-0.8741738081	-3.9277534403
H	-0.9732763171	-3.9512695052	-1.4920989063
H	-0.7477988107	-2.8339848651	-3.7052697219
K	-0.2954758355	1.0743314884	0.7515642252
C	-2.2874957280	-0.1211467178	-1.5964231961
O	-2.4245622984	1.0817817005	-0.8379423814
C	-3.3580289226	1.9175774500	-1.5256528782
C	-3.3421808574	1.4729276040	-3.0065632790
C	-2.2765198322	0.3641443810	-3.0379995236
H	-1.3717510845	-0.6305656229	-1.2838120106
H	-3.1459610049	-0.7850919499	-1.4065369787
H	-4.3534129076	1.7923358181	-1.0815549981
H	-3.0411521229	2.9526357539	-1.3803404002
H	-4.3193704096	1.0781523964	-3.2951475823
H	-3.1046187163	2.2967550096	-3.6815304766
H	-2.4960676629	-0.4293760626	-3.7543026034
H	-1.2882224947	0.7706704823	-3.2700211153
C	-1.2068576548	-1.6281629913	2.7127305310
O	-1.9008397307	-0.5526714423	2.0570324716
C	-3.1818941722	-1.0231644832	1.6538589594
C	-2.9291424758	-2.4690929712	1.2482522518
C	-1.9617698609	-2.9221802114	2.3504459104
H	-0.1731145115	-1.6151446302	2.3524509451
H	-1.2005309743	-1.4472594790	3.7932195442
H	-3.8874888269	-0.9685796066	2.4967732506
H	-3.5314105144	-0.3713383139	0.8498951838
H	-3.8397106438	-3.0700768227	1.2014471631
H	-2.4321519088	-2.4947762577	0.2727819372
H	-2.5197394788	-3.2946457205	3.2141017867

H	-1.2860954471	-3.7143808280	2.0217256547
C	1.7451824948	3.3933998946	2.1761779030
O	1.3261510438	3.1743223383	0.8228192897
C	2.4750765264	2.9325670755	-0.0070670291
C	3.6761734455	2.8746975128	0.9333055127
C	3.2194658074	3.7674296955	2.0891204574
H	1.1124461418	4.1758446818	2.6040087586
H	1.6228728184	2.4630648976	2.7496330141
H	2.3330081333	1.9878935293	-0.5459837110
H	2.5533508948	3.7534239654	-0.7299632926
H	3.8089506537	1.8471036052	1.2852410077
H	4.5971438885	3.2125315612	0.4541069362
H	3.7537804550	3.5733052613	3.0209401367
H	3.3294352009	4.8263626158	1.8338994518

V′

M06-2X/6-31G(d,p) Electronic E: -2909.801156 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2909.009242 a.u.

M06-2X/cc-pVTZ Electronic E: -2910.491168 a.u.

B	-1.1064180714	-0.1832409885	-0.0923665016
O	-1.6054380637	0.8666371323	-1.0561249025
O	-2.3099311086	-0.5655916474	0.6729746751
C	-2.8649941088	1.3150285755	-0.5808180092
C	-3.4507697398	0.0369307954	0.0983382003
C	-3.6585070014	1.8496802041	-1.7672315428
H	-4.6875615487	2.0984421013	-1.4860107384
H	-3.1742337555	2.7647531570	-2.1298369188
H	-3.6816510719	1.1231511661	-2.5844328722
C	-2.6575106703	2.4373846094	0.4382172071
H	-1.9417112775	3.1536843968	0.0231118381
H	-3.5921783899	2.9604872856	0.6690399019
H	-2.2468947036	2.0385945493	1.3655762779
C	-4.4667564681	0.3211667704	1.2015772384
H	-5.3175743470	0.8976002493	0.8205699816
H	-4.8454405590	-0.6257707539	1.5959108707
H	-4.0069974636	0.8675122705	2.0268398175
C	-4.0838928224	-0.9040195008	-0.9306014835
H	-4.2664813736	-1.8728956528	-0.4590786942
H	-5.0331776834	-0.5138826391	-1.3132536072
H	-3.4058517847	-1.0619342256	-1.7719394183
Si	0.3717002614	0.5839269760	1.1648309108

C	1.5974149966	-0.6611219124	1.9226424904
H	2.2374379640	-1.1495760531	1.1851904146
H	2.2447872795	-0.1633458765	2.6517355208
H	1.0500317791	-1.4513779769	2.4479684334
C	-0.1552781434	1.6241914193	2.6788185532
H	0.6766176808	1.7169361713	3.3841618845
H	-0.4963179441	2.6333832562	2.4332958304
H	-0.9796146820	1.1208718686	3.1966166727
C	1.4112731351	1.7393262740	0.0479463698
C	1.1504786989	3.1155952369	-0.0542367556
C	2.3797587463	1.2159280153	-0.8273167560
C	1.8125249134	3.9272838728	-0.9760245951
H	0.4153734546	3.5684891074	0.6078369959
C	3.0540860185	2.0172751161	-1.7485169121
H	2.6232226142	0.1563006459	-0.7805093684
C	2.7667341824	3.3802872148	-1.8331436921
H	1.5888693147	4.9907420623	-1.0191445484
H	3.8129971242	1.5801578867	-2.3913110343
H	3.2845714021	4.0082442562	-2.5534848066
K	-0.0934910663	2.0207458405	-2.9051083721
Si	-0.3815001010	-1.7827654564	-1.2514829214
C	-1.6360538661	-3.2173677241	-1.3425294602
H	-2.4245113826	-3.0353321483	-2.0779446186
H	-1.1401875234	-4.1557740052	-1.6103545607
H	-2.1188450368	-3.3416049362	-0.3682031217
C	1.2502777960	-2.6621700898	-0.8033951449
H	1.1890776880	-3.0844804627	0.2043647692
H	1.4281648792	-3.4890336258	-1.5003835341
H	2.1303624123	-2.0121656771	-0.8268746448
C	-0.1186997064	-1.2557738875	-3.0786449358
C	1.1304604132	-1.2860691776	-3.7191407492
C	-1.2145544562	-0.8331042945	-3.8544531263
C	1.2770247411	-0.9502788238	-5.0676626102
H	2.0067866925	-1.6128155141	-3.1632491717
C	-1.0797065824	-0.4853322025	-5.1960164581
H	-2.2018747328	-0.7913601279	-3.4002011119
C	0.1706505701	-0.5505257444	-5.8131706076
H	2.2525034306	-1.0230297753	-5.5430577496
H	-1.9559072139	-0.1910181962	-5.7667684528
H	0.2733526904	-0.3188362288	-6.8703739275
C	-2.6601531406	3.5906233069	-5.0595694561

O	-1.3135892758	3.1445912383	-5.1679118212
C	-1.1387396587	2.7414499424	-6.5242965949
C	-2.5218499465	2.2627236718	-7.0257207290
C	-3.4487177433	2.5351467468	-5.8259498583
H	-2.8998955534	3.6775373175	-4.0002186220
H	-2.7654228738	4.5806323772	-5.5345465997
H	-0.7976817567	3.6021437646	-7.1186691262
H	-0.3606465788	1.9747233276	-6.5364449574
H	-2.8330925997	2.8445845050	-7.8967422085
H	-2.5169465247	1.2115722363	-7.3202852532
H	-4.4452630499	2.8686473619	-6.1209538140
H	-3.5507041061	1.6429541063	-5.2001371294
C	-1.6827220463	5.3440811319	-1.4803842990
O	-1.0604210673	4.5592791811	-2.5008430101
C	-0.2501064427	5.4007598902	-3.3330432082
C	-0.2693183872	6.7869882143	-2.6891706292
C	-1.6272347870	6.7807047374	-1.9845726515
H	-2.6957840203	4.9640219802	-1.3232038418
H	-1.1209115850	5.2349020627	-0.5417671816
H	0.7526054388	4.9631371197	-3.4006581875
H	-0.6904342320	5.4168885912	-4.3370443075
H	0.5341042542	6.8848661015	-1.9516962438
H	-0.1582008408	7.5877463093	-3.4227499268
H	-1.7088558984	7.5144095592	-1.1808012181
H	-2.4316693386	6.9600534693	-2.7054428584
C	1.7704646250	4.0033546491	-5.7365775523
O	1.6757992181	2.9191544901	-4.8226281112
C	2.8266514949	2.1233996823	-5.0708310349
C	2.8903652227	2.0322434697	-6.5946395274
C	2.3459914831	3.4090297572	-7.0395843509
H	0.7747079036	4.4358375676	-5.8389955264
H	2.4495693699	4.7659349106	-5.3248375812
H	3.7200613039	2.6259849633	-4.6657139585
H	2.6925912108	1.1655061672	-4.5659975990
H	3.8970740331	1.8285964295	-6.9640687724
H	2.2301233061	1.2288803624	-6.9338185855
H	3.1318490061	4.0479755113	-7.4476147098
H	1.5750939545	3.3017722010	-7.8059145346

TS2

M06-2X/6-31G(d,p) Electronic E: -2207.342459 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2206.757451 a.u.

M06-2X/cc-pVTZ Electronic E: -2207.854203 a.u.

Si	2.5739166406	-0.8316501177	0.4625063113
C	3.3289632455	-2.2582507808	1.5053348172
H	2.5718120479	-2.9934554990	1.7995993430
H	4.1095577138	-2.7924394090	0.9536994467
H	3.7745124938	-1.8717172733	2.4289168018
C	4.1084912313	-0.2178943159	-0.5321302463
H	4.8846579661	0.0797370648	0.1812418585
H	4.5265242541	-1.0132178122	-1.1615504125
H	3.9175150760	0.6531569272	-1.1665264337
C	1.4921923576	-1.7257110208	-0.8305821158
C	1.4589630258	-1.3344929036	-2.1867014062
C	0.4786092666	-2.6196654039	-0.4200945480
C	0.4558242062	-1.7576485814	-3.0578225152
H	2.2390932369	-0.6782854009	-2.5683195176
C	-0.5224775942	-3.0560881406	-1.2853258379
H	0.4704376092	-2.9698262374	0.6119072606
C	-0.5555751353	-2.6103358836	-2.6083017220
H	0.4682836733	-1.4320477398	-4.0950702809
H	-1.2837454859	-3.7467782190	-0.9286926195
H	-1.3363683635	-2.9447533239	-3.2848452598
C	-0.3589858919	3.8209380243	2.1448732970
C	0.0823242461	2.5063280796	2.2607204228
C	-0.8262068163	1.4221786307	2.2156375544
C	-2.1844038167	1.7366907904	1.9658200184
C	-2.6132529300	3.0510341067	1.8344342406
C	-1.7063100081	4.1109283947	1.9338327801
H	0.3634249226	4.6298104069	2.2212817526
H	1.1373923694	2.3110635222	2.4236811403
H	-2.9012921378	0.9209666522	1.8920778150
H	-3.6676392823	3.2536357829	1.6655226553
H	-2.0445129738	5.1382349081	1.8479669605
C	-0.4018461191	0.0490519993	2.3612626352
H	-1.1729576798	-0.7086864996	2.2372810141
C	0.9042699164	-0.3463800869	2.5243009865
H	1.6554581318	0.3434609551	2.8868781294
H	1.1192579811	-1.3911387787	2.7258020262
K	-0.6985842726	0.2164694502	-0.5244336239
C	-0.4738983984	3.3971967444	-1.3714232501
O	0.1291818504	2.2799991593	-2.0390778146

C	1.5590053904	2.3716035901	-1.9531111747
C	1.8520755574	3.4766290705	-0.9426896600
C	0.6492495516	4.4017921285	-1.1370754864
H	-1.2784925138	3.7875261239	-2.0027896696
H	-0.9101228468	3.0674304292	-0.4177621508
H	1.9476421681	1.3997131927	-1.6355221000
H	1.9589526683	2.6089243265	-2.9474198789
H	1.8491404655	3.0597615572	0.0698183461
H	2.8138018913	3.9616542204	-1.1208015306
H	0.4475106223	5.0428968814	-0.2770722429
H	0.7892736811	5.0322222141	-2.0215341789
C	-2.4007668712	0.9438938829	-3.3727195622
O	-2.6372548605	1.2519715221	-2.0037625595
C	-3.6423658992	2.2606448385	-1.9403416225
C	-3.6155994720	2.9958330233	-3.3005794096
C	-2.4910197918	2.2895231665	-4.0813710792
H	-1.4173202133	0.4722049593	-3.4428050486
H	-3.1680155423	0.2420877064	-3.7377143389
H	-4.6195901914	1.7927542226	-1.7589354983
H	-3.4021963242	2.9022954843	-1.0880316551
H	-4.5741370759	2.8851057759	-3.8133249668
H	-3.4265016465	4.0651609087	-3.1843735230
H	-2.7104950251	2.1940651676	-5.1464532657
H	-1.5372538193	2.8096092213	-3.9637027390
C	-2.9345515326	-2.3234289856	1.0851232988
O	-2.9019386595	-1.2035385183	0.1983058394
C	-4.0777588774	-1.2559111136	-0.6004854082
C	-4.2461171483	-2.7385918821	-0.9079277053
C	-3.8522384593	-3.3821197776	0.4317745504
H	-1.9050541540	-2.6676146058	1.2132672419
H	-3.3202914308	-2.0050512272	2.0621313302
H	-4.9378446930	-0.8707144204	-0.0300898381
H	-3.9095520670	-0.6202877449	-1.4705790173
H	-5.2567034408	-3.0003349266	-1.2276125322
H	-3.5439063920	-3.0239271389	-1.6968588836
H	-4.7361044423	-3.5554296782	1.0506596462
H	-3.3475941625	-4.3417637652	0.3014998098

VI

M06-2X/6-31G(d,p) Electronic E: -2207.385512 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2206.798479 a.u.

M06-2X/cc-pVTZ   Electronic E: -2207.901962 a.u.

Si	3.0696985156	-1.3667808987	1.1925068509
C	4.6168068716	-2.4482796208	1.2907754050
H	4.3696455000	-3.4534653679	1.6456018363
H	5.1029595604	-2.5459463427	0.3153923710
H	5.3425873851	-2.0176862153	1.9879686504
C	3.5303256328	0.2988384157	0.4402260645
H	4.1947704370	0.8585015416	1.1058329256
H	4.0479389990	0.1746608171	-0.5177193186
H	2.6295292555	0.9039738560	0.2852002121
C	1.8401288651	-2.1666425294	-0.0180991103
C	1.7552089840	-1.7933707765	-1.3676767169
C	0.9045469965	-3.1038295581	0.4504067652
C	0.7687484519	-2.3132350465	-2.2112085033
H	2.4539784693	-1.0619342533	-1.7691235484
C	-0.0749430369	-3.6373536353	-0.3837385138
H	0.9296830640	-3.4040836977	1.4957999652
C	-0.1542136887	-3.2320694699	-1.7173814850
H	0.7216043517	-2.0019259063	-3.2506504929
H	-0.7782106641	-4.3674347316	0.0077327820
H	-0.9234868322	-3.6382268868	-2.3682740532
C	1.1032380402	3.1235669678	2.7954956320
C	1.4594215003	1.7872987067	2.7292513599
C	0.4797121774	0.7254926060	2.7588062483
C	-0.8882782654	1.1975470521	2.7844132617
C	-1.2155151184	2.5417937044	2.8431443336
C	-0.2340796351	3.5423445274	2.8475087447
H	1.8970045241	3.8698576986	2.8109806273
H	2.5136725764	1.5254023449	2.7205444808
H	-1.6854401947	0.4548311599	2.8440356162
H	-2.2668084832	2.8188747776	2.8989607844
H	-0.4964184284	4.5922828083	2.9095061556
C	0.7888171405	-0.6312949208	2.7411906706
H	-0.0258128487	-1.3238955519	2.9526148217
C	2.1916219928	-1.1906314176	2.8531261864
H	2.8289263859	-0.5899704500	3.5240679795
H	2.1607646219	-2.1863194205	3.3175720473
K	-0.4454016596	-0.1324139559	0.0632945914
C	0.0231192597	2.8535266767	-0.4905504781
O	0.7495179103	1.8895867825	-1.2854904711

C	1.9268318439	2.4998678152	-1.8114557585
C	2.2231921538	3.6574881980	-0.8676365140
C	0.8077796954	4.1618706918	-0.5757846950
H	-0.9973541119	2.9330692514	-0.8850184861
H	-0.0145687741	2.5019091955	0.5447194791
H	2.7146585133	1.7436433121	-1.8512471767
H	1.7314242124	2.8636637519	-2.8327414746
H	2.6768766044	3.2751424608	0.0534185115
H	2.8785061312	4.4118729504	-1.3076384166
H	0.7265685081	4.7231994904	0.3562278298
H	0.4488063016	4.7854892717	-1.4023959083
C	-1.1110051305	0.7186376961	-3.4062721947
O	-1.7753912575	0.4216419894	-2.1859967638
C	-3.0498558322	1.0471296650	-2.2590200064
C	-2.8355756925	2.3638804232	-3.0339160704
C	-1.4419596822	2.1871138741	-3.6805893283
H	-0.0463777065	0.5312828595	-3.2575723062
H	-1.4977364882	0.0654214669	-4.2041744306
H	-3.7500906767	0.3896788881	-2.7953694508
H	-3.4109043632	1.1817540983	-1.2361378160
H	-3.6191547263	2.5079195902	-3.7806574728
H	-2.8551704334	3.2275405156	-2.3659625243
H	-1.4372222954	2.4219915688	-4.7466805696
H	-0.7023311692	2.8198519836	-3.1840502542
C	-2.8973517058	-2.2147394187	1.4109136495
O	-2.7600708273	-1.3983686375	0.2397588597
C	-3.4973819869	-1.9576577471	-0.8484309960
C	-3.8024388302	-3.3960781035	-0.4444321087
C	-3.9608186708	-3.2602361602	1.0726095728
H	-1.9262314269	-2.6793901489	1.6260250550
H	-3.1714185078	-1.5756146747	2.2544755890
H	-4.4252731107	-1.3847736362	-0.9867153507
H	-2.8877816556	-1.8651373770	-1.7518291208
H	-4.6905924347	-3.7930094268	-0.9399087509
H	-2.9536617527	-4.0436023298	-0.6849831541
H	-4.9585306929	-2.8807699968	1.3135787921
H	-3.8113596352	-4.1969951403	1.6126690829

TS3

M06-2X/6-31G(d,p) Electronic E: -2395.904311 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2395.309153 a.u.

M06-2X/cc-pVTZ Electronic E: -2396.505142 a.u.

Si	2.1526979694	-0.9660685896	1.2674828523
C	3.2149962902	-2.5010729131	1.5599158569
H	2.6054498572	-3.3279674400	1.9381558556
H	3.7077424701	-2.8365809707	0.6426616735
H	3.9894199708	-2.2934053231	2.3055190032
C	3.2644201171	0.3572524432	0.5016982026
H	3.9287875623	0.7717574306	1.2664947581
H	3.8944593147	-0.0614736436	-0.2899243423
H	2.6920758952	1.1894189357	0.0801424575
C	0.8703179368	-1.4642127730	-0.0372052753
C	0.9712764297	-1.0503821720	-1.3745924222
C	-0.1812840179	-2.3370801230	0.2924935955
C	0.0646228315	-1.4817507220	-2.3446634923
H	1.7804840849	-0.3842460239	-1.6681821964
C	-1.0931727812	-2.7714869950	-0.6700354301
H	-0.2889635117	-2.6755511970	1.3210847260
C	-0.9763618463	-2.3398039630	-1.9918897015
H	0.1748954417	-1.1571412319	-3.3756964320
H	-1.8975791678	-3.4461422111	-0.3929224526
H	-1.6880486692	-2.6746598838	-2.7411291141
C	-0.6774594733	2.8738185343	0.9348788387
C	-0.0205989745	1.8385113263	1.5914969957
C	-0.7325967968	0.8733862331	2.3864142379
C	-2.1515119059	1.1064459805	2.4918830176
C	-2.7805478289	2.1373274158	1.8240127137
C	-2.0662733577	3.0279131651	0.9962737143
H	-0.0867982945	3.5872141930	0.3633545597
H	1.0634237808	1.7915541497	1.5521184880
H	-2.7202030849	0.4684327985	3.1612979986
H	-3.8533733724	2.2676133192	1.9526160652
H	-2.5639918247	3.8470907005	0.4899694676
C	-0.0973851850	-0.1814588490	3.0547584715
H	-0.7184205299	-0.9509218438	3.5051070087
C	1.3777539478	-0.4488032061	2.9258877441
H	1.9431296702	0.4372932746	3.2613070467
H	1.6587048228	-1.2352445499	3.6379452999
K	-1.7415136919	0.2877253055	-0.3849107109
C	-0.1988458705	0.9766528858	5.1130497190
O	-1.3062466483	0.7401188823	5.4504493851
O	0.8948542036	1.4179354425	5.1686820970
C	-3.6030563834	-1.8159129310	1.7374304640

O	-3.7507811987	-1.2524374826	0.4269918249
C	-4.6241414307	-2.0547061847	-0.3650910901
C	-5.2313702720	-3.0869357169	0.5858824406
C	-4.1217472881	-3.2462158705	1.6287911007
H	-2.5493250000	-1.7374828578	2.0269282426
H	-4.2013754301	-1.2324331161	2.4475853014
H	-5.3731932102	-1.4067317307	-0.8337843274
H	-4.0397969496	-2.5303618593	-1.1657223429
H	-6.1322805433	-2.6833346497	1.0581998349
H	-5.4965640587	-4.0178462528	0.0810442443
H	-4.4769039602	-3.6342438753	2.5850503510
H	-3.3387723127	-3.9165480427	1.2593927452
C	-4.3651514436	1.1612485075	-1.7264783470
O	-3.6435533424	0.0571223632	-2.2974316784
C	-4.3096534842	-0.4184245765	-3.4627650414
C	-5.2837901773	0.6860016947	-3.8643155072
C	-5.6828883702	1.2444280969	-2.4962779281
H	-4.5020480422	0.9687282417	-0.6557781681
H	-3.7589448487	2.0693468270	-1.8488342738
H	-3.5583971183	-0.6394006690	-4.2272994220
H	-4.8468631505	-1.3479683841	-3.2239866926
H	-4.7685507925	1.4529296816	-4.4518049329
H	-6.1271503772	0.3133743786	-4.4486010410
H	-6.0790281784	2.2603750439	-2.5371152484
H	-6.4381097128	0.6009994855	-2.0328931645
C	-1.4087317293	1.4760640724	-3.8456796350
O	-1.0750913542	1.7400584485	-2.4827689150
C	0.2253392002	2.3288655824	-2.3935444490
C	0.9048299483	2.0043808998	-3.7185808051
C	-0.2801740841	2.0784905223	-4.6855359007
H	-1.4810609958	0.3896657450	-3.9812530396
H	-2.3895541767	1.9135165184	-4.0621810098
H	0.1253380594	3.4129547693	-2.2514587868
H	0.7295880127	1.9091290644	-1.5165809296
H	1.7113064032	2.6982160835	-3.9621900749
H	1.3165034124	0.9894227324	-3.6949460596
H	-0.4995183755	3.1227006760	-4.9284534529
H	-0.1183000081	1.5365059731	-5.6192635660

VII

M06-2X/6-31G(d,p) Electronic E: -2395.927671 a.u.

M06-2X/6-31G(d,p) Gibbs free E: -2395.329021 a.u.

M06-2X/cc-pVTZ Electronic E: -2396.545105 a.u.

Si	3.3848932242	-0.9472556171	1.4129025127
C	4.3008845769	-2.5088282328	1.9350655165
H	3.6029790542	-3.2594771841	2.3186990290
H	4.8553395834	-2.9526793492	1.1032697880
H	5.0097739597	-2.2820432019	2.7375573294
C	4.6501499526	0.2422021803	0.6664152543
H	5.2955644109	0.6392250599	1.4561225098
H	5.2916740731	-0.2791653256	-0.0515409143
H	4.1976952333	1.0963455509	0.1526834246
C	2.2098913043	-1.4709129091	0.0083125704
C	2.3604551592	-1.0112525126	-1.3099285870
C	1.1819568715	-2.4000165723	0.2513794075
C	1.5194664687	-1.4459131385	-2.3373764937
H	3.1590623036	-0.3108573327	-1.5461119256
C	0.3335271569	-2.8361667183	-0.7651236571
H	1.0409161117	-2.7946597927	1.2556698334
C	0.4967459483	-2.3538329785	-2.0655168826
H	1.6659027899	-1.0824140140	-3.3506289898
H	-0.4528902467	-3.5521342827	-0.5425878275
H	-0.1601491203	-2.6929395486	-2.8615584940
C	1.0239878437	3.0972315466	0.5785500400
C	1.4411002788	2.0058077756	1.3460331153
C	0.5357077294	1.2535900508	2.1080465407
C	-0.8089279451	1.6811126335	2.1183443508
C	-1.2243792395	2.7644070326	1.3494242509
C	-0.3162099598	3.4698474261	0.5536299458
H	1.7570687612	3.6615040349	0.0088419021
H	2.4947154632	1.7507338191	1.3592885766
H	-1.4967049418	1.1485912138	2.7685662525
H	-2.2664641320	3.0710301660	1.3817702035
H	-0.6435775557	4.3132742023	-0.0463235275
C	0.9473218857	-0.0024621001	2.8476905899
H	0.4506365239	-0.8385739228	2.3295295110
C	2.4587403249	-0.2517314612	2.9067220628
H	2.9591470202	0.6588149338	3.2602159764
H	2.6096127679	-0.9583172979	3.7305427540
K	-0.4160488472	0.2790320325	-0.5251627053
C	0.2930585869	-0.0506027304	4.3060073249
O	-0.9519385613	-0.2218149455	4.2873169261
O	1.0777013395	0.0677531521	5.2488587959

C	-2.5938922504	-1.5315179641	1.9683136137
O	-2.3163319582	-1.1451640979	0.6113517349
C	-3.0084533188	-2.0567866784	-0.2364876065
C	-3.1915108481	-3.3631236021	0.5704753309
C	-2.5105369773	-3.0494724118	1.9137807063
H	-1.8794394820	-1.0548475378	2.6495027298
H	-3.6125700137	-1.2076086733	2.2312337221
H	-3.9788062318	-1.6250439384	-0.5271498749
H	-2.4127782565	-2.1857005170	-1.1455859164
H	-4.2536709160	-3.5749773686	0.7169123645
H	-2.7528273191	-4.2268715858	0.0643489846
H	-2.9928206711	-3.5329809151	2.7645070522
H	-1.4579812961	-3.3513411610	1.9007545488
C	-3.2693203799	1.1778049538	-1.5023761459
O	-2.4727778226	0.2133462122	-2.2148508065
C	-3.2145018518	-0.3251207465	-3.3060716973
C	-4.3210546915	0.6869702214	-3.5789486478
C	-4.6511599658	1.1505452775	-2.1580729859
H	-3.2892836985	0.8966065827	-0.4434145354
H	-2.7875687076	2.1592716935	-1.6057851469
H	-2.5300732369	-0.4711407897	-4.1468904366
H	-3.6350534556	-1.3003847921	-3.0216260179
H	-3.9318097133	1.5213901742	-4.1720487460
H	-5.1724464910	0.2533126084	-4.1063733194
H	-5.1497876322	2.1202936033	-2.1191940604
H	-5.2931854685	0.4154689944	-1.6626943146
C	-0.2069367331	1.3634732121	-3.9622168622
O	0.2685479778	1.6777711949	-2.6504006479
C	1.5453457290	2.3165171386	-2.7239493862
C	2.0797996583	1.9961561846	-4.1149918048
C	0.7881272390	1.9956053749	-4.9370044396
H	-0.2382052405	0.2703046605	-4.0669488985
H	-1.2267516968	1.7460611903	-4.0686545386
H	1.4186544275	3.3983563143	-2.5834911045
H	2.1668206174	1.9308323421	-1.9094609728
H	2.8172197268	2.7220789040	-4.4617549199
H	2.5427715952	1.0035095064	-4.1242630830
H	0.4930045100	3.0231761573	-5.1701463529
H	0.8662386857	1.4411976365	-5.8739568090

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