Supporting information

The Synthesis of Highly Functionalized 2-Pyranone from Silyl Ketene

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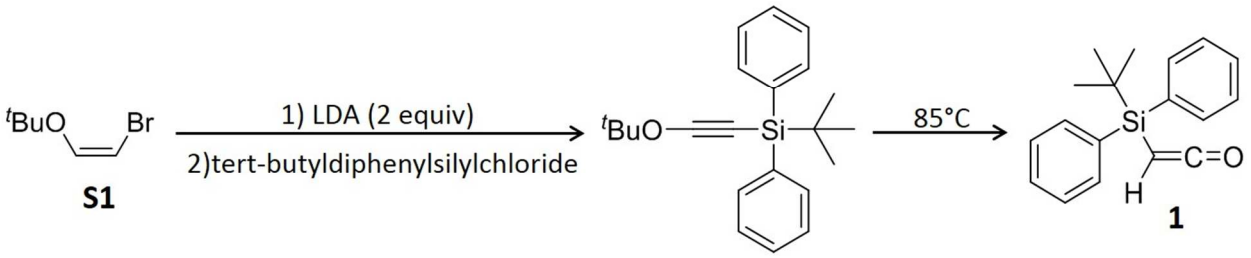
General Considerations. All operations were conducted under an inert atmosphere. All ^{1}H, ^{13}C, ^{29}Si, HSQC, HMBC and NOESY NMR were collected on Bruker Ascend III HD 500MHz NMR instrument equipped with prodigy probe and shifts are reported relative to residual solvent peak, as noted. All NMR spectra were collected using $CDCl_3$ as the solvent unless otherwise noted. FTIR spectra were acquired using an Aglient Cary 630 FT-IR in ATR mode. Melting points were determined using. Melt-TEMP 50/60 cycle apparatus. ESI spectra were obtained on THERMO Finniagn LCQ DECA ion trap mass spectrometer equipped with an external AP ESI ion source.

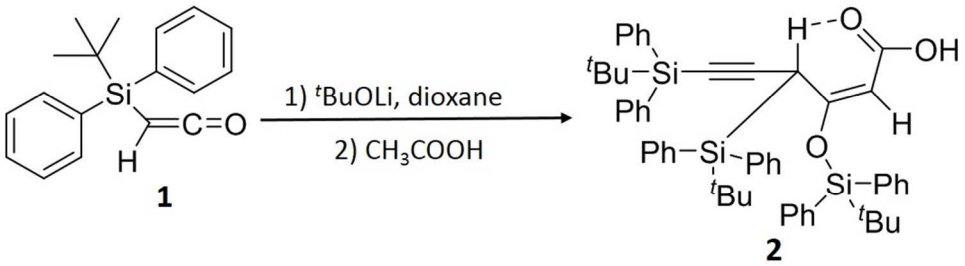
Materials. All purchased chemicals were used directly as received, unless otherwise stated. LDA solution, tert-butyldiphenylsilylchloride, ^{t}BuOLi solution and acetic acid was purchased from sigma aldrich. Dioxane was purchased from fishier and dried over CaH_2 under reflux for 8 hours and used immediately or stored in the schlenk flask.

Other Systems Explored. The transformation reported herein (silyl ketene to 2-pyranone) was attempted with many other silyl groups, solvents, and catalysts; the formation of 2 in high yield was only realized with the system reported herein, with all other conditions leading to a complex mixture of products, as determined by TLC and ^{1}H NMR. Similar reactions were explored with trimethylsilyl (TMS) ketene, triethylsilylketene (TES), *tert*-butyldimethylsilyl ketene (TBDMS), triisopropylsilyl (TIPS) ketene, methyldiphenylsilyl (MDPS) ketene, phenyldimethylsilyl (PDMS) ketene, and triphenylsilyl (TPhS) ketene in dry hexane, cyclohexane, toluene, THF and 1,4-dioxane, with the counterion of Li^+, Na^+, K^+ and NH_4^+ and anion of MeO^-, $^{t}BuO^-$ and LDA.

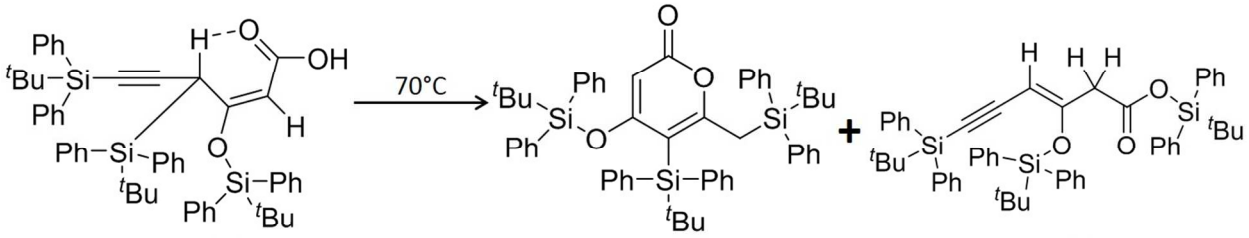
Materials Preparation



Preparation of Triisopropylsilylketene (TBDPS ketene, 1)[2]: (Z)-1-bromo-2-tert-butoxylethene (**S1**) was preparaed using the previously established protocol. [1] An LDA (2mol/L in THF-ethylbenzene-hexane) in THF (48 mL, 0.096 mol LDA) was added to dry THF (48 mL) in an oven-dried round bottom flask placed under N_2, cooled to -78 °C in a dry ice-acetone bath. A mixture **S1** (7.08 g, 0.04 moL) and dry THF (16 mL) was prepared in an addition funnel and added dropwise to LDA solution. After complete addition, the reaction was warmed to room temperature naturally and stirred for 3 hours. The vessel was then cooled to -20 °C using a salt water ice bath and *tert*-butyldiphenylsilyl chloride (12.1 mL, 0.048 mol) was then added and the resulting solution again warmed to room temperature and stirred for 4 hours. The mixture was then transferred to a separation funnel containing an aqueous solution of saturated $NaHCO_3$ (80 mL). The organic layer was isolated and the aqueous layer washed with hexane (2 x 20 mL). The combined organic layers were washed with 0.5 N HCl (2 x 80 mL), water (120 mL), and an aqueous solution of saturated NaCl (120 mL); the organic phase was dried over Na_2SO_4, then filtered and solvent removed under reduced pressure. The isolated crude product was run through a plug column of silica gel, with eluent of 2.5 vol% NEt_3 in hexanes. A pale, yellow oil was obtained, placed under an inert environement (N_2) and then heated to 85 °C for 2 hours (or until disappeareance of the alkyne stretching frequency in the FTIR spectrum). Compound **1** was isolated by vacuum distillation (41%, 4.2 g, 0.016 mol) as a transparent oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 6.5 Hz, 4H), 7.46 (dq, J = 14.0, 7.0 Hz, 6H), 2.30 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.96, 135.99, 134.15, 129.99, 128.14, 27.49, 19.45, -3.23. ^{29}Si NMR (99 MHz, $CDCl_3$) δ -3.59.



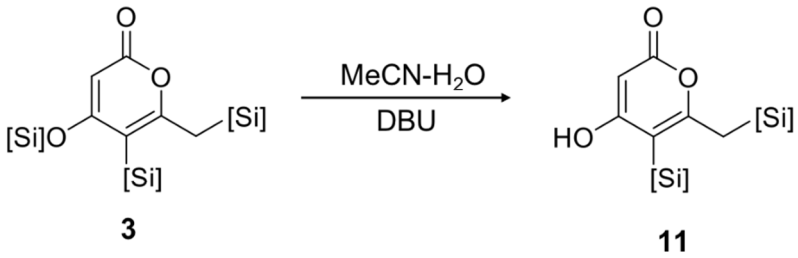
Preparation of (Z)-4,6-bis(tert-butyldiphenylsilyl)-3-((*tert*-butyldiphenylsilyl)oxy)-hex-2-en-5-ynoic acid (2): To a round bottom flask, a THF solution of ^{t}BuOLi (1 M, 0.33 mmol) was diluted with dry dioxane (2 mL) at 25°C. Then TBDPS-ketene (1mmol, 0.28g) was added dropwise. After the addition, the mixture was stirred at 25°C for ~30 s. Then neat acetic acid (0.02 g, 0.33mmol) was add. Then the whole mixture was loaded on the column and the final product was obtained by eluting with Hexane : Et_2O = 2 :1 and was pure enough for the next step reaction with the yield of 50%. The spectrum pure title product was obtained after recrystallization from diethyl ether as a white solid (mp = 166 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 7.0 Hz, 2H), 7.70 (dd, J = 15.0, 6.8 Hz, 5H), 7.59 (d, J = 7.0 Hz, 2H), 7.54 (d, J = 7.0 Hz, 2H), 7.40 – 7.24 (m, 15H), 7.18 – 7.06 (m, 7H), 6.03 (s, 1H), 4.43 (s, 1H), 1.16 (s, 9H), 1.03 (s, 9H), 0.73 (s, 9H).^{13}C NMR (126 MHz, $CDCl_3$) δ 170.98, 170.52, 137.22, 136.96, 135.96, 135.94, 135.42, 135.24, 133.72, 132.48, 132.01, 131.33, 130.10, 129.96, 129.88, 129.56, 129.43, 129.20, 129.17, 127.79, 127.73, 127.56, 127.52, 127.43, 127.27, 108.25, 99.49, 82.87, 28.73, 27.35, 26.41, 25.27, 19.63, 19.25, 18.70. ^{29}Si NMR (99 MHz, $CDCl_3$) δ -2.13, -2.74, -18.31.



Preparation of 5-(tert-butyldiphenylsilyl)-6-((tert-butyldiphenylsilyl)methyl)-4-((tert-butyldiphenylsilyl)oxy)-2H-pyran-2-one (3): Compound **2** (0.3g,0.36mmol) was dissloved in dry dioxane (2 mL) under N_2 and stirred at 70°C. After complete consumption of **2**, the solvent was removed under reduced pressure, and the viscouse residue was subjected to column chromatography (elutent of hexanes:ethyl acetate, 10:1, v:v). Byproduct **10** and the compound **3** were isolated (R_f values of 0.8 and 0.5, respectively).

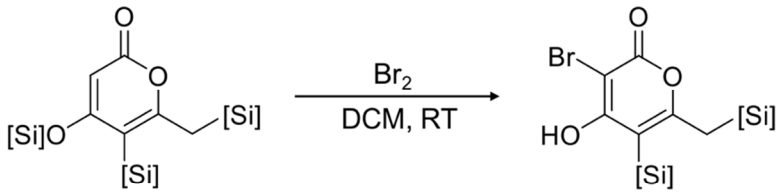
Compound 3 (75%, 0.23g, 0.27mmol, white solid, mp = 160 °C)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.25 (m, 25H), 7.17 (t, J = 7.5 Hz, 4H), 7.02 (d, J = 7.0 Hz, 4H), 5.16 (s, 1H), 2.43 (s, 2H), 0.96 (s, 9H), 0.86 (s, 9H), 0.74 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.21, 172.87, 163.43, 136.80, 136.49, 136.30, 135.43, 133.95, 131.75, 130.34, 129.67, 129.63, 128.34, 128.09, 127.78, 104.50, 97.14, 30.85, 28.77, 28.16, 24.82, 20.22, 20.14, 18.84. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 1.09, -2.24, -6.13.

Compound 10 (15%, 0.045g, 0.054mmol, light yellow oil): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 4H), 7.64 (d, J = 7.0 Hz, 4H), 7.57 – 7.53 (m, 4H), 7.38 – 7.13 (m, 26H), 5.00 (s, 1H), 2.87 (s, 2H), 1.01 (s, 18H), 0.94 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.99, 157.32, 136.13, 136.04, 135.92, 135.87, 135.78, 135.73, 135.48, 134.16, 133.03, 131.75, 130.47, 130.45, 129.56, 128.35, 128.17, 128.03, 127.88, 105.35, 93.68, 93.14, 43.86, 27.57, 27.18, 26.96, 19.91, 19.58, 19.00. ^{29}Si NMR (99 MHz, $CDCl_3$) δ -0.58, -4.98, -17.47.



3 **11**

Preparation of 5-(tert-butyldiphenylsilyl)-6-((tert-butyldiphenylsilyl)methyl)-4-hydroxy-2H-pyran-2-one (11): First, 0.23g (0.27 mmol) 3 was dissloved with MeCN/H_2O (10 : 1) at room temperature. Then 0.03ml DB ws added and the mixture was stirred at room temperature for 30mins. Then the mixture was washed with 10ml sat. NH_4Cl solution. The aqueous phase was washed with DCM. Then the organic phase was combined and dried under Na_2SO_4 for 30min. Then the solvent was eaporated and the residue was laded on the column and eluted with Hex : EA = 5 : 1 first to get rid of the tert-butyldiphenylsilyl alcohol and then Hex : EtOH = 10 : 1 to get the titled compound as a white solid (0.1g, 0.16mmol, 61%). ^{1}H NMR (500 MHz, CDCl3) δ 7.47 (d, J = 7.0 Hz, 4H), 7.32 (t, J = 7.0 Hz, 3H), 7.26 (t, J = 7.0 Hz, 5H), 7.18 – 7.10 (m, 7H), 7.04 (t, J = 7.5 Hz, 4H), 5.44 (s, 1H), 2.03 (s, 2H), 1.00 (s, 10H), 0.63 (s, 9H). ^{13}C NMR (126 MHz, CDCl3) δ 176.87, 174.81, 166.53, 105.13, 89.13, 30.21, 27.90, 23.35, 20.08, 18.51. ^{29}Si NMR (99 MHz, CDCl3) δ -2.90, -6.29.

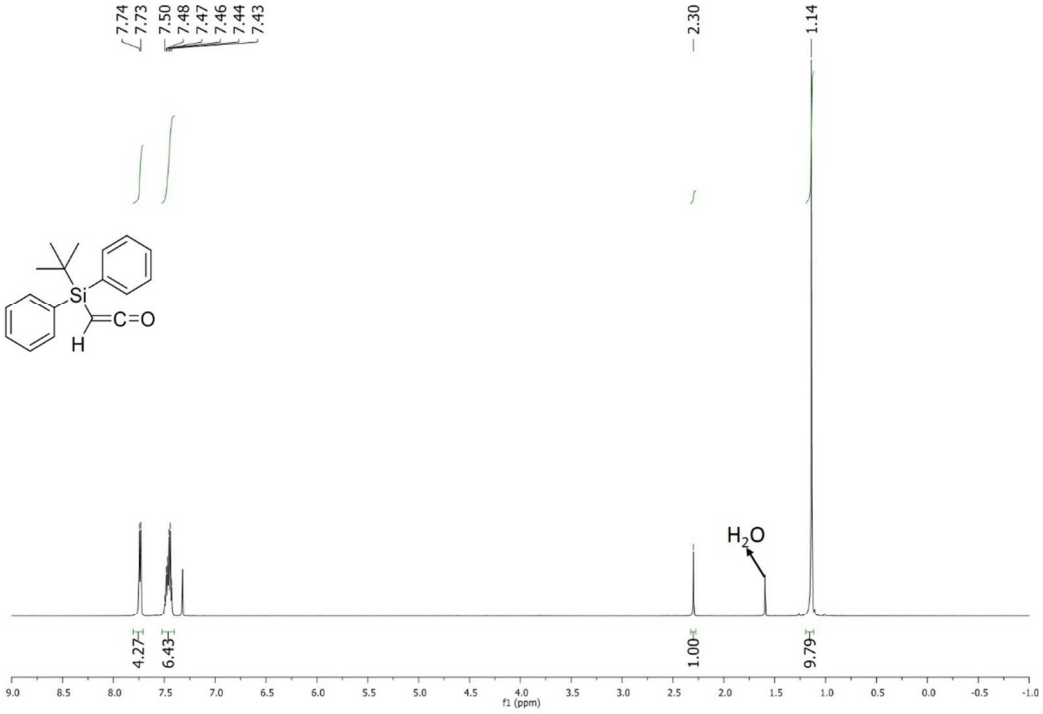


3 **12**

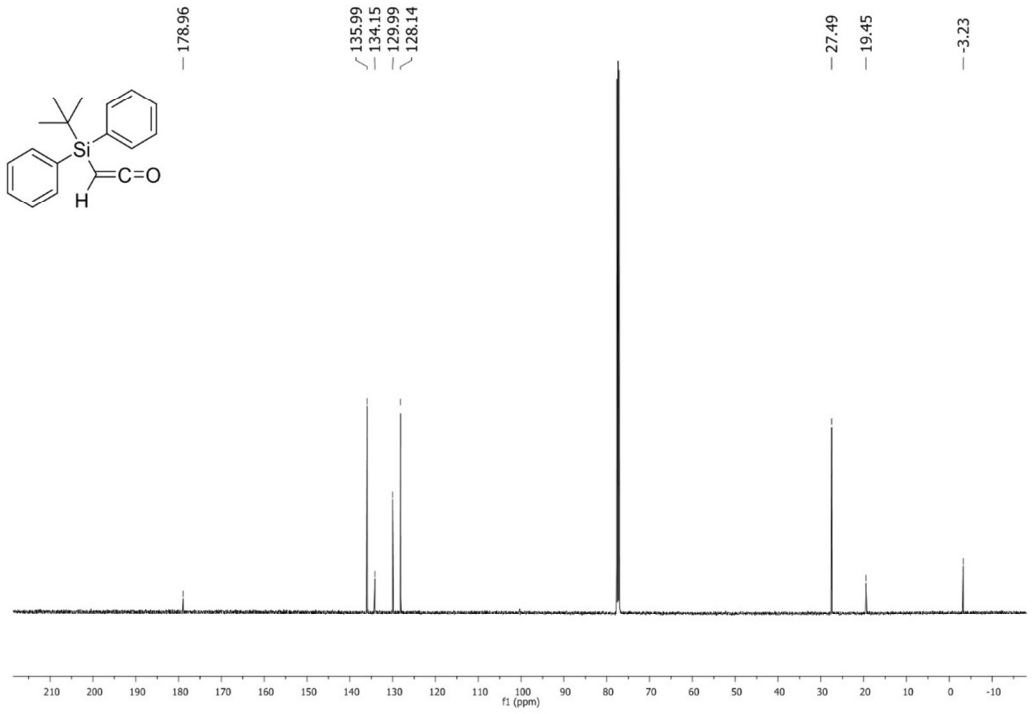
Preparation of 5-(tert-butyldiphenylsilyl)-6-((tert-butyldiphenylsilyl)methyl)-4-((tert-butyldiphenylsilyl)oxy)-2-bromo-pyran-2-one (12): First, 0.5g 3 was diluted with 3ml dry DCM and sitrred at room temperature. Then 0.4ml Br_2/DCM solution (1.66M) was added dropwisely. After the addition, the mixture was kept stirred in the dark for 3hrs. Then the mixture was loaded on the column and eluted with Hex:EA = 5 : 1 to get the titled compound as a white solid with the yield of 30% (0.12g). ^{1}H NMR (500 MHz, CDCl3) δ 7.64 (d, J = 6.5 Hz, 3H), 7.43 (d, J = 7.0 Hz, 3H), 7.34 – 7.31 (m, 5H), 7.26 (t, J = 7.0 Hz, 7H), 7.20 (d, J = 7.0 Hz, 4H), 6.42 (s, 1H), 2.08 (s, 2H), 1.00 (s, 9H), 0.68 (s, 10H). ^{13}C NMR (126 MHz, CDCl3) δ 173.73, 167.82, 158.96, 102.00, 87.84, 30.05, 27.90, 23.15, 20.05, 18.62. ^{29}Si NMR (99 MHz, CDCl3) δ 2.33, -1.27.

Figure S1: Characterization of **1:** A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) FTIR; E) Gas chromatogram; F) Mass spectrum from GC-MS.

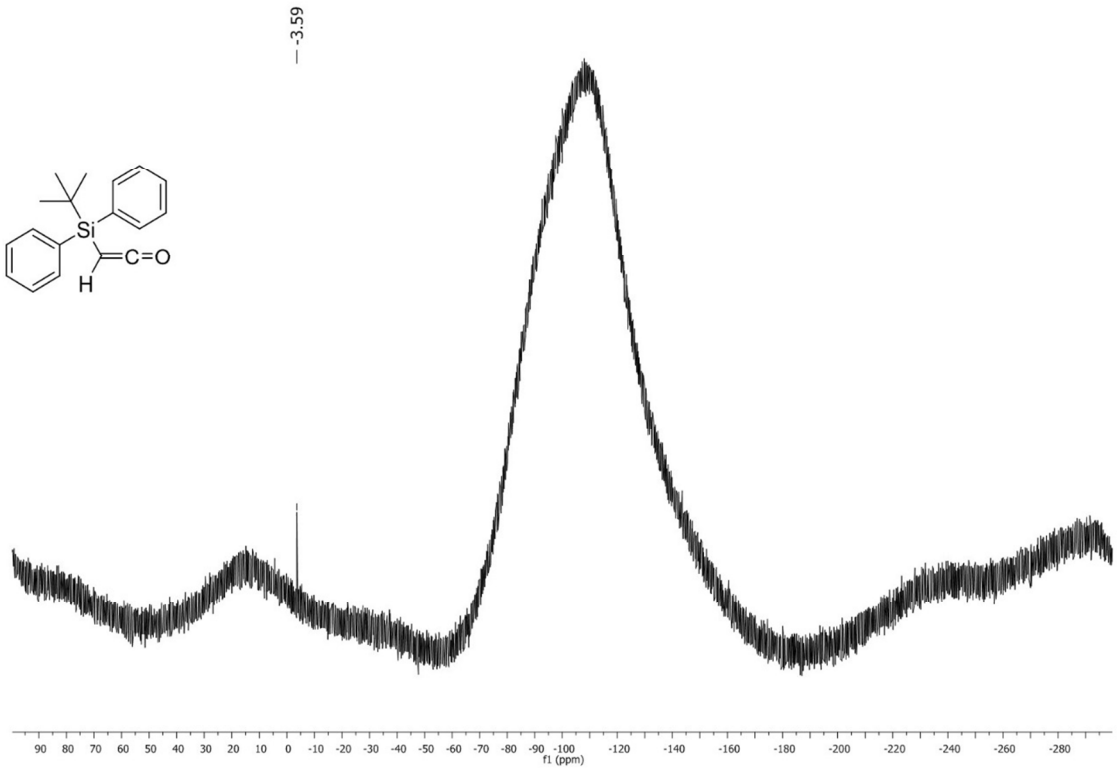
A)



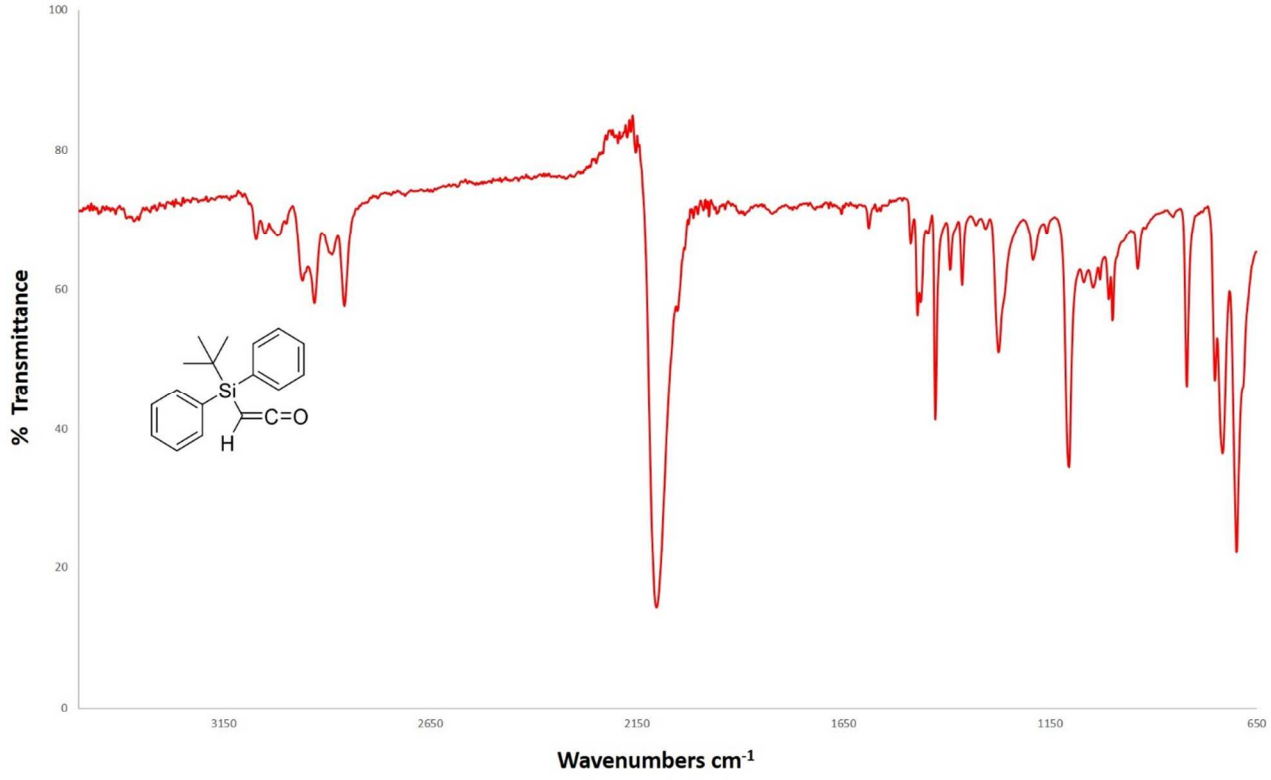
B)



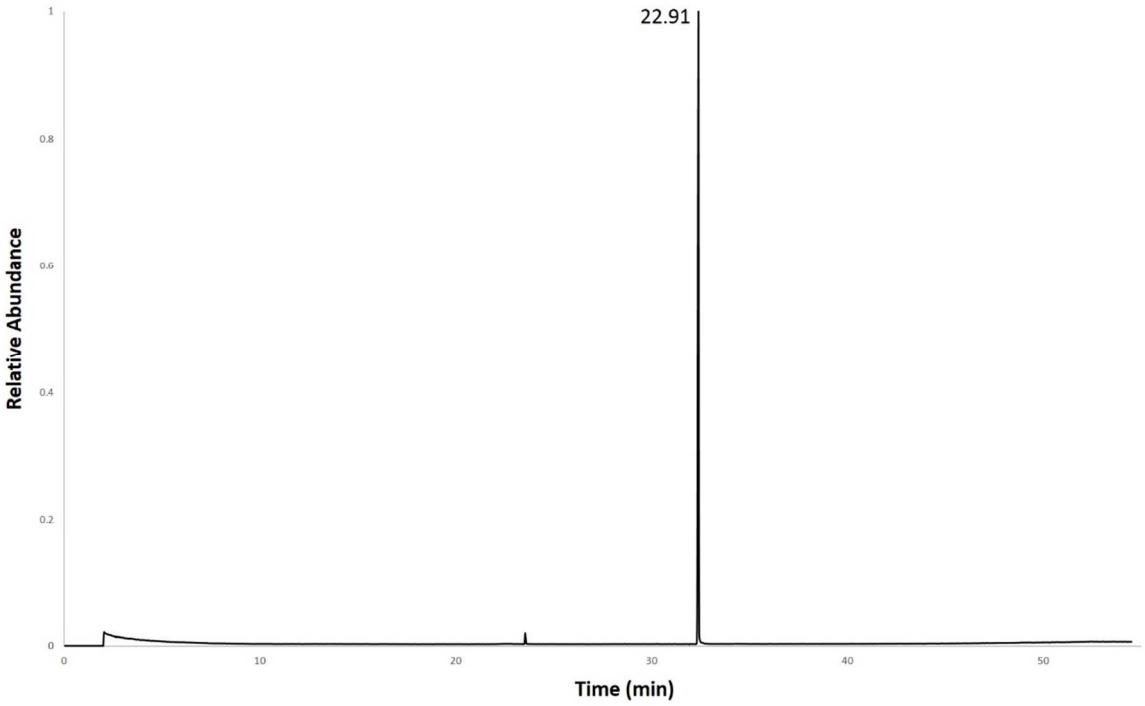
C)


-3.59
Si
C=O
H
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

D)


100
80
60
40
20
0
% Transmittance
Si
C=O
H
3150
2650
2150
1650
1150
650
Wavenumbers cm-1

E)


22.91
Relative Abundance
Time (min)

F)

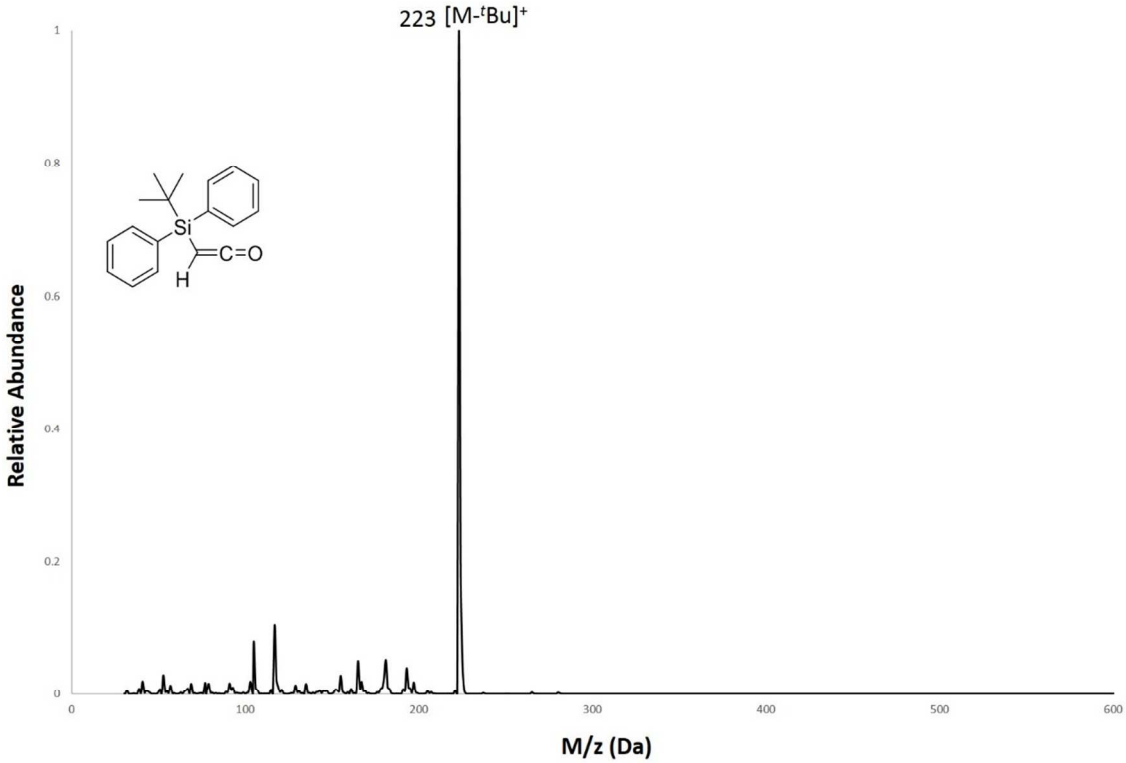
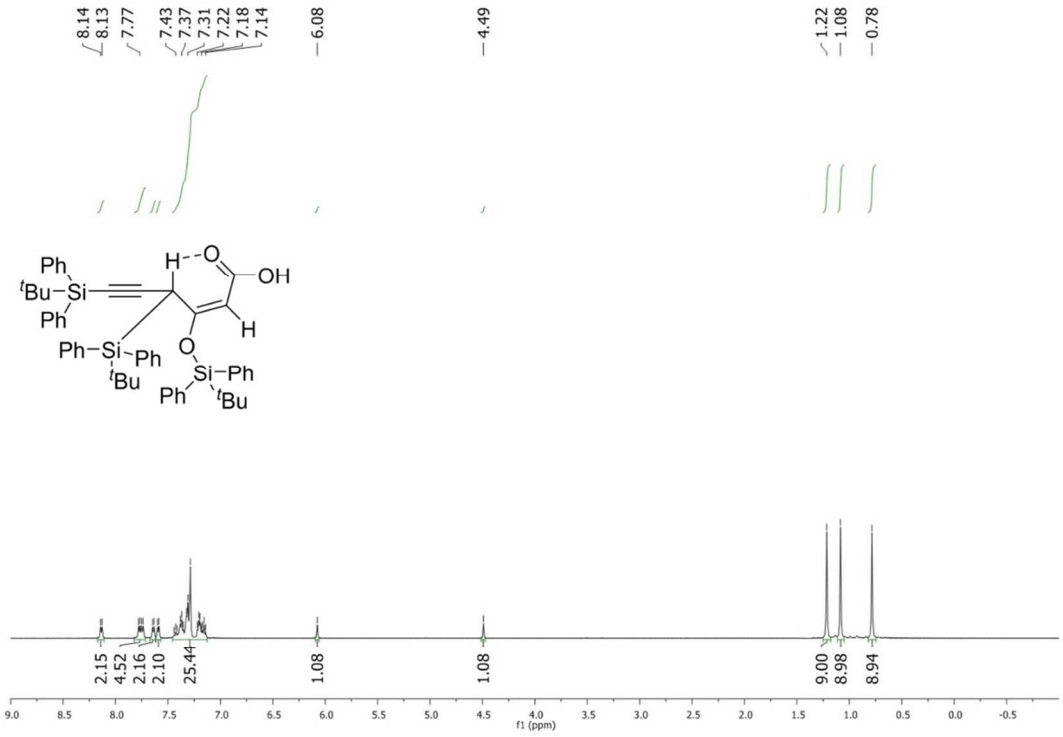
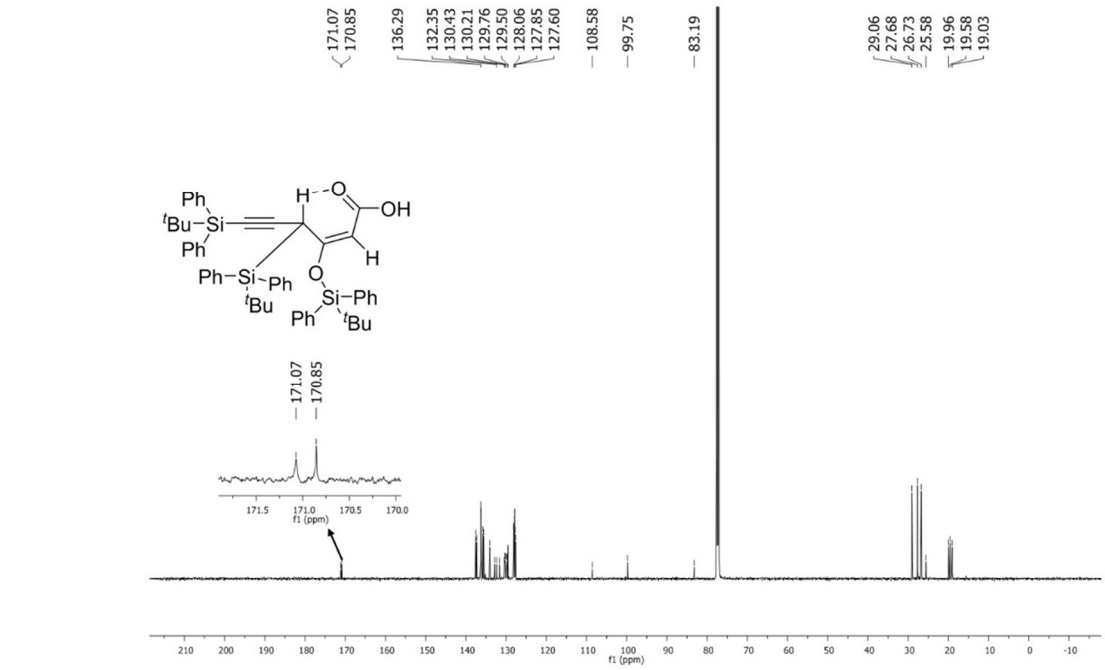

223 [M-tBu]+
Si
C=O
H
Relative Abundance
M/z (Da)

Figure S2: Characterization of **2**: A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) HSQC NMR; E) HMBC NMR; F) NOESY NMR; G) FTIR; H) Electronspray ionlization mass spectrum.

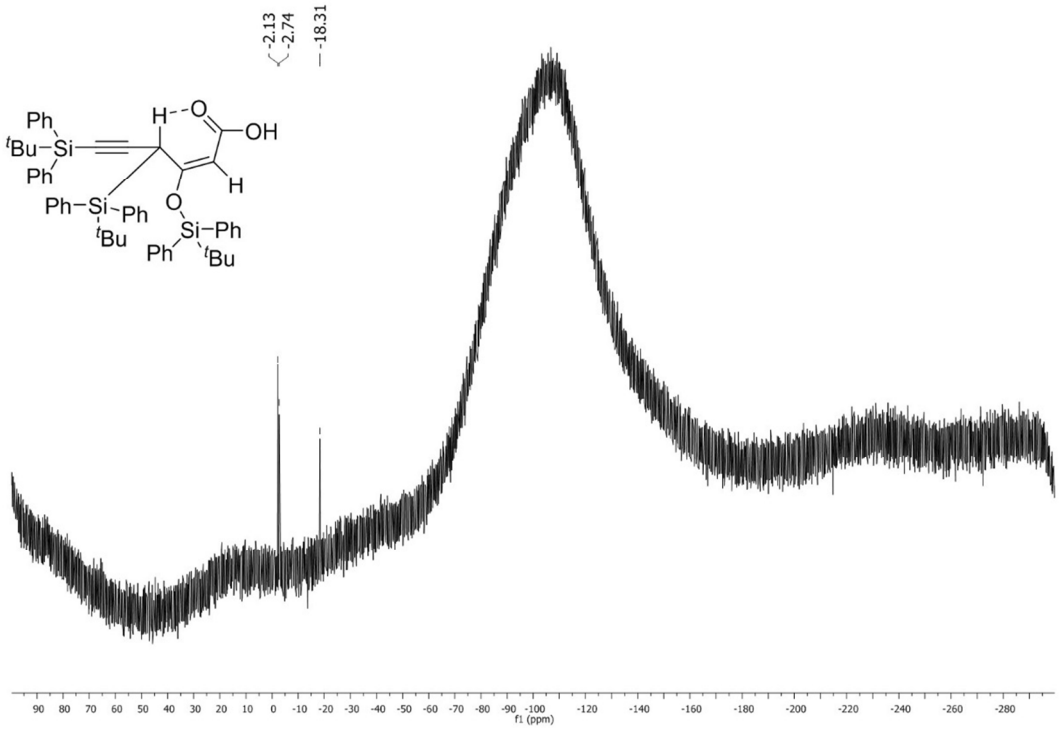
A)



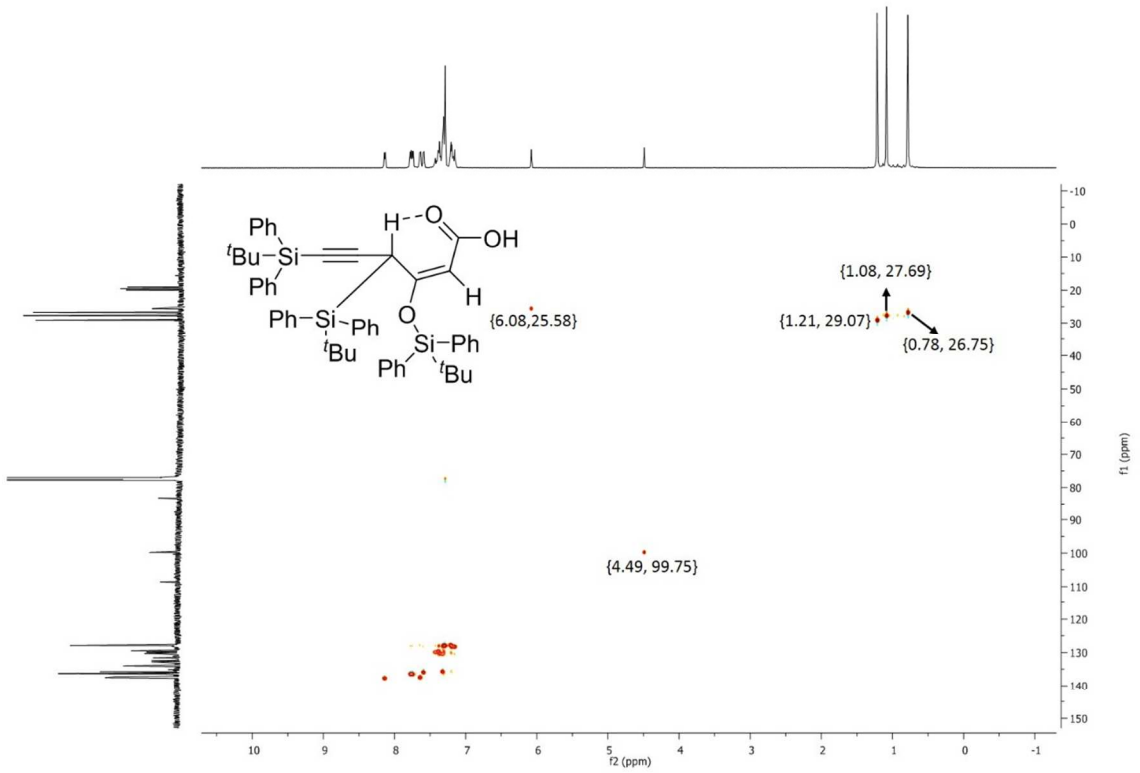
B)



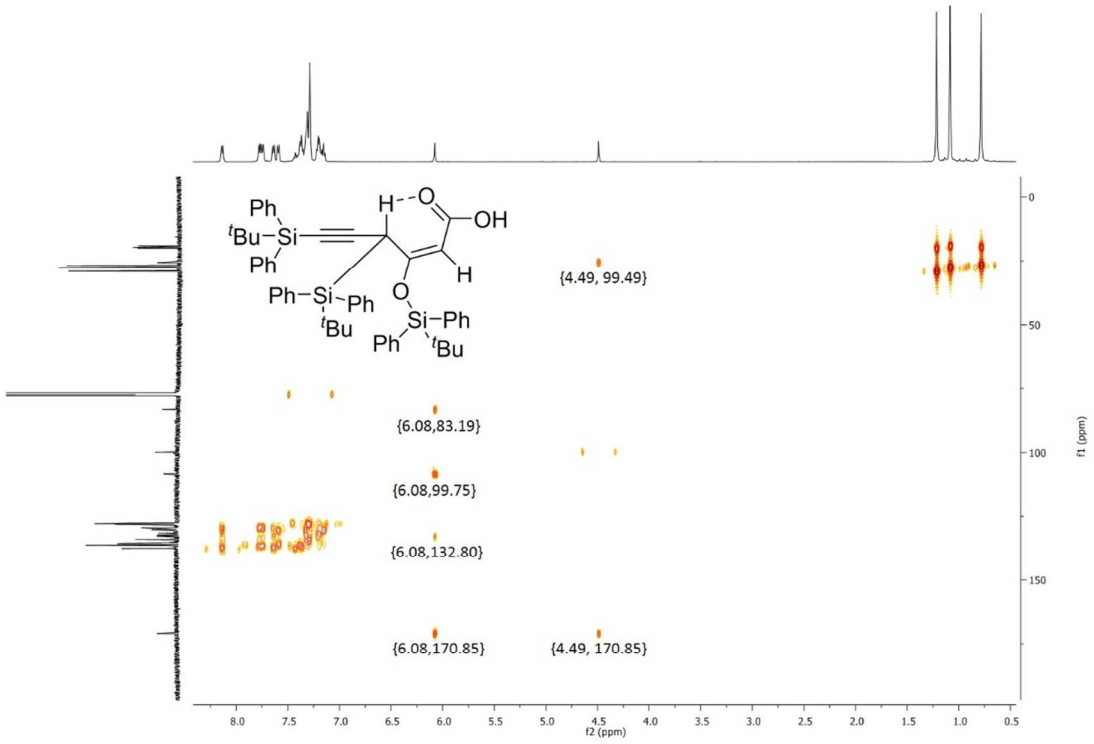
C)


-2.13
-2.74
-18.31
f1 (ppm)

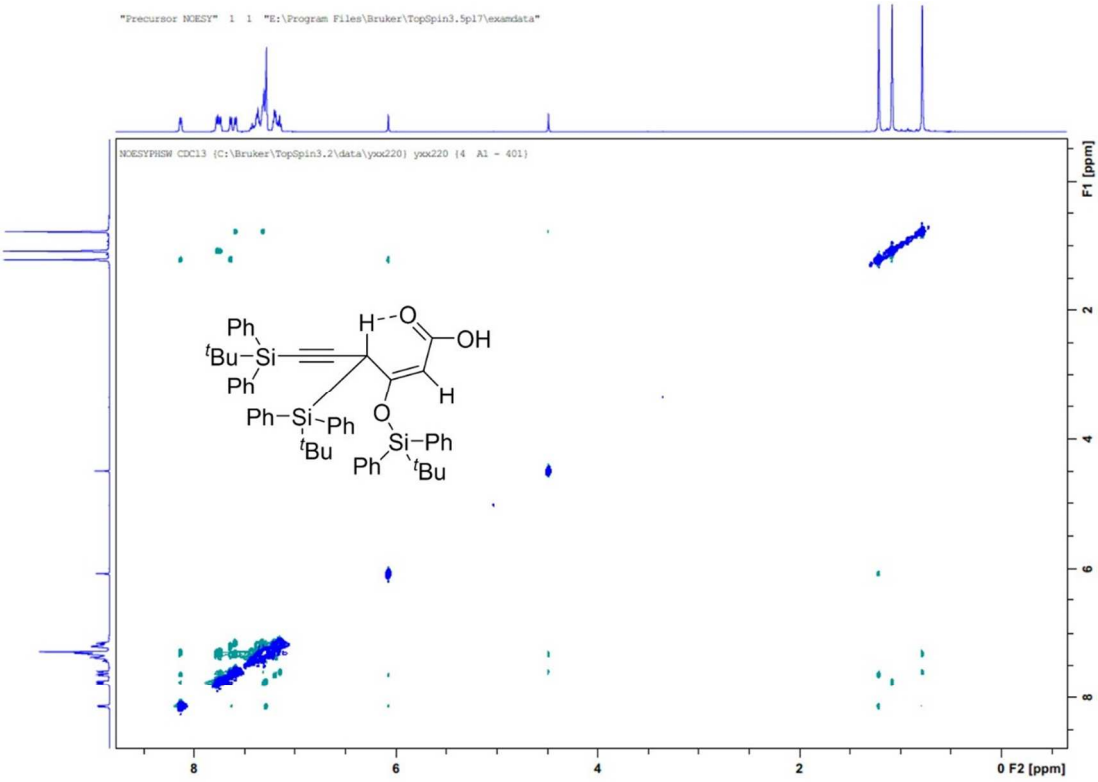
D)


{6.08,25.58}
{1.08, 27.69}
{1.21, 29.07}
{0.78, 26.75}
{4.49, 99.75}
f2 (ppm)
f1 (ppm)

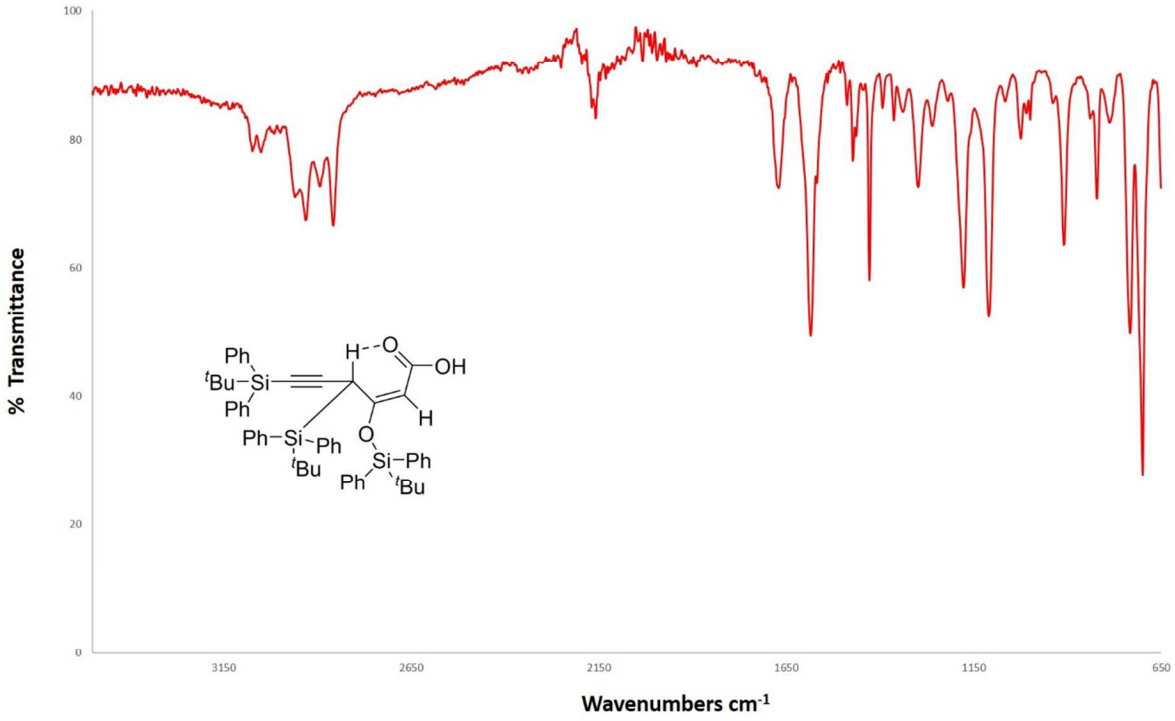
E)


{4.49, 99.49}
{6.08,83.19}
{6.08,99.75}
{6.08,132.80}
{6.08,170.85}
{4.49, 170.85}
f2 (ppm)
f1 (ppm)

F)


F1 [ppm]
0 F2 [ppm]

G)


% Transmittance
100
80
60
40
20
0
3150
2650
2150
1650
1150
650
Wavenumbers cm-1
Ph
tBu–Si
Ph
H
O
OH
H
Ph–Si–Ph
tBu
O
Si–Ph
Ph
tBu

H)

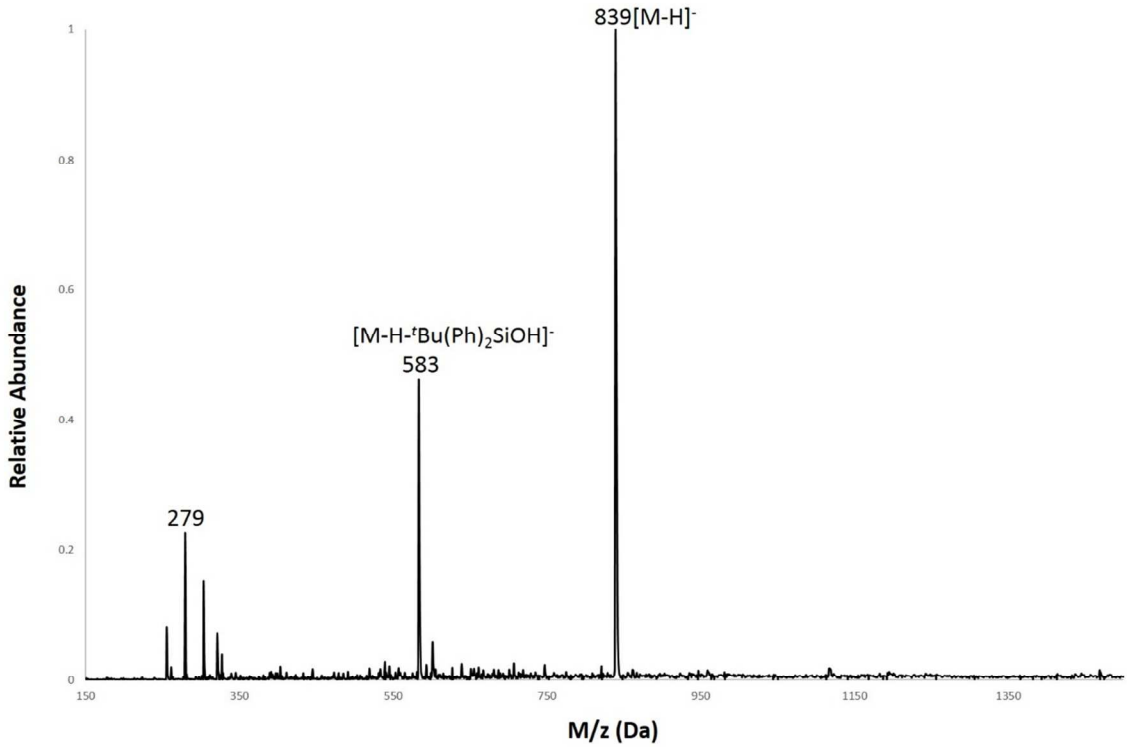
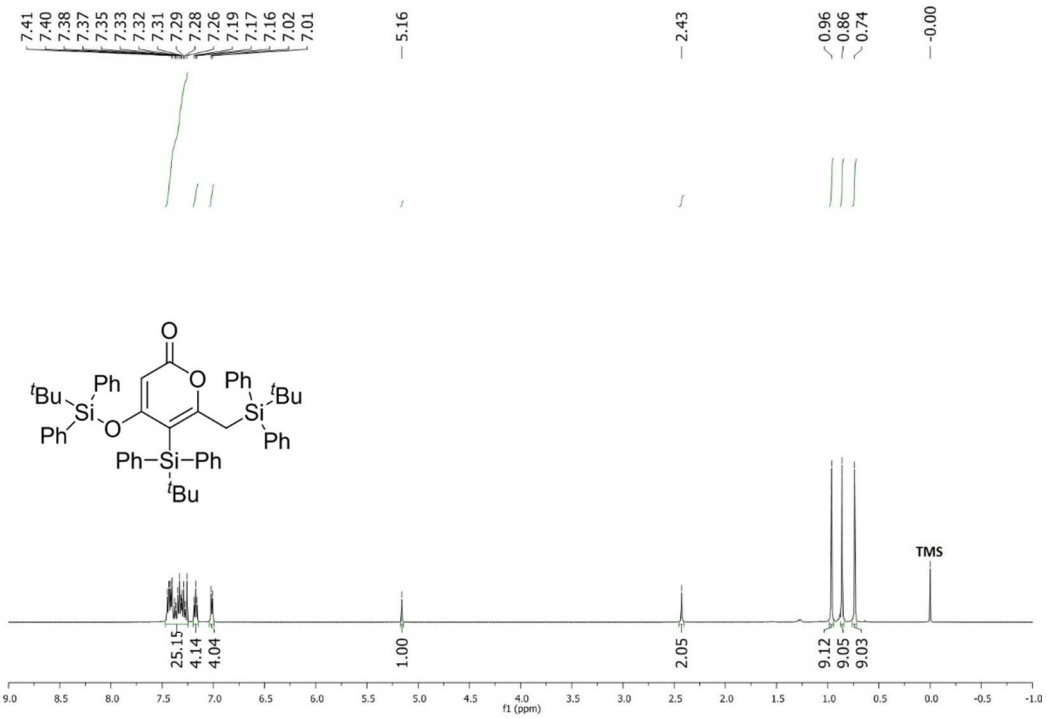
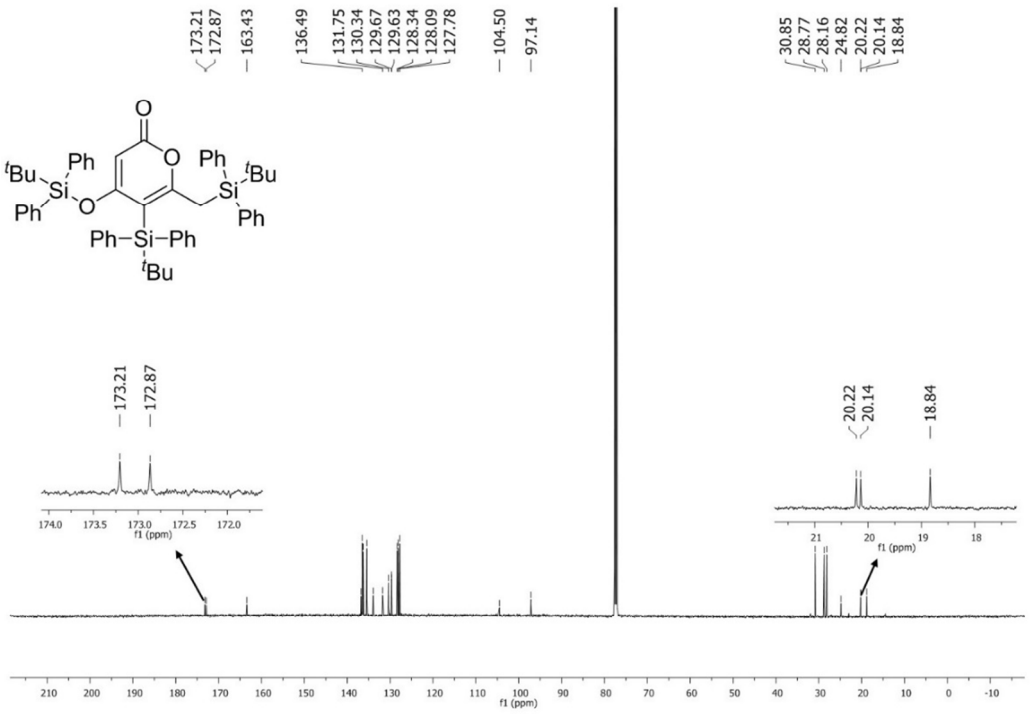

839[M-H]-
[M-H-tBu(Ph)2SiOH]-
583
279
Relative Abundance
1
0.8
0.6
0.4
0.2
0
150
350
550
750
950
1150
1350
M/z (Da)

Figure S3: Characterizatin of **3**: A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) HSQC NMR; E) HMBC NMR; F) NOESY NMR; G) FTIR; H) Electronspray ionlization mass spectrum.

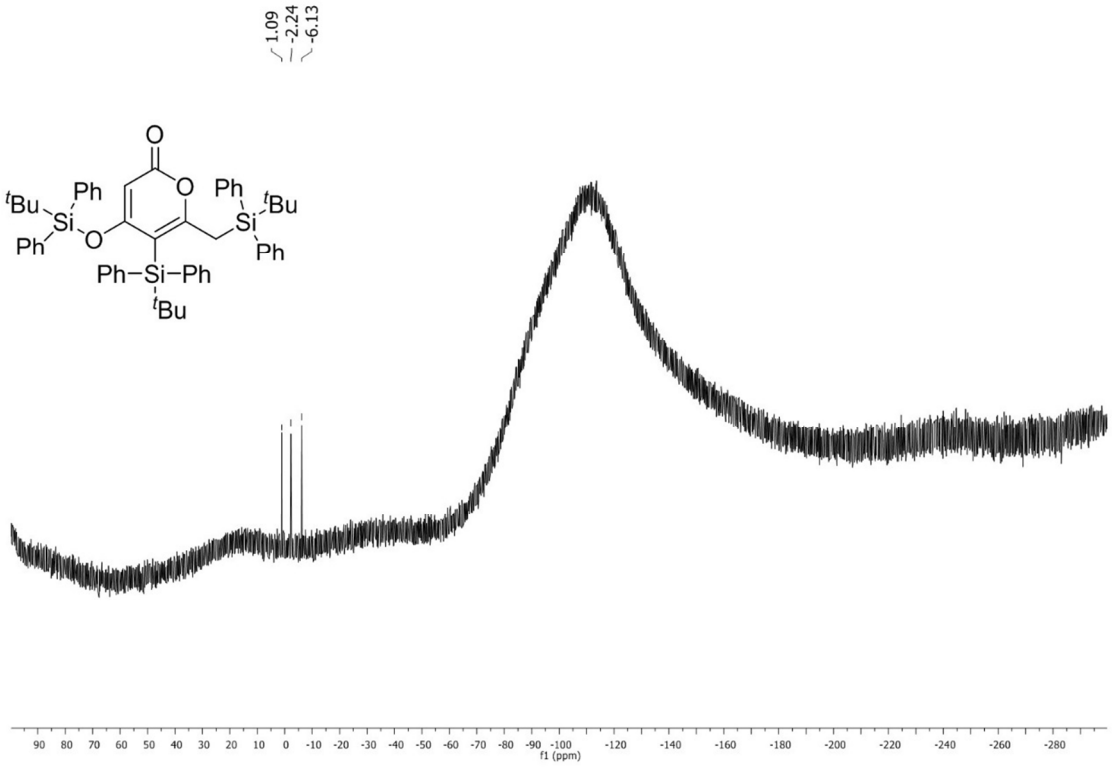
A)



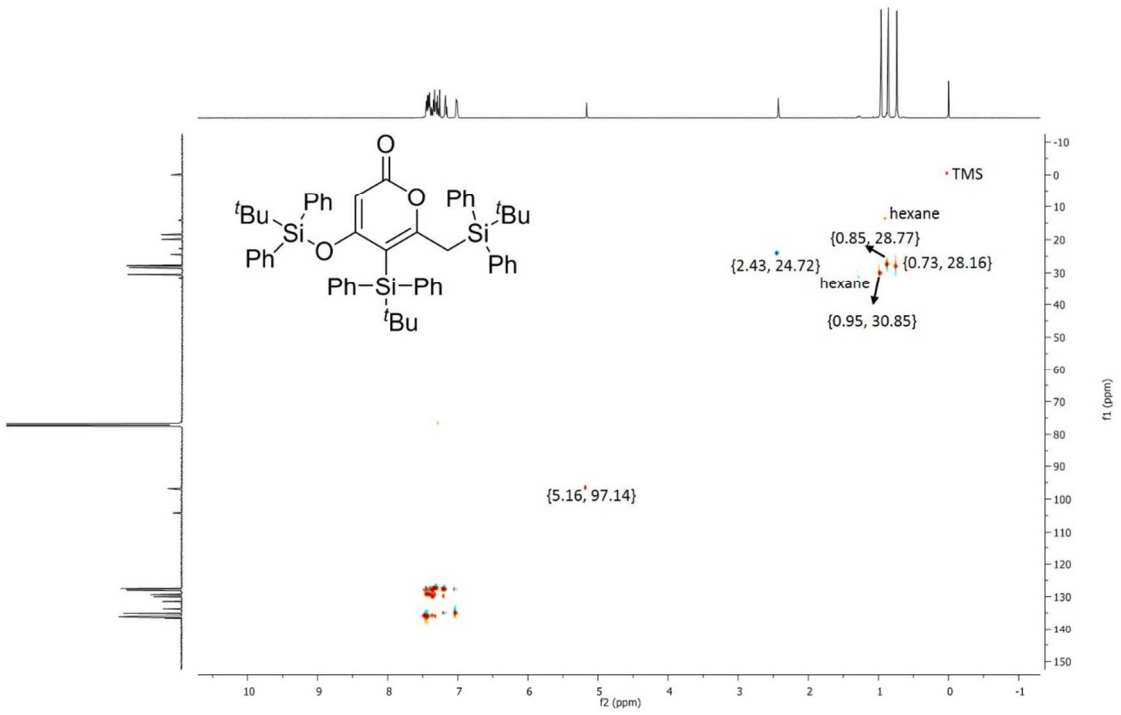
B)



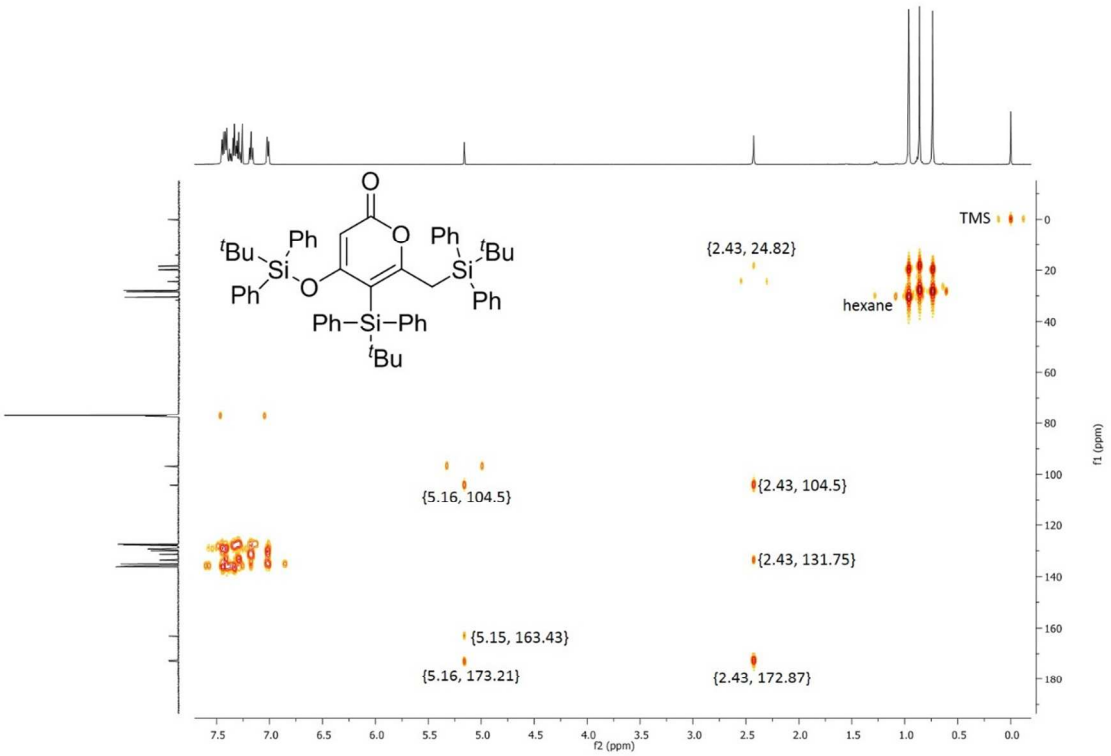
C)


1.09
2.24
6.13
f1 (ppm)

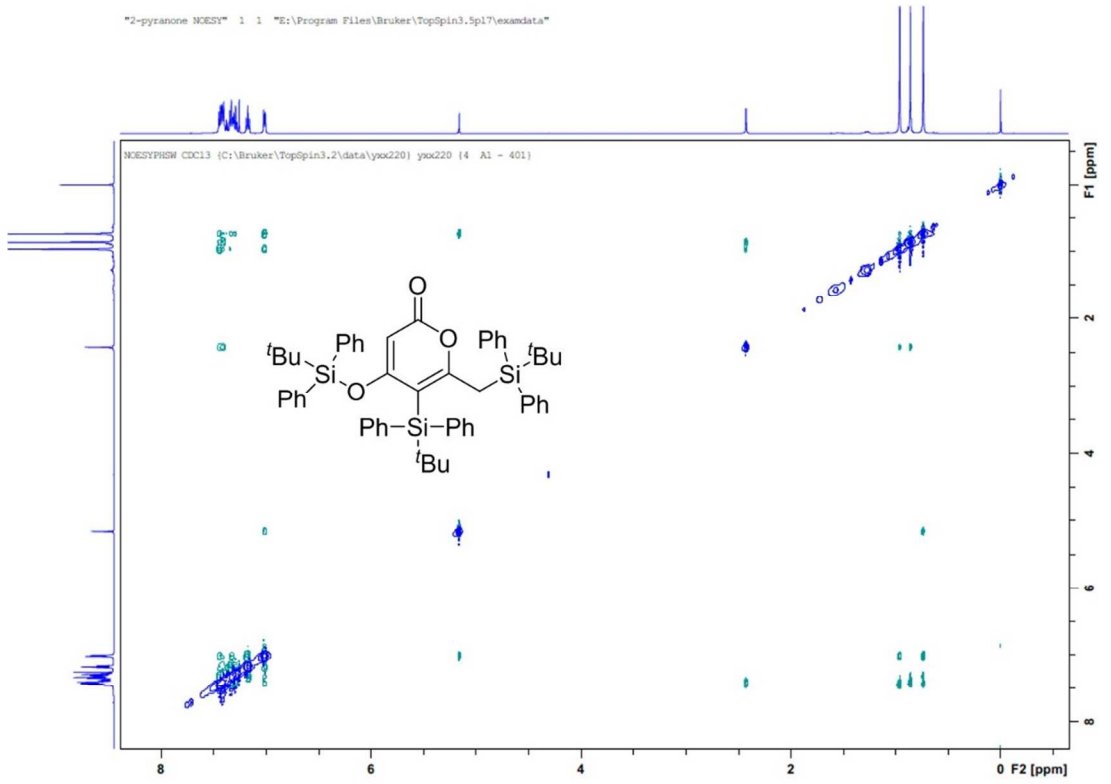
D)


TMS
hexane
{0.85, 28.77}
{2.43, 24.72}
{0.73, 28.16}
hexane
{0.95, 30.85}
{5.16, 97.14}
f2 (ppm)
f1 (ppm)

E)


TMS
hexane
{2.43, 24.82}
{5.16, 104.5}
{2.43, 104.5}
{2.43, 131.75}
{5.15, 163.43}
{5.16, 173.21}
{2.43, 172.87}
f2 (ppm)
f1 (ppm)

F)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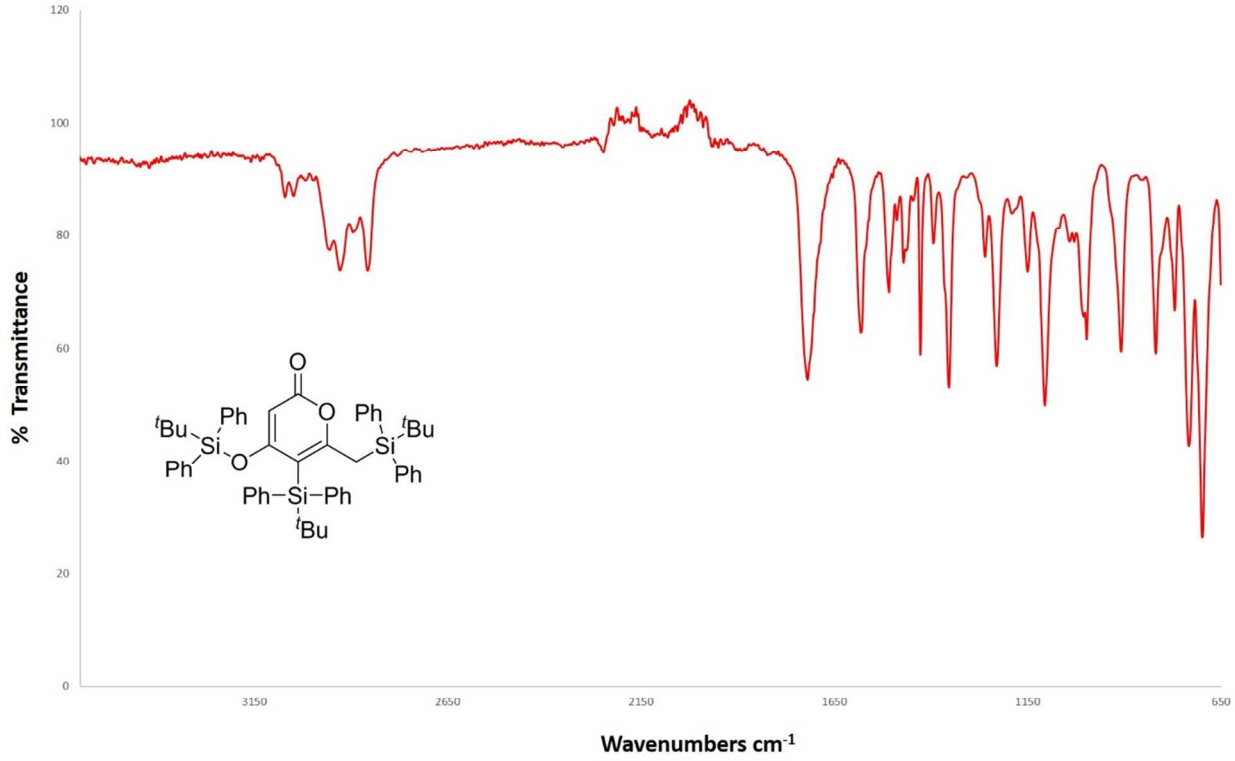
NOESYPHSW CDC13 (C:\Bruker\TopSpin3.2\data\yxx220) yxx220 (4 A1 - 401)
F1 [ppm]
F2 [ppm]

G)


120
100
80
60
40
20
0
% Transmittance
3150
2650
2150
1650
1150
650
Wavenumbers cm-1
O
O
Ph
tBu
Si
O
Ph
Ph
Si
tBu
Ph
Ph–Si–Ph
tBu

H)

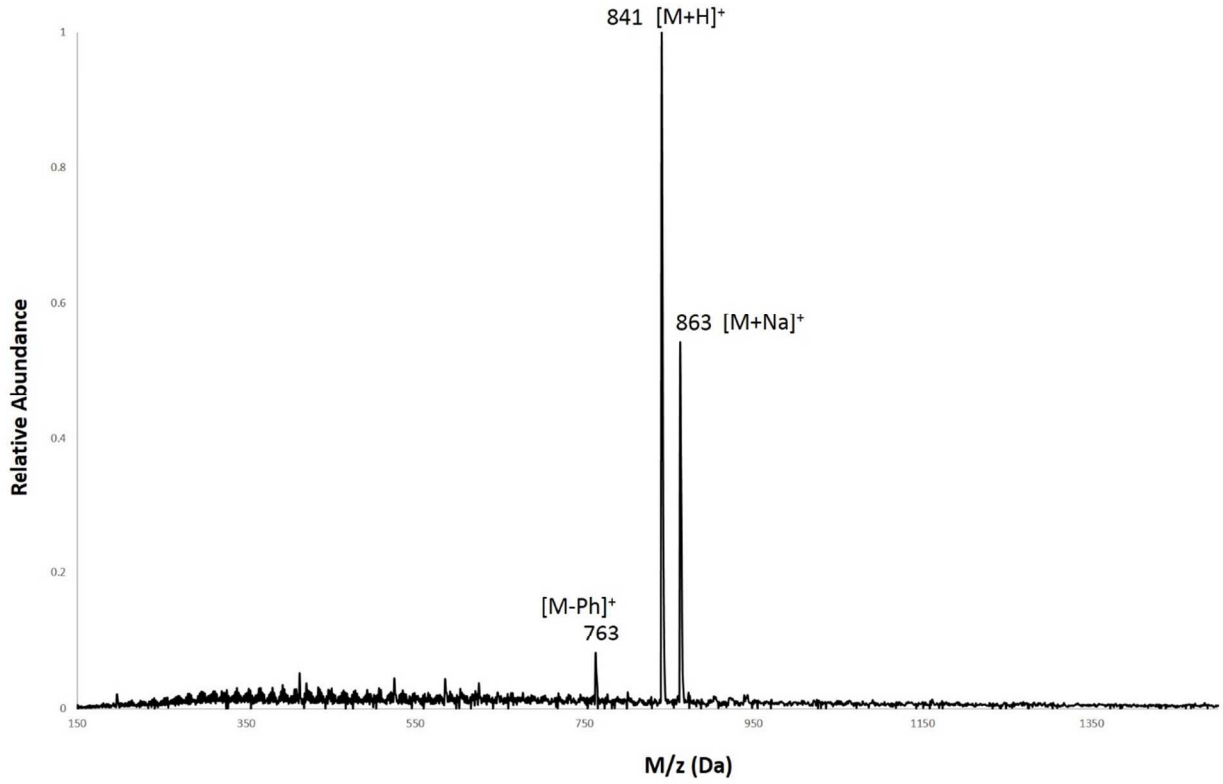

841 [M+H]+
863 [M+Na]+
[M-Ph]+
763
1
0.8
0.6
0.4
0.2
0
Relative Abundance
150
350
550
750
950
1150
1350
M/z (Da)

Figure S4: Full ^{1}H NMR spectra before and after 13 and 78 hours of heating **2** in dioxane with the chemical shifts of starting material **2**, product **3**, intermediate **6**, and byproduct **10** identified by boxes of the relevant colors.

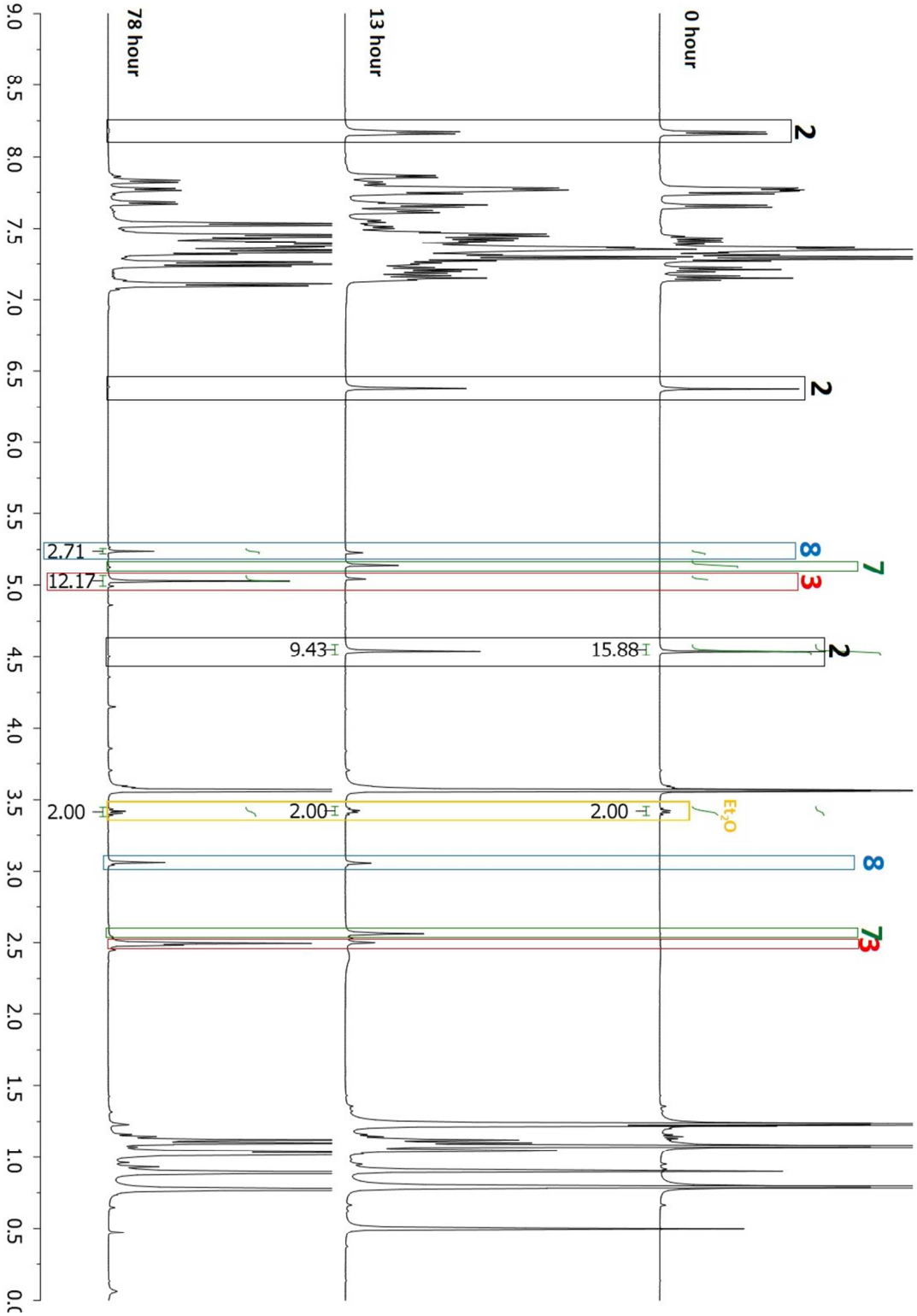
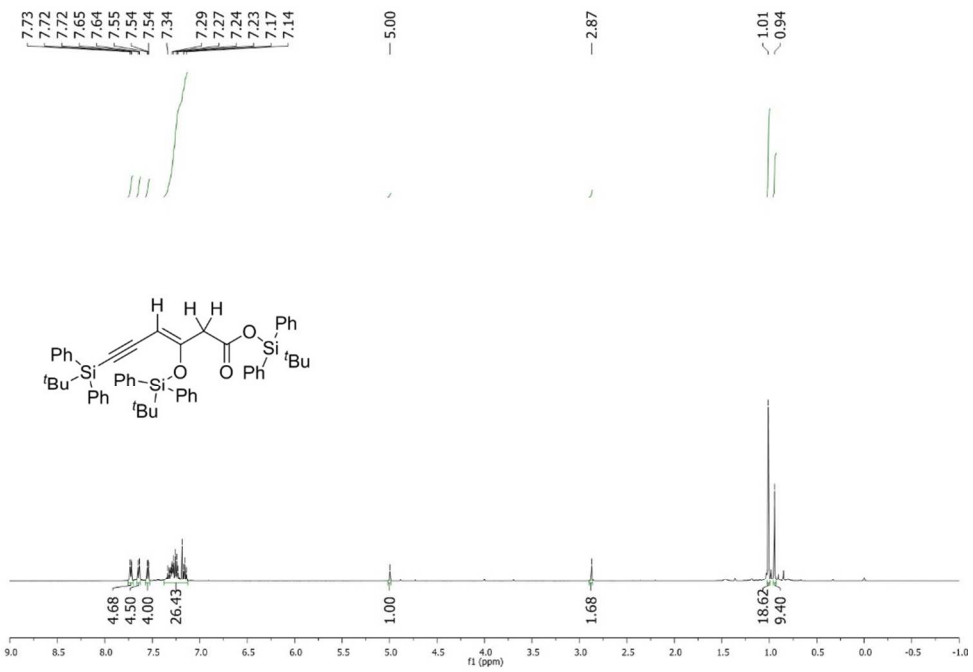
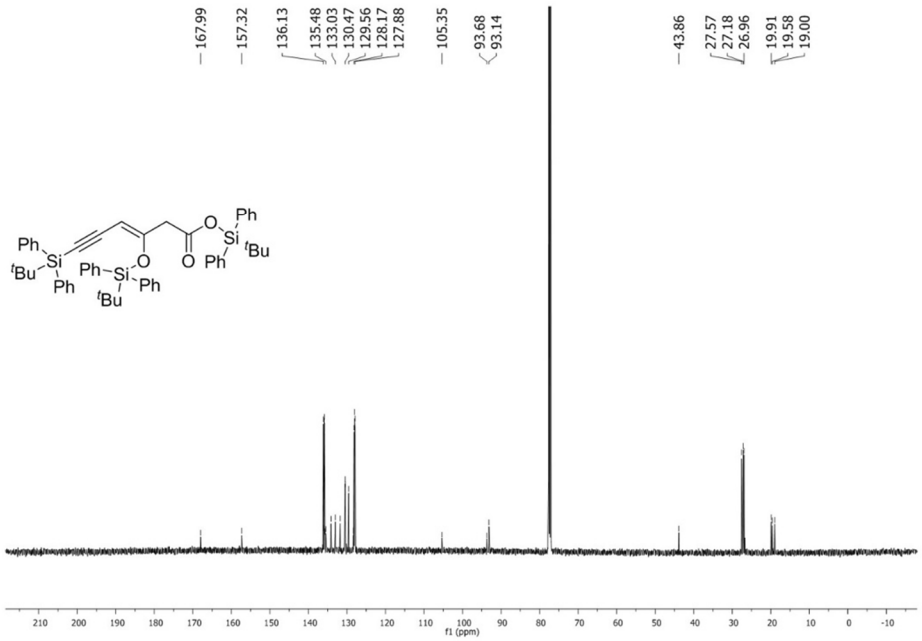


Figure S5. Characterization of **10**: A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) HSQC NMR; E) HMBC NMR; F) NOESY NMR; G) FTIR; H) Electronspray ionlization mass spectrum.

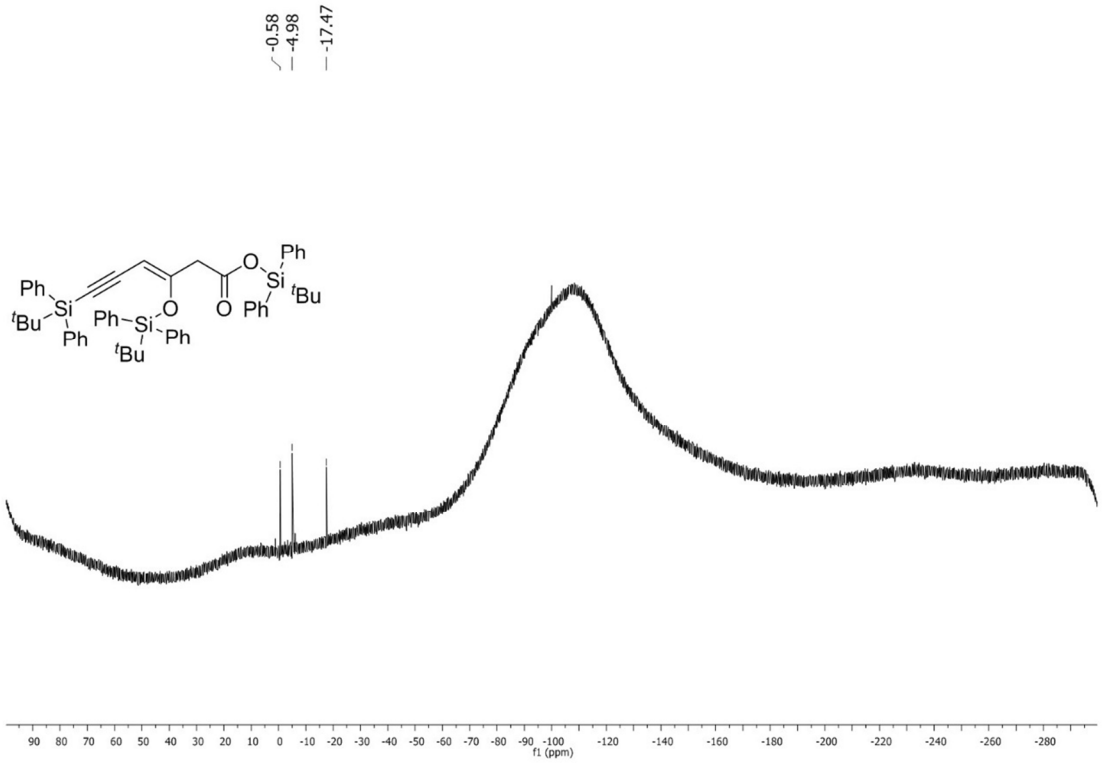
A)



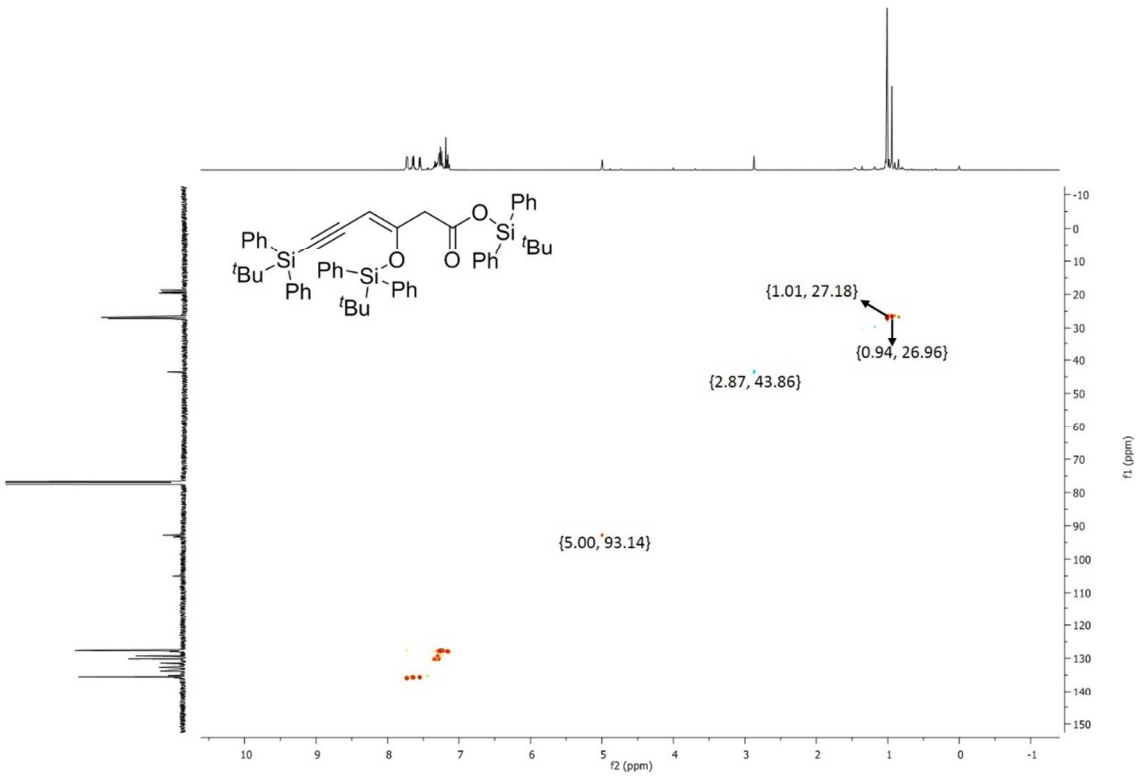
B)



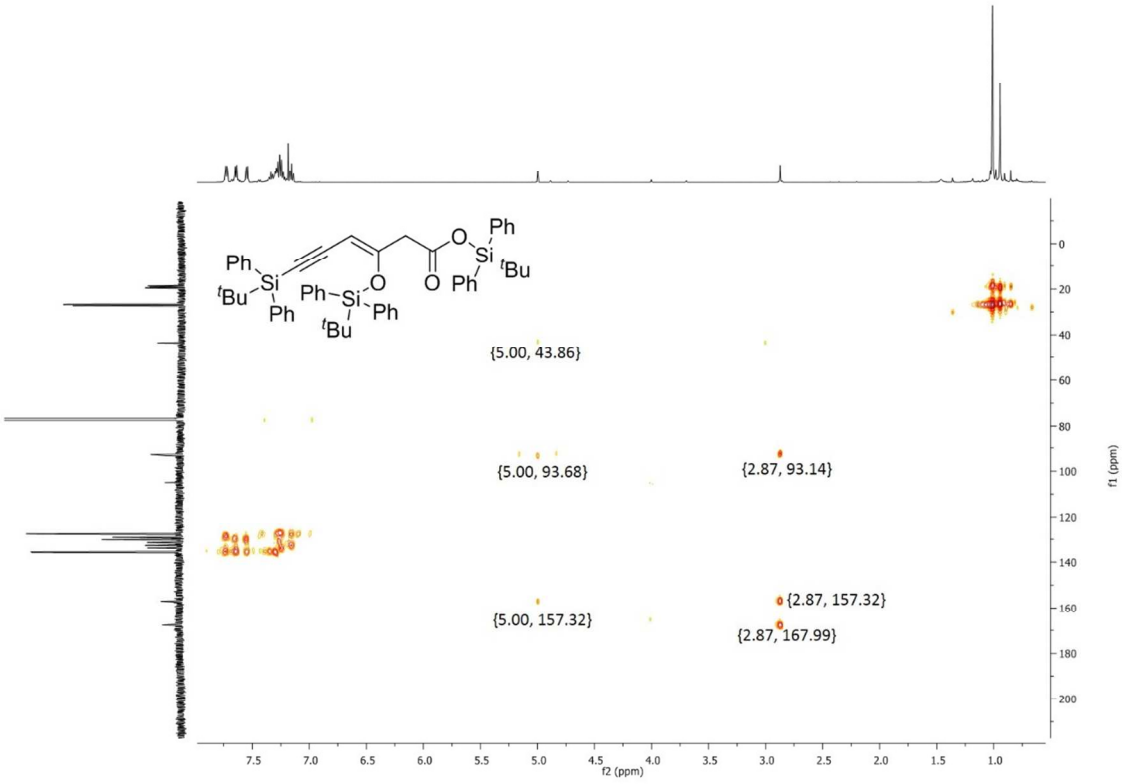
C)


-0.58
-4.98
-17.47
f1 (ppm)

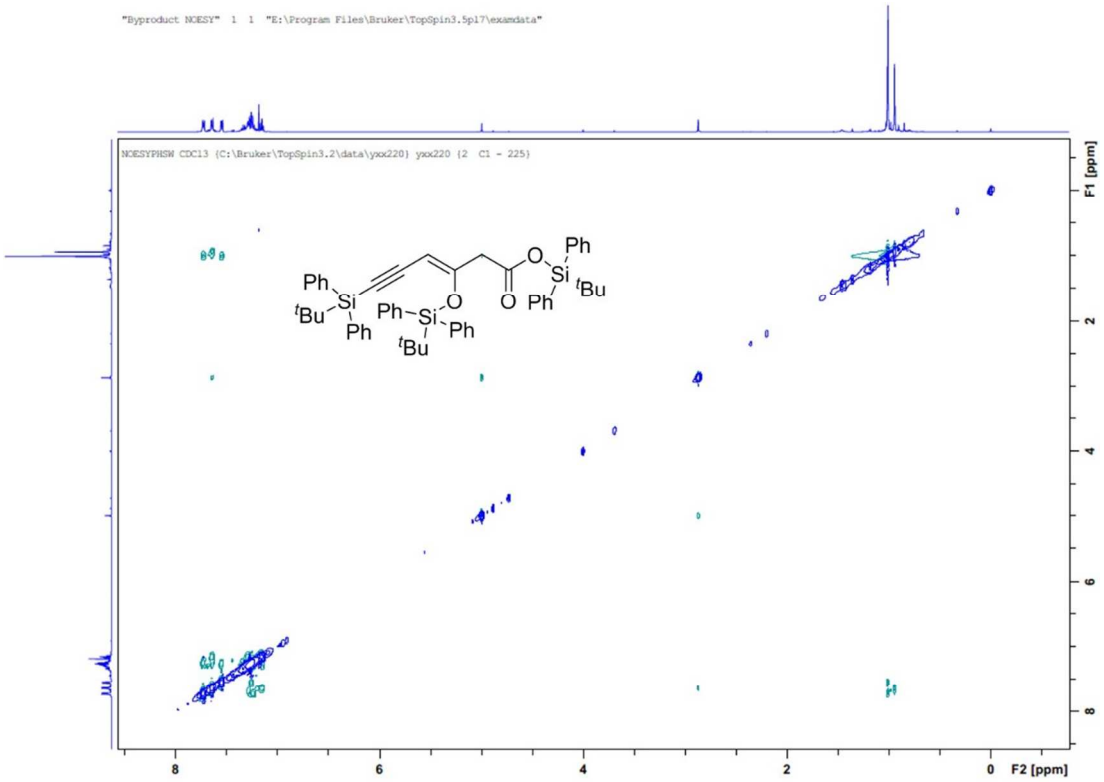
D)


{1.01, 27.18}
{0.94, 26.96}
{2.87, 43.86}
{5.00, 93.14}
f2 (ppm)
f1 (ppm)

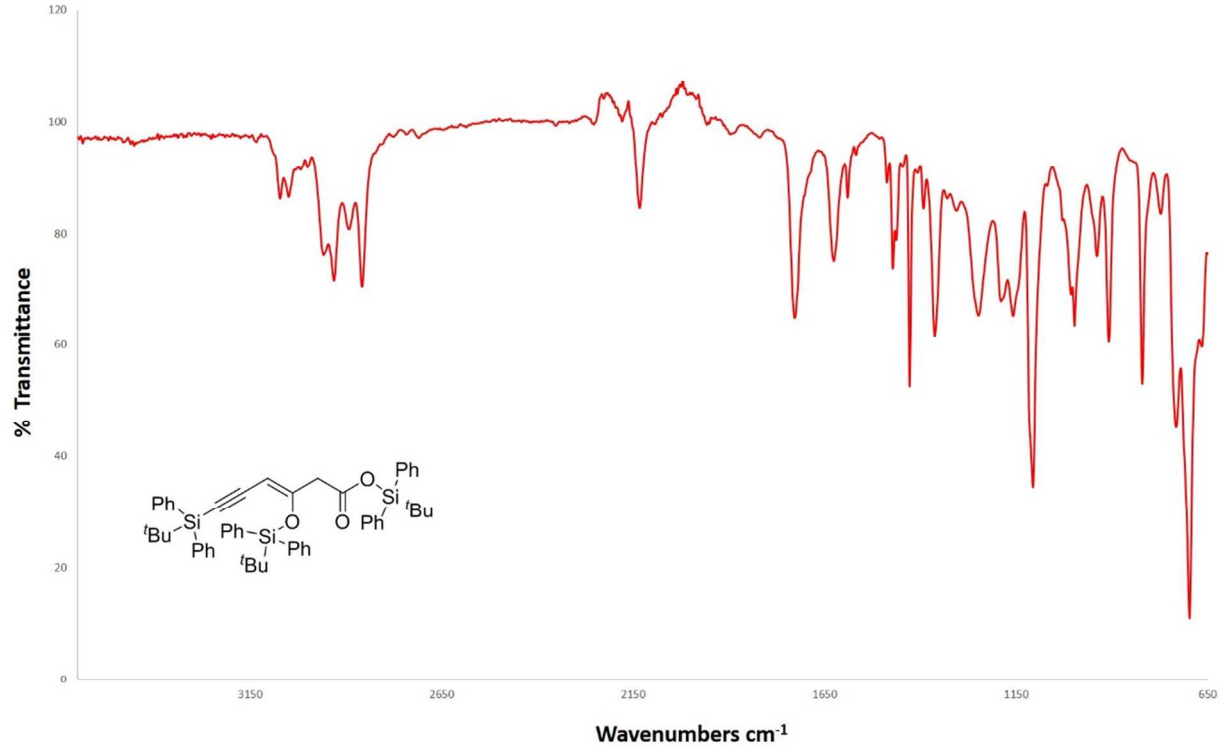
E)


{5.00, 43.86}
{5.00, 93.68}
{2.87, 93.14}
{2.87, 157.32}
{5.00, 157.32}
{2.87, 167.99}
f2 (ppm)
f1 (ppm)

F)


"Byproduct NOESY" 1 1 "E:\Program Files\Bruker\TopSpin3.5pl7\examdata"
F2 [ppm]
F1 [ppm]

G)


% Transmittance
120
100
80
60
40
20
0
3150
2650
2150
1650
1150
650
Wavenumbers cm-1

H)

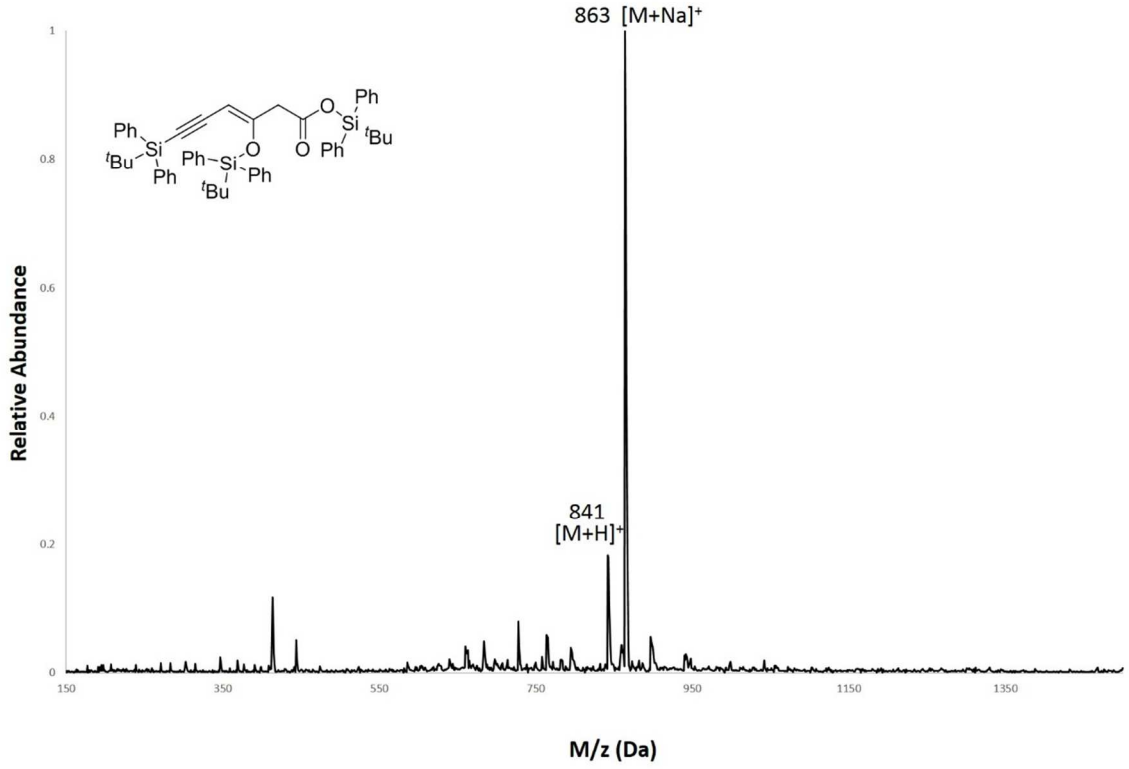
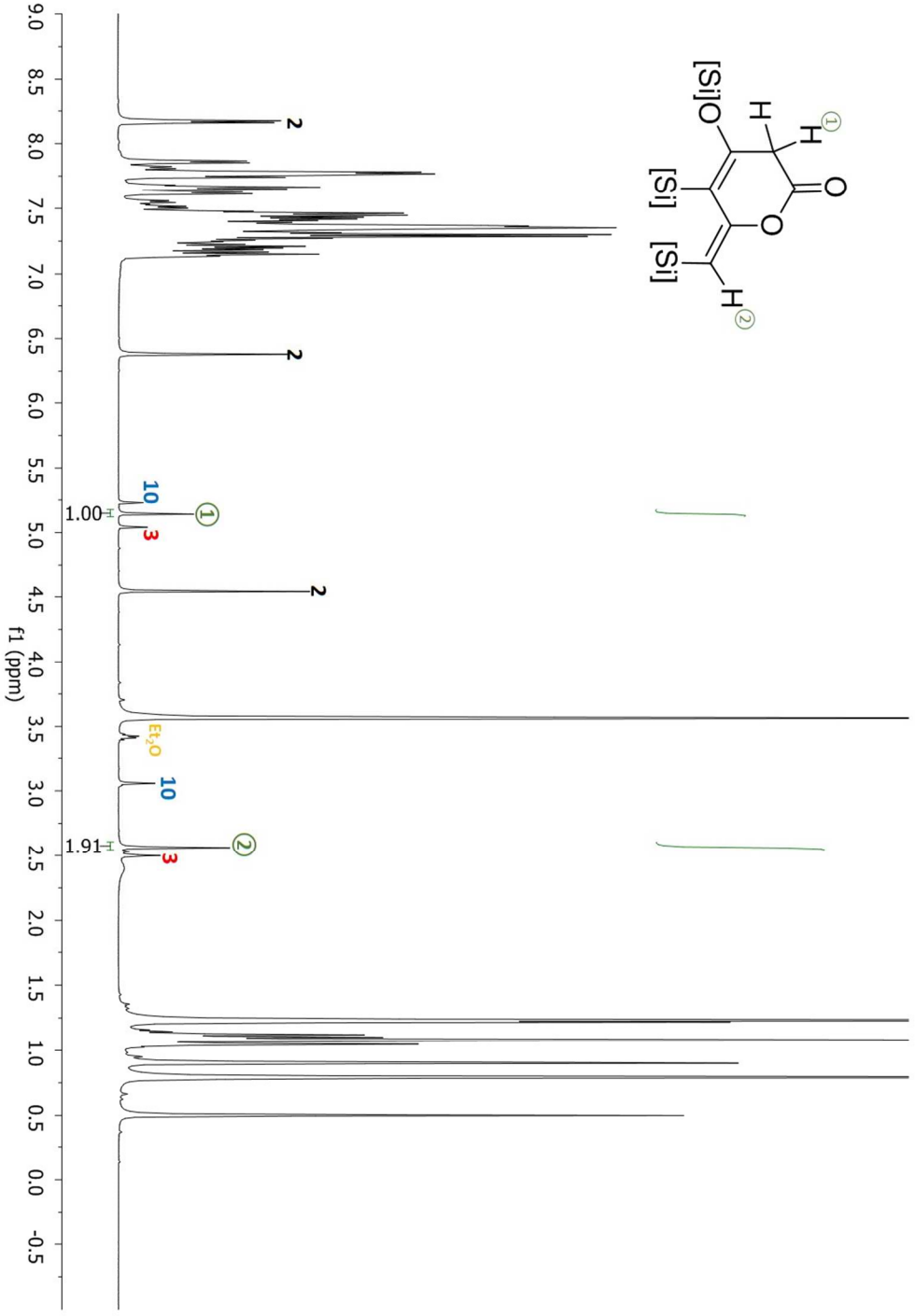
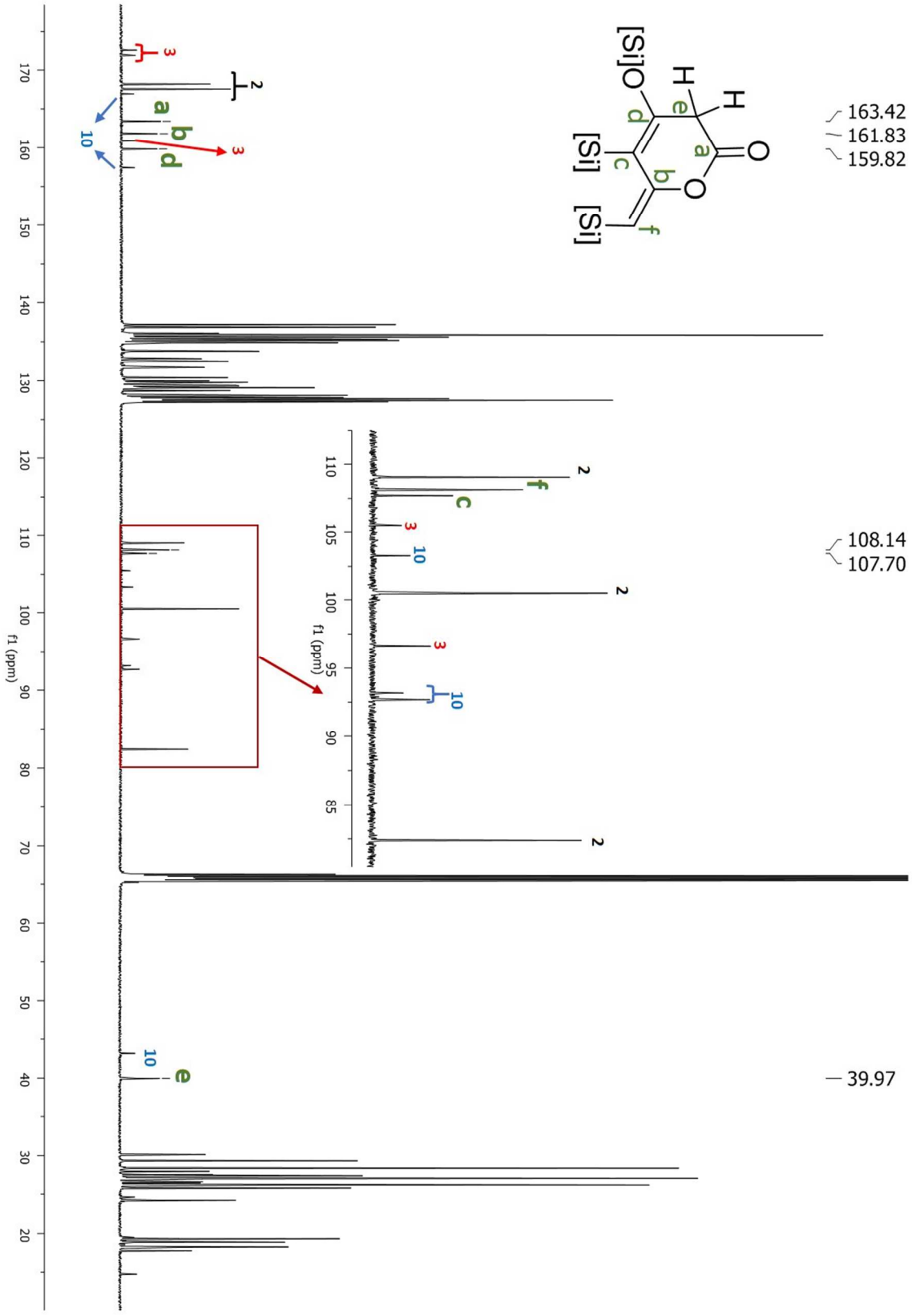

863 [M+Na]+
841
[M+H]+
Relative Abundance
1
0.8
0.6
0.4
0.2
0
150
350
550
750
950
1150
1350
M/z (Da)

Figure S6. Proposed structure of compound **6** based on NMR spectrum of the reaction mixture at 13 hours: A) ^{1}H NMR; B) ^{13}C NMR; C) HSQC NMR; D) HMBC NMR. (Peaks labeled as **2**, **10**, **3** stand for compound **2**, compound **10** and compound **3**, respectively.)

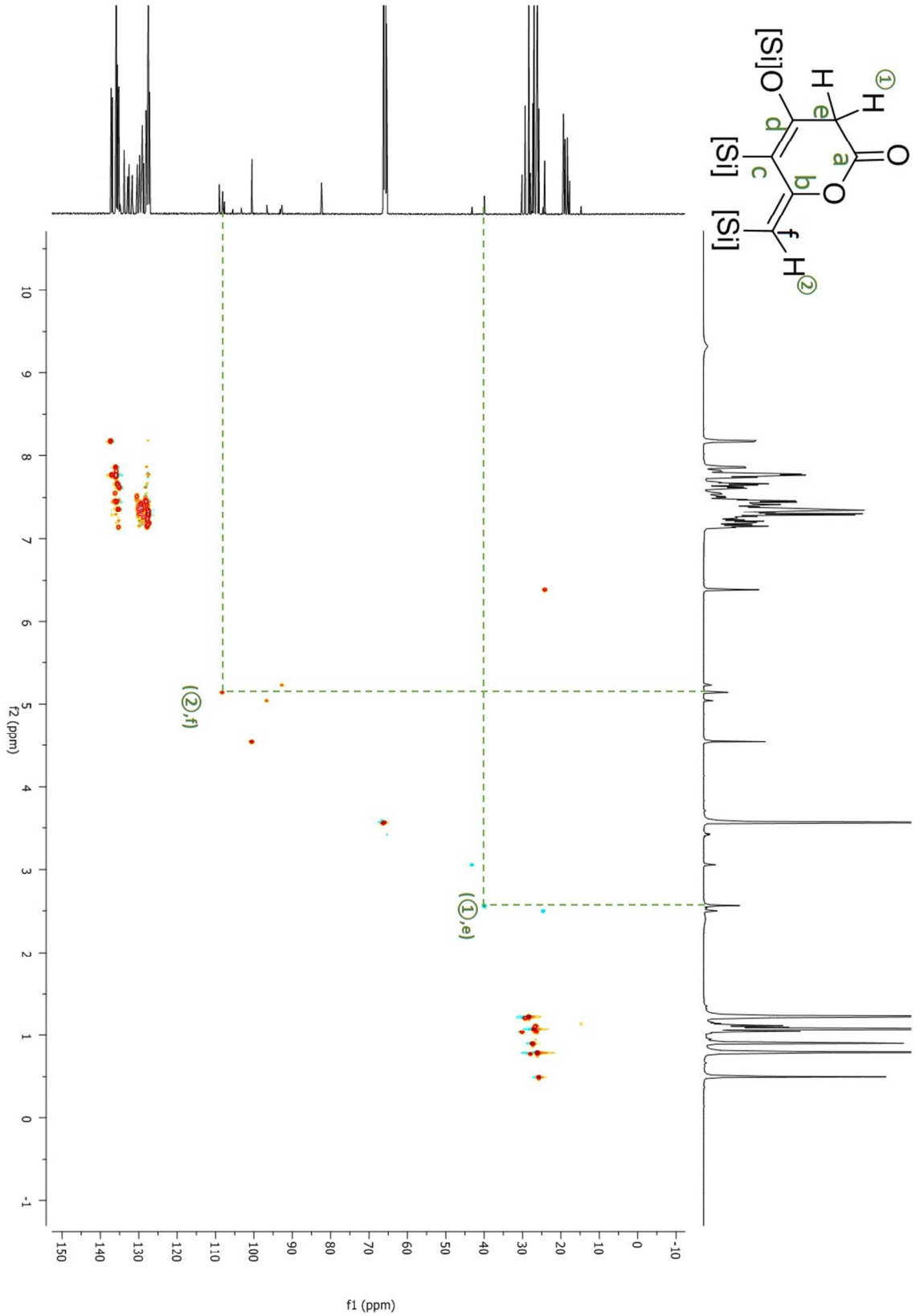
A)



B)



C)



D)

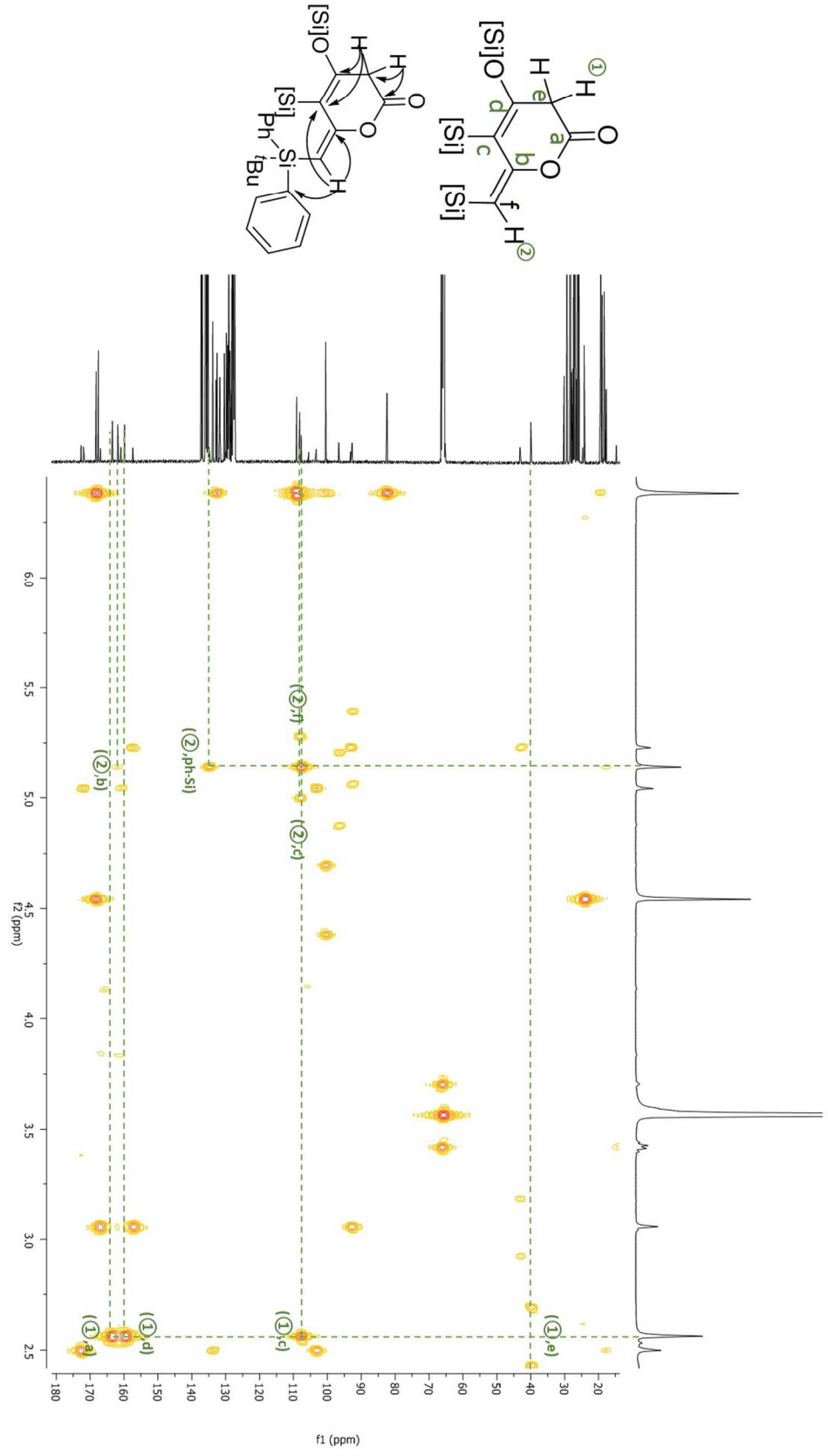
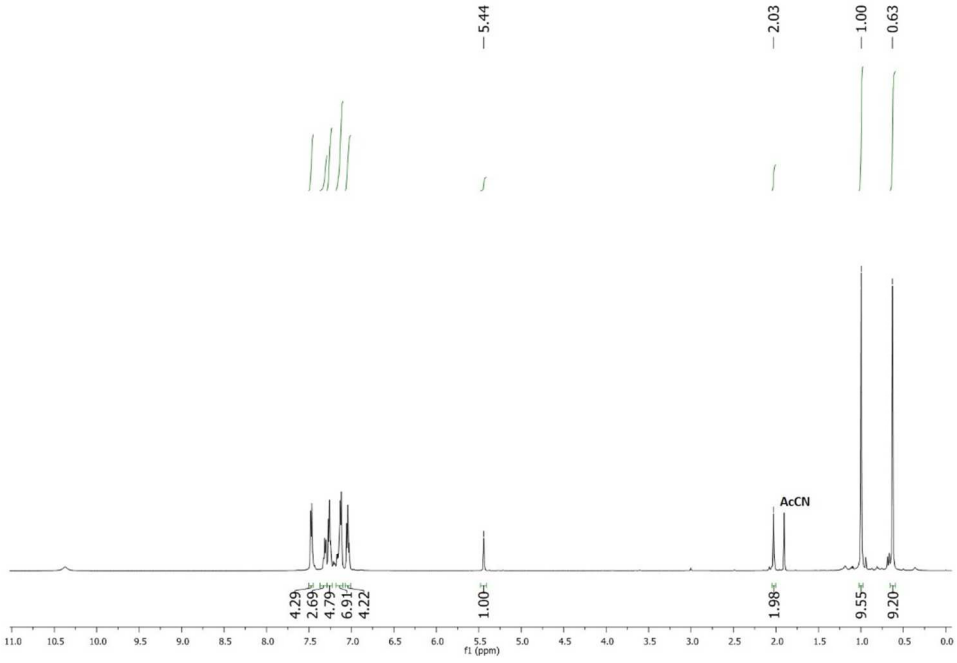
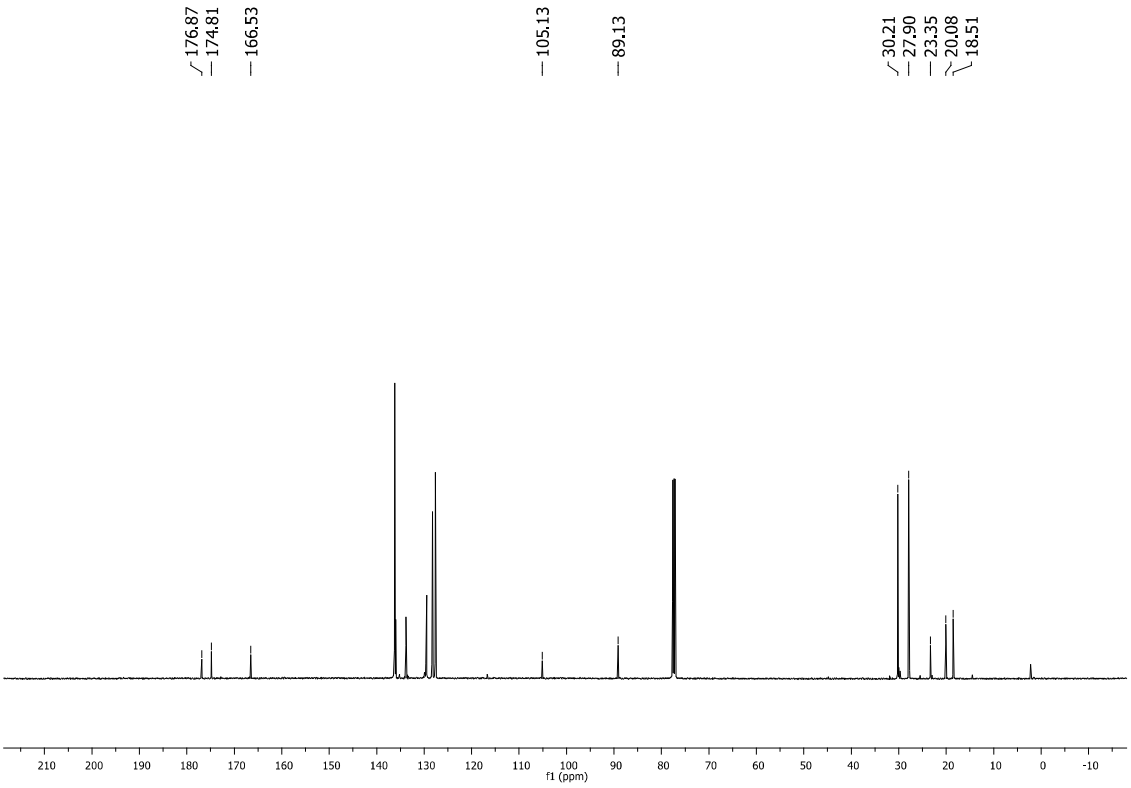

[Si]O
H
H
O
O
[Si]
Ph
Si
tBu
H
[Si]O
H
H
O
O
[Si]
[Si]
f
H②
①
a
b
c
d
e
(①),a
(①),d
(①),c
(①),e
(②),b
(②),ph-Si
(②),f
(②),d
f1 (ppm)
f2 (ppm)

Figure S7. Characterization data for compound **11**: A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) FTIR; E) Electronspray ionization mass spectrum.

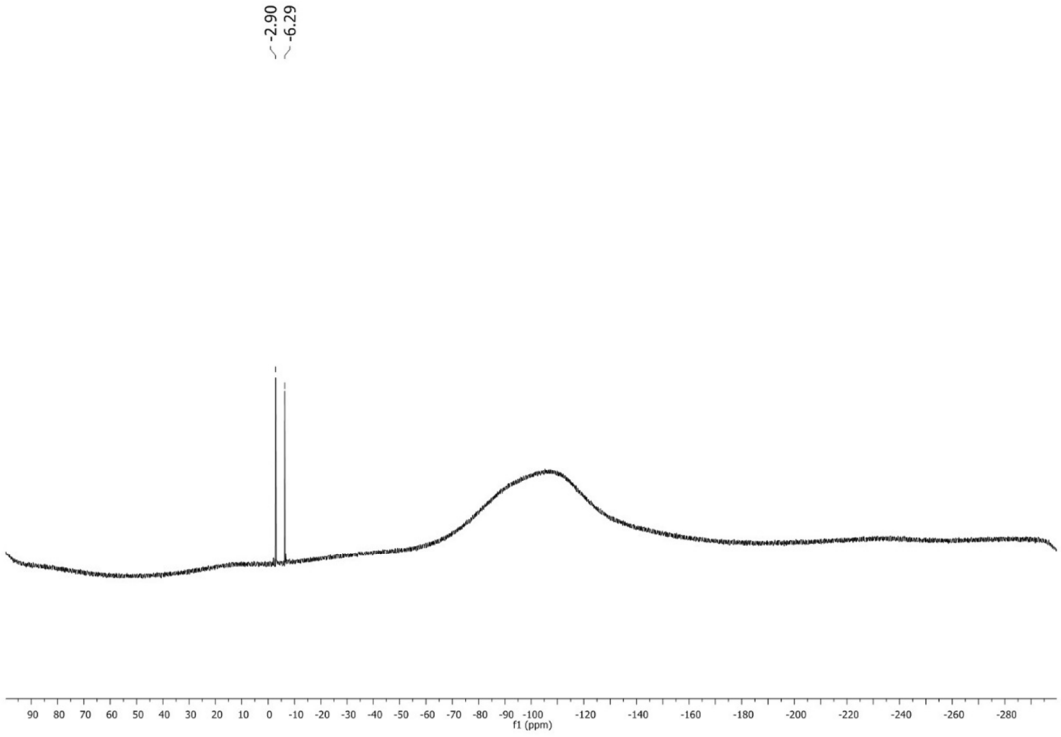
A)



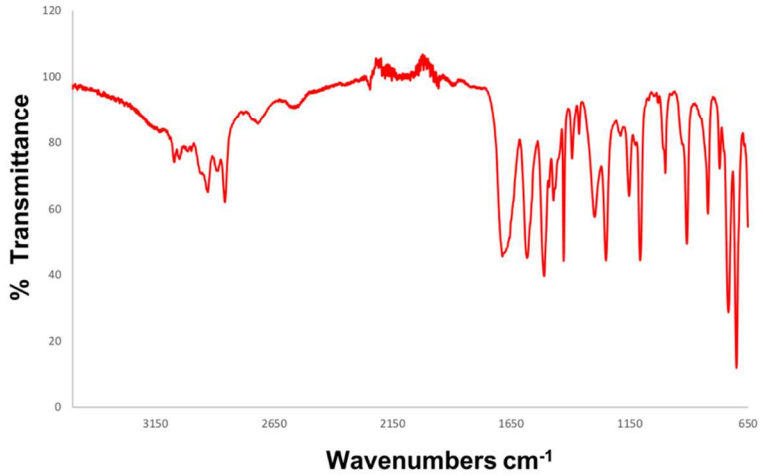
B)



C)


-2.90
-6.29
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

D)


% Transmittance
120
100
80
60
40
20
0
3150
2650
2150
1650
1150
650
Wavenumbers cm-1

E)

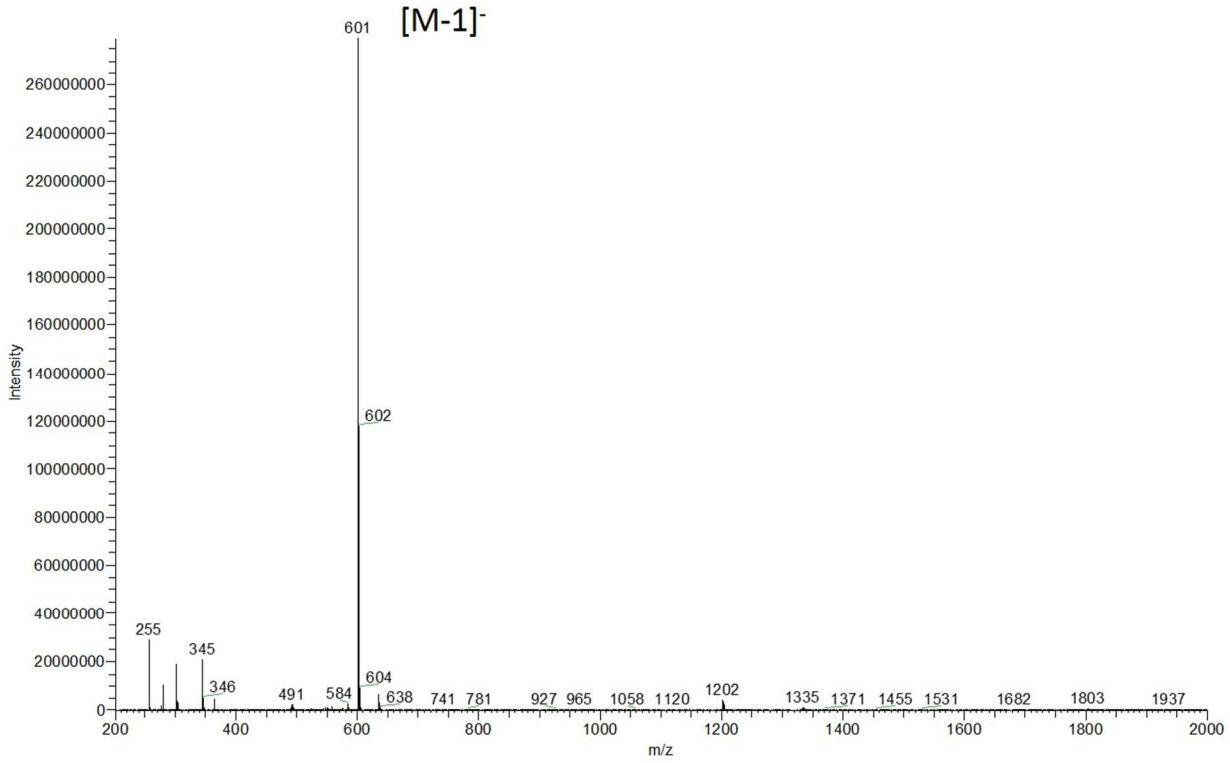
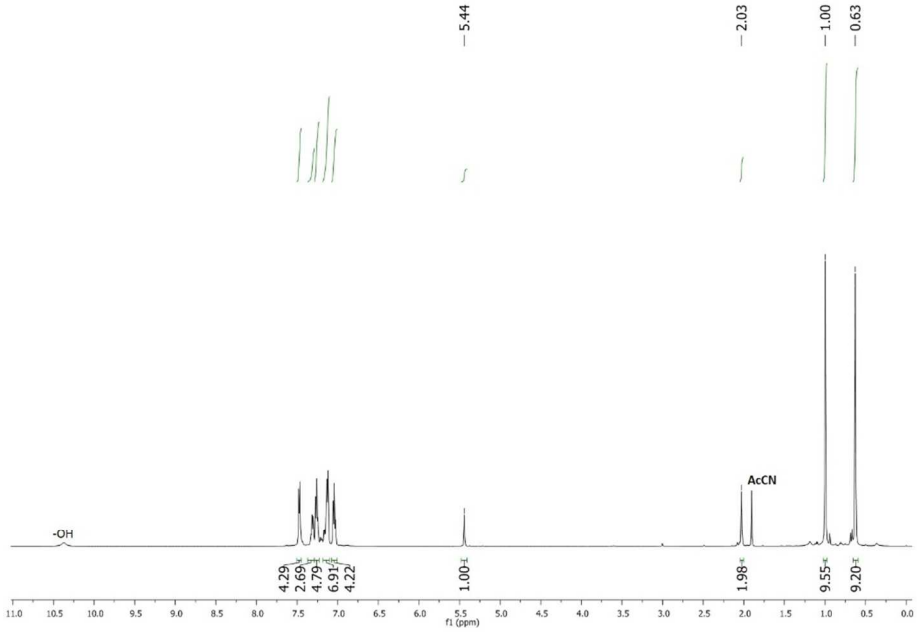
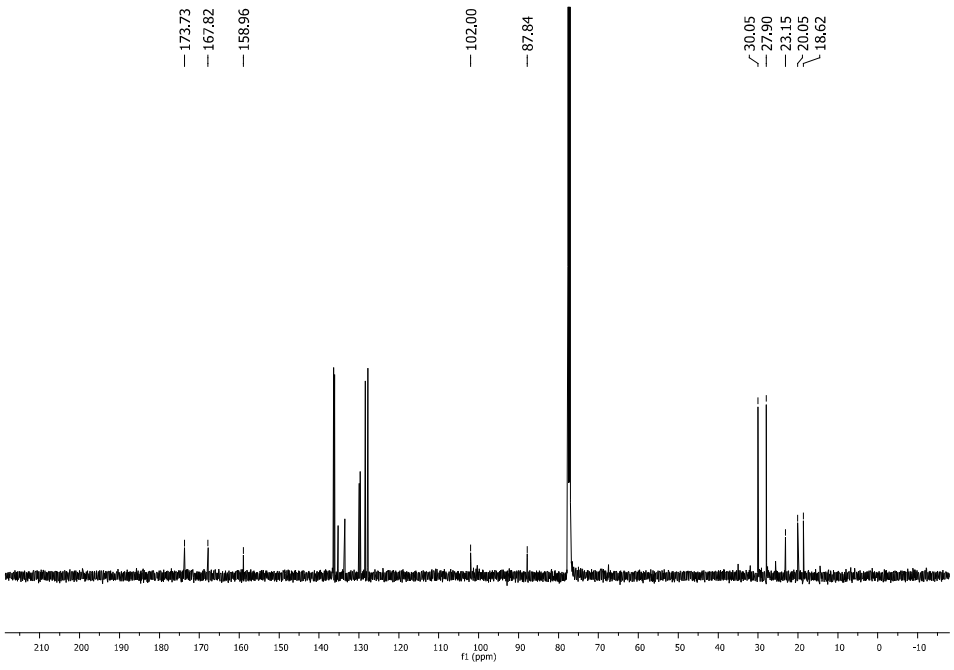

[M-1]-
601
602
604
255
345
346
491
584
638
741
781
927
965
1058
1120
1202
1335
1371
1455
1531
1682
1803
1937
Intensity
m/z
0
20000000
40000000
60000000
80000000
100000000
120000000
140000000
160000000
180000000
200000000
220000000
240000000
260000000
200
400
600
800
1000
1200
1400
1600
1800
2000

Figure S8. Characterization data for compound **12**: A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) FTIR; E) Electronspray ionlization mass spectrum.

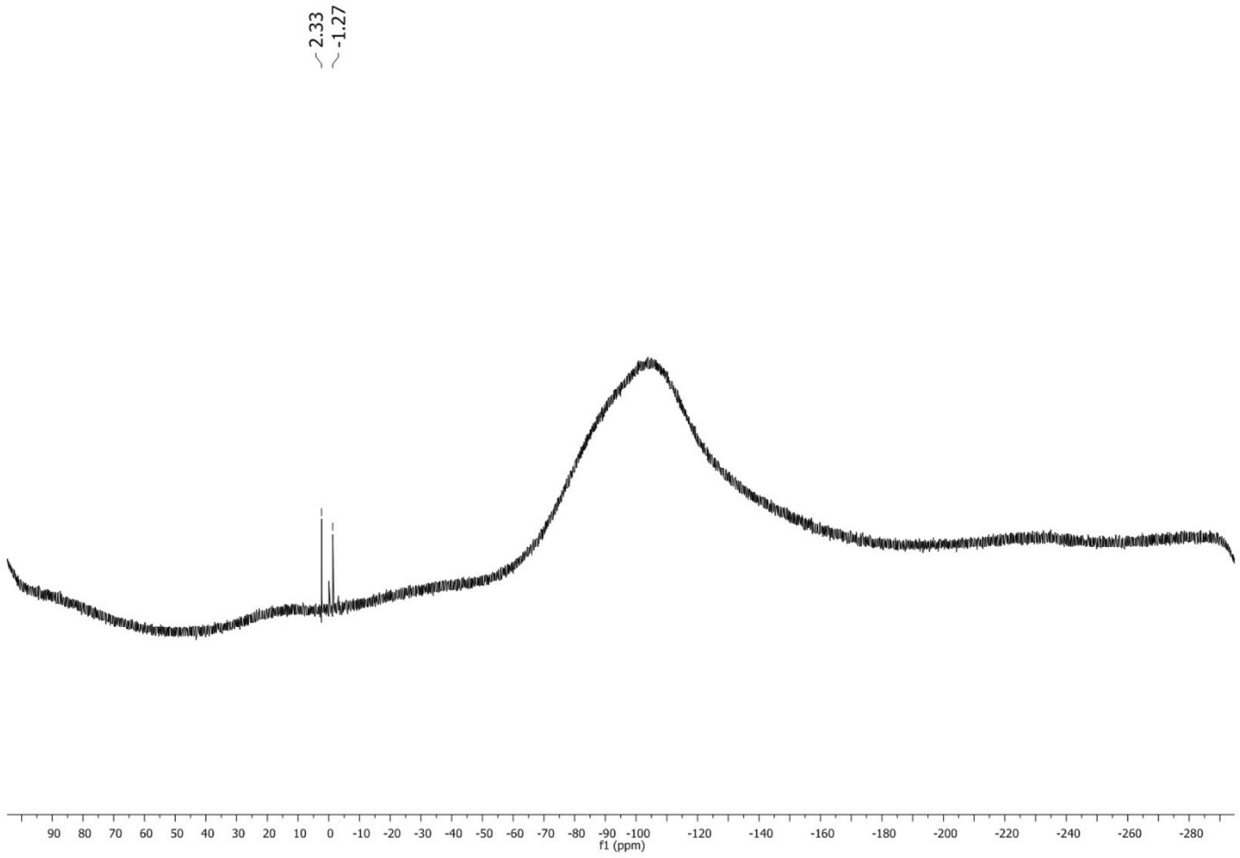
A)



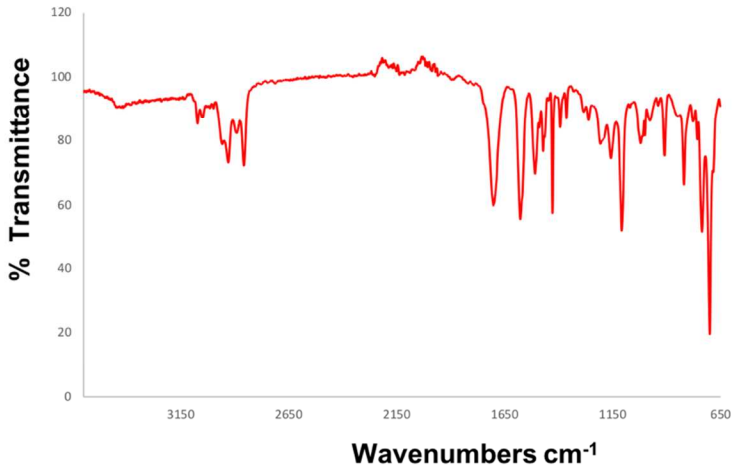
B)



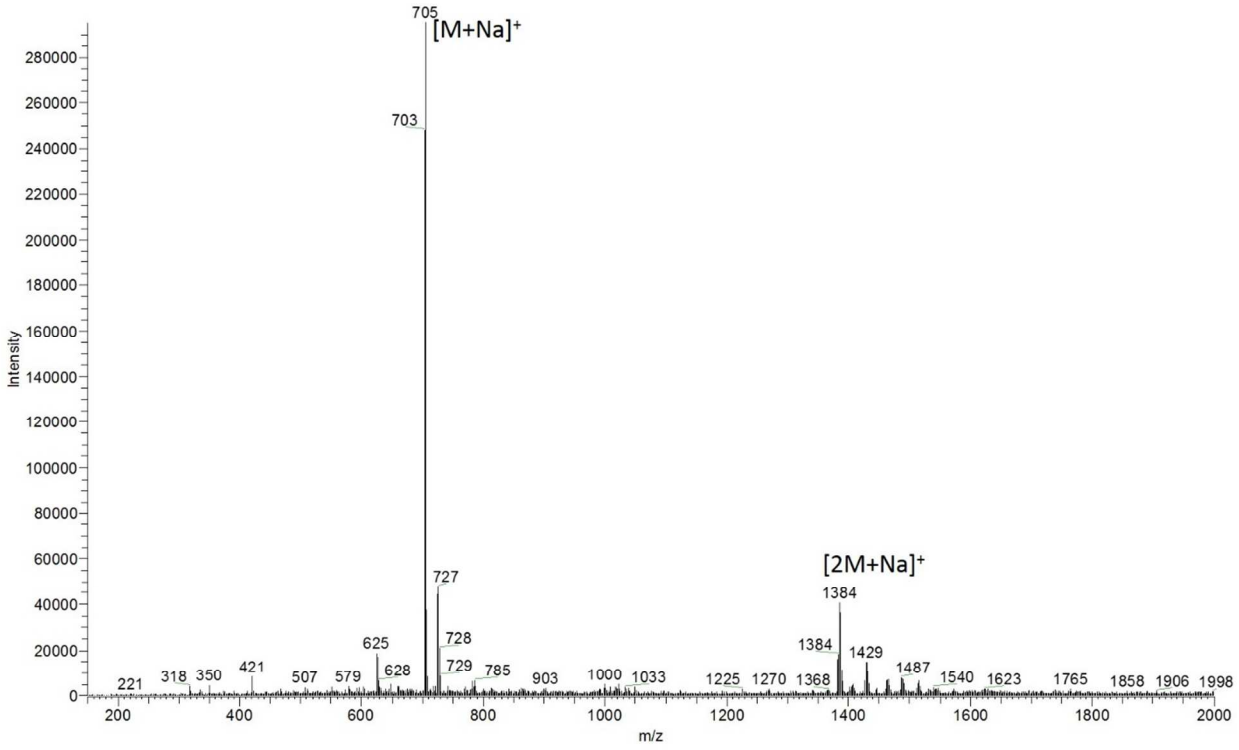
C)


2.33
-1.27
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

D)


% Transmittance
120
100
80
60
40
20
0
3150
2650
2150
1650
1150
650
Wavenumbers cm-1

E)


705
[M+Na]+
703
727
728
625
729
628
785
[2M+Na]+
1384
1384
1429
1487
Intensity
m/z
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
200
400
600
800
1000
1200
1400
1600
1800
2000
221
318
350
421
507
579
903
1000
1033
1225
1270
1368
1540
1623
1765
1858
1906
1998

Appendix 1. XRD characterization data. The thermal ellipsoid probability of the X-ray structures is 50%.

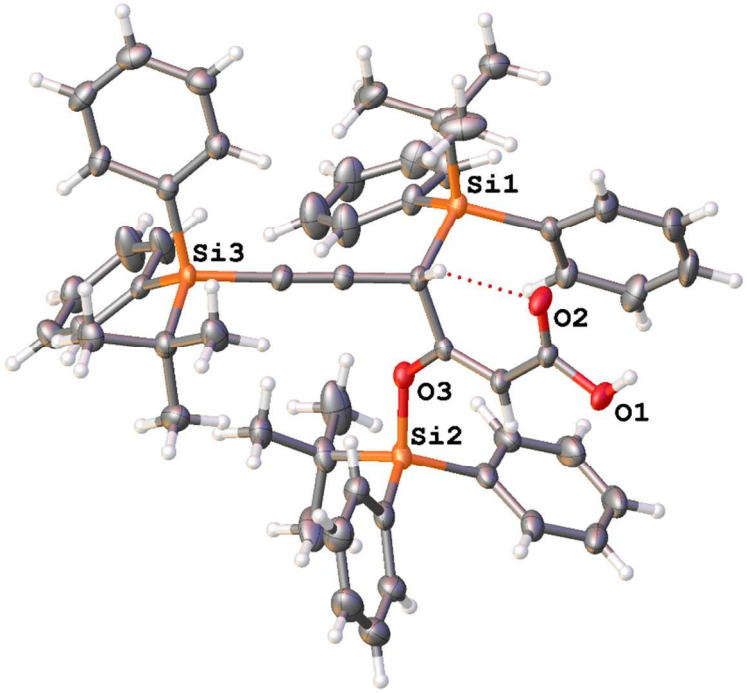


Table S1. Crystal data and structure refinement for Compound **2**.

Identification code	Compound **2**	
Empirical formula	C54 H60 O3 Si3	
Formula weight	841.29	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.7333(5) Å	□= 90.326(2)°.
	b = 14.5236(5) Å	□= 109.495(2)°.
	c = 15.4513(5) Å	□ = 93.507(2)°.
Volume	2898.63(18) Å^3	
Z	2	
Density (calculated)	0.964 Mg/m^3	
Absorption coefficient	1.015 mm^{-1}	
F(000)	900	
Crystal size	0.3 x 0.27 x 0.24 mm^3	
Theta range for data collection	3.035 to 68.326°.	
Index ranges	-14<=h<=16, -17<=k<=17, -18<=l<=18	
Reflections collected	36276	
Independent reflections	10419 [R(int) = 0.0523]	
Completeness to theta = 67.679°	97.90%	

Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6285	
Refinement method	Full-matrix least-squares on F_2	
Data / restraints / parameters	10419 / 0 / 551	
Goodness-of-fit on F_2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1340	
R indices (all data)	R1 = 0.0646, wR2 = 0.1417	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.129 and -0.387 e.$Å^{-3}$	
SQUEEZE	155e/uc (4 DCM = 168e/uc)	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	7230(1)	7633(1)	5169(1)	22(1)
Si(2)	5712(1)	8485(1)	1845(1)	26(1)
Si(3)	7346(1)	4711(1)	2772(1)	23(1)
O(3)	6377(1)	8002(1)	2837(1)	24(1)
O(1)	9021(1)	10313(1)	3954(1)	32(1)
O(2)	9359(1)	8997(1)	4713(1)	30(1)
C(6)	8783(2)	9443(1)	4091(1)	23(1)
C(28)	7734(2)	2961(1)	3605(2)	31(1)
C(3)	7732(2)	7528(1)	4135(1)	21(1)
C(45)	6551(2)	8532(2)	1112(2)	30(1)
C(29)	5932(2)	4325(1)	2269(2)	24(1)
C(12)	6443(2)	9417(2)	4974(2)	31(1)
C(1)	7462(2)	5867(1)	3314(2)	25(1)
C(35)	8050(2)	4766(2)	1902(2)	29(1)
C(24)	8723(2)	4231(2)	4547(2)	29(1)
C(5)	7792(2)	9098(1)	3440(1)	23(1)
C(2)	7572(2)	6611(1)	3690(1)	22(1)
C(17)	5843(2)	7171(1)	4872(2)	29(1)
C(7)	7280(2)	8904(1)	5450(2)	25(1)
C(25)	9183(2)	3625(2)	5231(2)	37(1)
C(23)	7988(2)	3914(1)	3719(2)	24(1)
C(39)	5364(2)	9665(2)	2094(2)	30(1)
C(27)	8200(2)	2354(2)	4287(2)	35(1)
C(44)	5778(2)	10472(2)	1819(2)	35(1)
C(40)	4695(2)	9772(2)	2599(2)	37(1)
C(51)	4560(2)	7637(2)	1324(2)	37(1)
C(46)	7402(2)	7981(2)	1299(2)	33(1)
C(36)	8160(2)	3792(2)	1568(2)	36(1)
C(4)	7318(2)	8261(1)	3450(1)	21(1)
C(33)	4400(2)	3635(2)	1091(2)	36(1)
C(32)	3814(2)	3749(2)	1642(2)	41(1)

C(43)	5527(2)	11337(2)	2027(2)	41(1)
C(10)	7281(2)	10806(2)	5815(2)	48(1)
C(8)	8120(2)	9381(2)	6104(2)	39(1)
C(11)	6444(2)	10357(2)	5153(2)	43(1)
C(50)	6326(2)	9050(2)	308(2)	38(1)
C(34)	5442(2)	3923(2)	1398(2)	34(1)
C(16)	7748(3)	5913(2)	5961(2)	48(1)
C(13)	8087(2)	6952(2)	6153(2)	33(1)
C(18)	5255(2)	7483(2)	5373(2)	38(1)
C(37)	7488(2)	5347(2)	1078(2)	39(1)
C(38)	9141(2)	5219(2)	2385(2)	40(1)
C(9)	8121(2)	10317(2)	6285(2)	49(1)
C(15)	7936(2)	7242(2)	7058(2)	38(1)
C(30)	5331(2)	4412(2)	2824(2)	46(1)
C(26)	8920(2)	2687(2)	5101(2)	37(1)
C(53)	4956(2)	6688(2)	1242(2)	36(1)
C(19)	4252(2)	7127(2)	5236(2)	42(1)
C(41)	4443(2)	10637(2)	2804(2)	47(1)
C(49)	6910(2)	9032(2)	-263(2)	46(1)
C(47)	7984(2)	7952(2)	724(2)	43(1)
C(48)	7740(2)	8483(2)	-61(2)	48(1)
C(31)	4286(2)	4129(2)	2523(2)	58(1)
C(20)	3798(2)	6464(2)	4589(2)	51(1)
C(42)	4856(2)	11422(2)	2513(2)	49(1)
C(14)	9232(2)	7085(2)	6250(2)	52(1)
C(52)	3836(2)	7576(2)	1882(3)	66(1)
C(22)	5322(2)	6550(2)	4142(2)	52(1)
C(54)	3957(2)	7960(2)	350(2)	61(1)
C(21)	4310(2)	6209(2)	3999(3)	61(1)

Table S3. Bond lengths [Å] and angles [°] for compound **2**.

Si(1)-C(3)	1.947(2)
Si(1)-C(17)	1.883(2)
Si(1)-C(7)	1.887(2)
Si(1)-C(13)	1.908(2)
Si(2)-O(3)	1.6828(15)
Si(2)-C(45)	1.865(3)
Si(2)-C(39)	1.878(2)
Si(2)-C(51)	1.889(2)
Si(3)-C(29)	1.883(2)
Si(3)-C(1)	1.846(2)
Si(3)-C(35)	1.900(2)
Si(3)-C(23)	1.881(2)
O(3)-C(4)	1.352(2)
O(1)-H(1)	0.8400
O(1)-C(6)	1.321(2)
O(2)-C(6)	1.237(2)
C(6)-C(5)	1.454(3)
C(28)-H(28)	0.9500
C(28)-C(23)	1.402(3)
C(28)-C(27)	1.388(3)
C(3)-H(3)	1.0000
C(3)-C(2)	1.466(3)
C(3)-C(4)	1.504(3)
C(45)-C(46)	1.408(3)
C(45)-C(50)	1.410(3)
C(29)-C(34)	1.394(3)
C(29)-C(30)	1.384(3)
C(12)-H(12)	0.9500
C(12)-C(7)	1.401(3)
C(12)-C(11)	1.392(3)
C(1)-C(2)	1.201(3)
C(35)-C(36)	1.534(3)
C(35)-C(37)	1.537(3)
C(35)-C(38)	1.537(3)

C(24)-H(24)	0.9500
C(24)-C(25)	1.387(3)
C(24)-C(23)	1.393(3)
C(5)-H(5)	0.9500
C(5)-C(4)	1.346(3)
C(17)-C(18)	1.384(3)
C(17)-C(22)	1.404(4)
C(7)-C(8)	1.396(3)
C(25)-H(25)	0.9500
C(25)-C(26)	1.384(4)
C(39)-C(44)	1.403(3)
C(39)-C(40)	1.404(4)
C(27)-H(27)	0.9500
C(27)-C(26)	1.378(4)
C(44)-H(44)	0.9500
C(44)-C(43)	1.387(3)
C(40)-H(40)	0.9500
C(40)-C(41)	1.385(3)
C(51)-C(53)	1.532(3)
C(51)-C(52)	1.517(4)
C(51)-C(54)	1.547(4)
C(46)-H(46)	0.9500
C(46)-C(47)	1.380(4)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(33)-H(33)	0.9500
C(33)-C(32)	1.369(4)
C(33)-C(34)	1.386(3)
C(32)-H(32)	0.9500
C(32)-C(31)	1.390(4)
C(43)-H(43)	0.9500
C(43)-C(42)	1.378(4)
C(10)-H(10)	0.9500
C(10)-C(11)	1.382(4)
C(10)-C(9)	1.382(4)

C(8)-H(8)	0.9500
C(8)-C(9)	1.385(4)
C(11)-H(11)	0.9500
C(50)-H(50)	0.9500
C(50)-C(49)	1.377(4)
C(34)-H(34)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(16)-C(13)	1.548(4)
C(13)-C(15)	1.541(3)
C(13)-C(14)	1.530(4)
C(18)-H(18)	0.9500
C(18)-C(19)	1.388(4)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(9)-H(9)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(30)-H(30)	0.9500
C(30)-C(31)	1.387(4)
C(26)-H(26)	0.9500
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(19)-H(19)	0.9500
C(19)-C(20)	1.347(4)
C(41)-H(41)	0.9500
C(41)-C(42)	1.386(4)
C(49)-H(49)	0.9500
C(49)-C(48)	1.381(4)

C(47)-H(47)	0.9500
C(47)-C(48)	1.397(4)
C(48)-H(48)	0.9500
C(31)-H(31)	0.9500
C(20)-H(20)	0.9500
C(20)-C(21)	1.385(4)
C(42)-H(42)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(22)-H(22)	0.9500
C(22)-C(21)	1.391(4)
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(21)-H(21)	0.9500

C(17)-Si(1)-C(3)	112.20(10)
C(17)-Si(1)-C(7)	107.32(10)
C(17)-Si(1)-C(13)	109.37(11)
C(7)-Si(1)-C(3)	106.60(9)
C(7)-Si(1)-C(13)	113.44(10)
C(13)-Si(1)-C(3)	107.95(9)
O(3)-Si(2)-C(45)	107.38(9)
O(3)-Si(2)-C(39)	109.40(9)
O(3)-Si(2)-C(51)	103.69(10)
C(45)-Si(2)-C(39)	111.89(11)
C(45)-Si(2)-C(51)	109.85(11)
C(39)-Si(2)-C(51)	114.11(11)
C(29)-Si(3)-C(35)	114.06(10)
C(1)-Si(3)-C(29)	108.46(9)
C(1)-Si(3)-C(35)	108.74(10)
C(1)-Si(3)-C(23)	106.57(9)

C(23)-Si(3)-C(29)	108.63(9)
C(23)-Si(3)-C(35)	110.11(10)
C(4)-O(3)-Si(2)	129.69(13)
C(6)-O(1)-H(1)	109.5
O(1)-C(6)-C(5)	112.31(17)
O(2)-C(6)-O(1)	122.07(19)
O(2)-C(6)-C(5)	125.61(18)
C(23)-C(28)-H(28)	119.3
C(27)-C(28)-H(28)	119.3
C(27)-C(28)-C(23)	121.4(2)
Si(1)-C(3)-H(3)	106.1
C(2)-C(3)-Si(1)	115.56(14)
C(2)-C(3)-H(3)	106.1
C(2)-C(3)-C(4)	111.54(17)
C(4)-C(3)-Si(1)	110.75(13)
C(4)-C(3)-H(3)	106.1
C(46)-C(45)-Si(2)	120.69(18)
C(46)-C(45)-C(50)	116.5(2)
C(50)-C(45)-Si(2)	122.61(18)
C(34)-C(29)-Si(3)	125.72(17)
C(30)-C(29)-Si(3)	117.35(17)
C(30)-C(29)-C(34)	116.9(2)
C(7)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(11)-C(12)-C(7)	121.5(2)
C(2)-C(1)-Si(3)	177.5(2)
C(36)-C(35)-Si(3)	110.72(16)
C(36)-C(35)-C(37)	109.98(19)
C(36)-C(35)-C(38)	108.24(19)
C(37)-C(35)-Si(3)	111.16(16)
C(38)-C(35)-Si(3)	107.63(16)
C(38)-C(35)-C(37)	109.0(2)
C(25)-C(24)-H(24)	119.4
C(25)-C(24)-C(23)	121.2(2)
C(23)-C(24)-H(24)	119.4
C(6)-C(5)-H(5)	117.2

C(4)-C(5)-C(6)	125.62(19)
C(4)-C(5)-H(5)	117.2
C(1)-C(2)-C(3)	178.1(2)
C(18)-C(17)-Si(1)	119.26(17)
C(18)-C(17)-C(22)	115.7(2)
C(22)-C(17)-Si(1)	125.03(18)
C(12)-C(7)-Si(1)	119.26(16)
C(8)-C(7)-Si(1)	123.72(17)
C(8)-C(7)-C(12)	117.0(2)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-C(24)	120.2(2)
C(26)-C(25)-H(25)	119.9
C(28)-C(23)-Si(3)	120.01(17)
C(24)-C(23)-Si(3)	122.57(16)
C(24)-C(23)-C(28)	117.4(2)
C(44)-C(39)-Si(2)	122.35(19)
C(44)-C(39)-C(40)	117.0(2)
C(40)-C(39)-Si(2)	120.58(18)
C(28)-C(27)-H(27)	120.0
C(26)-C(27)-C(28)	119.9(2)
C(26)-C(27)-H(27)	120.0
C(39)-C(44)-H(44)	119.3
C(43)-C(44)-C(39)	121.3(3)
C(43)-C(44)-H(44)	119.3
C(39)-C(40)-H(40)	119.3
C(41)-C(40)-C(39)	121.5(2)
C(41)-C(40)-H(40)	119.3
C(53)-C(51)-Si(2)	108.50(16)
C(53)-C(51)-C(54)	108.8(2)
C(52)-C(51)-Si(2)	112.51(18)
C(52)-C(51)-C(53)	110.1(2)
C(52)-C(51)-C(54)	108.8(3)
C(54)-C(51)-Si(2)	108.00(19)
C(45)-C(46)-H(46)	119.2
C(47)-C(46)-C(45)	121.6(2)
C(47)-C(46)-H(46)	119.2

C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
O(3)-C(4)-C(3)	112.41(16)
C(5)-C(4)-O(3)	122.07(18)
C(5)-C(4)-C(3)	125.49(18)
C(32)-C(33)-H(33)	119.9
C(32)-C(33)-C(34)	120.2(2)
C(34)-C(33)-H(33)	119.9
C(33)-C(32)-H(32)	120.4
C(33)-C(32)-C(31)	119.1(2)
C(31)-C(32)-H(32)	120.4
C(44)-C(43)-H(43)	119.8
C(42)-C(43)-C(44)	120.4(3)
C(42)-C(43)-H(43)	119.8
C(11)-C(10)-H(10)	120.3
C(11)-C(10)-C(9)	119.4(2)
C(9)-C(10)-H(10)	120.3
C(7)-C(8)-H(8)	119.2
C(9)-C(8)-C(7)	121.6(2)
C(9)-C(8)-H(8)	119.2
C(12)-C(11)-H(11)	120.0
C(10)-C(11)-C(12)	120.1(2)
C(10)-C(11)-H(11)	120.0
C(45)-C(50)-H(50)	118.9
C(49)-C(50)-C(45)	122.2(2)
C(49)-C(50)-H(50)	118.9
C(29)-C(34)-H(34)	119.0
C(33)-C(34)-C(29)	121.9(2)
C(33)-C(34)-H(34)	119.0
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
C(16)-C(13)-Si(1)	108.52(18)
C(15)-C(13)-Si(1)	109.53(16)
C(15)-C(13)-C(16)	108.4(2)
C(14)-C(13)-Si(1)	112.36(16)
C(14)-C(13)-C(16)	108.1(2)
C(14)-C(13)-C(15)	109.8(2)
C(17)-C(18)-H(18)	118.8
C(17)-C(18)-C(19)	122.4(2)
C(19)-C(18)-H(18)	118.8
C(35)-C(37)-H(37A)	109.5
C(35)-C(37)-H(37B)	109.5
C(35)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(35)-C(38)-H(38A)	109.5
C(35)-C(38)-H(38B)	109.5
C(35)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(10)-C(9)-C(8)	120.4(2)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(29)-C(30)-H(30)	119.2
C(29)-C(30)-C(31)	121.7(2)
C(31)-C(30)-H(30)	119.2

C(25)-C(26)-H(26)	120.1
C(27)-C(26)-C(25)	119.8(2)
C(27)-C(26)-H(26)	120.1
C(51)-C(53)-H(53A)	109.5
C(51)-C(53)-H(53B)	109.5
C(51)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(18)-C(19)-H(19)	119.6
C(20)-C(19)-C(18)	120.8(2)
C(20)-C(19)-H(19)	119.6
C(40)-C(41)-H(41)	119.9
C(40)-C(41)-C(42)	120.1(3)
C(42)-C(41)-H(41)	119.9
C(50)-C(49)-H(49)	120.0
C(50)-C(49)-C(48)	119.9(3)
C(48)-C(49)-H(49)	120.0
C(46)-C(47)-H(47)	119.9
C(46)-C(47)-C(48)	120.1(3)
C(48)-C(47)-H(47)	119.9
C(49)-C(48)-C(47)	119.7(3)
C(49)-C(48)-H(48)	120.2
C(47)-C(48)-H(48)	120.2
C(32)-C(31)-H(31)	119.9
C(30)-C(31)-C(32)	120.2(3)
C(30)-C(31)-H(31)	119.9
C(19)-C(20)-H(20)	120.6
C(19)-C(20)-C(21)	118.7(3)
C(21)-C(20)-H(20)	120.6
C(43)-C(42)-C(41)	119.6(2)
C(43)-C(42)-H(42)	120.2
C(41)-C(42)-H(42)	120.2
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5

H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(51)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52B)	109.5
C(51)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(17)-C(22)-H(22)	119.4
C(21)-C(22)-C(17)	121.2(3)
C(21)-C(22)-H(22)	119.4
C(51)-C(54)-H(54A)	109.5
C(51)-C(54)-H(54B)	109.5
C(51)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(20)-C(21)-C(22)	120.5(3)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	23(1)	17(1)	28(1)	-2(1)	10(1)	1(1)
Si(2)	24(1)	22(1)	26(1)	-6(1)	1(1)	2(1)
Si(3)	27(1)	16(1)	23(1)	-4(1)	6(1)	1(1)
O(3)	22(1)	20(1)	27(1)	-3(1)	3(1)	-2(1)
O(1)	30(1)	19(1)	34(1)	2(1)	-2(1)	-7(1)
O(2)	24(1)	18(1)	37(1)	2(1)	-2(1)	-2(1)
C(6)	25(1)	17(1)	26(1)	-1(1)	6(1)	-1(1)
C(28)	32(1)	19(1)	40(1)	-3(1)	12(1)	2(1)
C(3)	20(1)	17(1)	25(1)	-3(1)	6(1)	-1(1)
C(45)	31(1)	23(1)	29(1)	-7(1)	3(1)	0(1)
C(29)	31(1)	16(1)	26(1)	0(1)	9(1)	0(1)
C(12)	34(1)	22(1)	36(1)	-4(1)	9(1)	2(1)
C(1)	26(1)	20(1)	28(1)	0(1)	7(1)	1(1)
C(35)	33(1)	25(1)	30(1)	-4(1)	12(1)	1(1)
C(24)	31(1)	26(1)	30(1)	-2(1)	9(1)	3(1)
C(5)	23(1)	19(1)	24(1)	-2(1)	2(1)	-2(1)
C(2)	20(1)	21(1)	24(1)	-1(1)	6(1)	1(1)
C(17)	28(1)	21(1)	40(1)	-6(1)	17(1)	-1(1)
C(7)	29(1)	23(1)	25(1)	-4(1)	11(1)	0(1)
C(25)	38(1)	40(1)	30(1)	3(1)	7(1)	7(1)
C(23)	25(1)	22(1)	28(1)	-2(1)	11(1)	3(1)
C(39)	32(1)	26(1)	22(1)	-4(1)	-3(1)	6(1)
C(27)	38(1)	21(1)	53(2)	7(1)	23(1)	7(1)
C(44)	34(1)	28(1)	32(1)	-7(1)	-2(1)	2(1)
C(40)	52(2)	33(1)	26(1)	0(1)	10(1)	10(1)
C(51)	28(1)	34(1)	42(1)	-15(1)	2(1)	0(1)
C(46)	37(1)	27(1)	34(1)	-1(1)	11(1)	2(1)
C(36)	38(1)	34(1)	38(1)	-7(1)	18(1)	5(1)
C(4)	21(1)	20(1)	22(1)	-6(1)	6(1)	1(1)
C(33)	32(1)	45(1)	28(1)	-5(1)	5(1)	-2(1)
C(32)	34(1)	40(1)	50(2)	-9(1)	15(1)	-9(1)

C(43)	53(2)	24(1)	34(1)	-2(1)	-3(1)	4(1)
C(10)	72(2)	21(1)	56(2)	-12(1)	31(2)	-6(1)
C(8)	42(1)	30(1)	38(1)	-5(1)	4(1)	-6(1)
C(11)	46(2)	24(1)	62(2)	-1(1)	23(1)	7(1)
C(50)	41(1)	35(1)	29(1)	0(1)	2(1)	2(1)
C(34)	31(1)	42(1)	29(1)	-8(1)	8(1)	2(1)
C(16)	75(2)	31(1)	50(2)	11(1)	36(2)	16(1)
C(13)	35(1)	34(1)	36(1)	10(1)	20(1)	9(1)
C(18)	34(1)	36(1)	46(2)	-15(1)	20(1)	-3(1)
C(37)	53(2)	34(1)	32(1)	2(1)	18(1)	4(1)
C(38)	40(1)	43(1)	41(1)	-11(1)	19(1)	-11(1)
C(9)	63(2)	32(1)	43(2)	-12(1)	9(1)	-15(1)
C(15)	43(2)	38(1)	33(1)	5(1)	13(1)	1(1)
C(30)	52(2)	47(2)	40(2)	-21(1)	25(1)	-22(1)
C(26)	36(1)	38(1)	40(1)	15(1)	16(1)	15(1)
C(53)	37(1)	28(1)	40(1)	-11(1)	9(1)	-5(1)
C(19)	33(1)	41(1)	63(2)	-4(1)	30(1)	4(1)
C(41)	69(2)	41(2)	37(1)	-4(1)	22(1)	17(1)
C(49)	58(2)	45(2)	30(1)	0(1)	10(1)	-3(1)
C(47)	42(2)	39(1)	51(2)	-3(1)	20(1)	3(1)
C(48)	57(2)	51(2)	42(2)	-6(1)	26(1)	-10(1)
C(31)	54(2)	65(2)	65(2)	-34(2)	39(2)	-29(2)
C(20)	34(2)	48(2)	78(2)	-14(2)	30(1)	-13(1)
C(42)	75(2)	31(1)	34(1)	-7(1)	8(1)	19(1)
C(14)	38(2)	73(2)	52(2)	31(2)	19(1)	24(1)
C(52)	42(2)	71(2)	90(3)	-41(2)	32(2)	-22(2)
C(22)	43(2)	49(2)	69(2)	-23(1)	29(2)	-10(1)
C(54)	48(2)	45(2)	60(2)	-16(1)	-23(2)	5(1)
C(21)	47(2)	58(2)	77(2)	-26(2)	25(2)	-18(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for comopund **2**.

	x	y	z	U(eq)
H(1)	9569	10501	4371	47
H(28)	7232	2726	3049	37
H(3)	8498	7666	4390	25
H(12)	5861	9116	4519	37
H(24)	8912	4873	4644	35
H(5)	7449	9497	2966	28
H(25)	9681	3855	5792	44
H(27)	8022	1710	4193	42
H(44)	6241	10426	1483	42
H(40)	4408	9239	2804	45
H(46)	7580	7620	1834	39
H(36A)	8538	3433	2095	53
H(36B)	8540	3835	1133	53
H(36C)	7471	3489	1265	53
H(33)	4091	3357	496	44
H(32)	3094	3572	1426	50
H(43)	5818	11875	1834	50
H(10)	7280	11446	5946	57
H(8)	8705	9056	6434	47
H(11)	5869	10691	4819	51
H(50)	5752	9425	154	45
H(34)	5835	3845	1003	41
H(16A)	7032	5804	5949	72
H(16B)	8203	5552	6447	72
H(16C)	7795	5726	5367	72
H(18)	5548	7958	5828	45
H(37A)	6812	5037	738	59
H(37B)	7903	5418	673	59
H(37C)	7389	5956	1299	59
H(38A)	9090	5862	2549	61

H(38B)	9548	5197	1972	61
H(38C)	9481	4884	2943	61
H(9)	8703	10624	6734	59
H(15A)	8205	7884	7219	57
H(15B)	8309	6841	7549	57
H(15C)	7197	7188	6981	57
H(30)	5642	4672	3426	55
H(26)	9235	2274	5571	44
H(53A)	5418	6734	876	55
H(53B)	4368	6247	942	55
H(53C)	5337	6475	1856	55
H(19)	3880	7354	5604	51
H(41)	3986	10692	3144	57
H(49)	6742	9396	-795	55
H(47)	8551	7571	863	52
H(48)	8143	8467	-455	58
H(31)	3892	4194	2919	70
H(20)	3140	6178	4538	61
H(42)	4679	12015	2648	58
H(14A)	9333	6849	5692	79
H(14B)	9645	6749	6780	79
H(14C)	9453	7744	6338	79
H(52A)	4220	7406	2511	99
H(52B)	3272	7107	1602	99
H(52C)	3549	8175	1894	99
H(22)	5666	6360	3737	62
H(54A)	3744	8586	391	92
H(54B)	3342	7540	73	92
H(54C)	4402	7958	-31	92
H(21)	3967	5799	3493	73

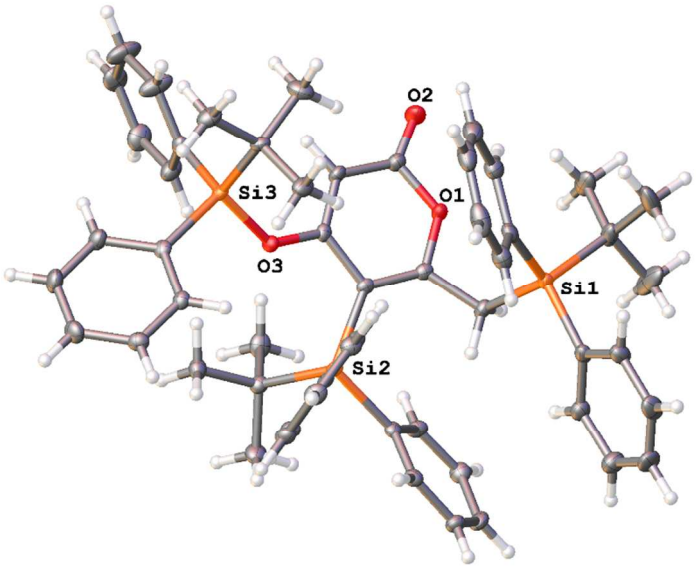


Table S6. Crystal data and structure refinement for compound **3**.

Identification code	Compound **3**	
Empirical formula	C54 H60 O3 Si3	
Formula weight	841.29	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.5118(9) Å	□= 68.488(2)°.
	b = 12.5949(11) Å	□= 89.117(2)°.
	c = 16.5326(15) Å	□ = 75.576(2)°.
Volume	2339.1(3) $Å^3$	
Z	2	
Density (calculated)	1.194 Mg/m^3	
Absorption coefficient	0.144 mm^{-1}	
F(000)	900	
Crystal size	0.32 x 0.3 x 0.28 mm^3	
Theta range for data collection	1.687 to 26.395°.	
Index ranges	-15<=h<=12, -15<=k<=15, -20<=l<=20	
Reflections collected	33116	
Independent reflections	9529 [R(int) = 0.0718]	
Completeness to theta = 25.242°	99.50%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4874 and 0.4488	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	9529 / 0 / 550	
Goodness-of-fit on F_2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1132	
R indices (all data)	R1 = 0.0674, wR2 = 0.1267	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.366 and -0.376 e.$Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(2)	4165(1)	4270(1)	3246(1)	13(1)
Si(3)	1477(1)	2226(1)	3443(1)	14(1)
Si(1)	2794(1)	7449(1)	408(1)	16(1)
O(1)	3259(1)	4726(1)	687(1)	17(1)
O(3)	2489(1)	2931(1)	3116(1)	15(1)
O(2)	2631(1)	3653(1)	101(1)	26(1)
C(22)	3062(2)	4968(2)	3812(1)	14(1)
C(3)	2822(2)	3425(2)	2310(1)	14(1)
C(38)	1569(2)	1891(2)	4644(1)	14(1)
C(39)	1613(2)	2745(2)	4984(1)	16(1)
C(6)	3098(2)	8666(2)	688(1)	20(1)
C(23)	3213(2)	4877(2)	4674(1)	18(1)
C(4)	2549(2)	3163(2)	1627(1)	16(1)
C(1)	3574(2)	4949(2)	1389(1)	14(1)
C(27)	2035(2)	5646(2)	3354(1)	16(1)
C(33)	6034(2)	5042(2)	2400(1)	18(1)
C(44)	1867(2)	817(2)	3248(1)	17(1)
C(2)	3471(2)	4266(2)	2227(1)	14(1)
C(5)	2804(2)	3793(2)	771(1)	17(1)
C(31)	6705(2)	6615(2)	2502(1)	21(1)
C(54)	3928(2)	6064(2)	1051(1)	17(1)
C(34)	5033(2)	2706(2)	3966(1)	17(1)
C(29)	5131(2)	6118(2)	3252(1)	16(1)
C(32)	6775(2)	5732(2)	2170(1)	20(1)
C(25)	1359(2)	6056(2)	4604(1)	21(1)
C(40)	1701(2)	2480(2)	5874(1)	20(1)
C(43)	1616(2)	745(2)	5242(1)	21(1)
C(26)	1191(2)	6177(2)	3748(1)	19(1)
C(11)	2313(2)	9748(2)	532(1)	25(1)
C(41)	1754(2)	1340(2)	6451(1)	24(1)

C(12)	1383(2)	7257(2)	722(1)	20(1)
C(7)	4176(2)	8563(2)	988(1)	23(1)
C(37)	5481(2)	2001(2)	3392(2)	25(1)
C(28)	5179(2)	5219(2)	2939(1)	15(1)
C(42)	1713(2)	477(2)	6131(2)	26(1)
C(30)	5892(2)	6799(2)	3045(1)	19(1)
C(45)	2978(2)	247(2)	3269(2)	24(1)
C(50)	56(2)	3216(2)	2926(1)	18(1)
C(24)	2374(2)	5410(2)	5070(1)	20(1)
C(35)	4397(2)	1988(2)	4671(1)	21(1)
C(17)	842(2)	6638(2)	384(1)	24(1)
C(18)	2876(2)	7877(2)	-817(1)	28(1)
C(53)	-834(2)	2686(2)	3472(2)	24(1)
C(16)	-236(2)	6581(2)	550(2)	31(1)
C(36)	6031(2)	2811(2)	4442(2)	25(1)
C(10)	2594(2)	10670(2)	667(2)	31(1)
C(47)	2520(2)	-1365(2)	3038(2)	29(1)
C(13)	792(2)	7786(2)	1262(1)	27(1)
C(51)	-62(2)	4442(2)	2962(2)	23(1)
C(52)	-178(2)	3382(2)	1972(2)	28(1)
C(14)	-290(2)	7726(2)	1434(2)	34(1)
C(19)	2984(2)	6859(2)	-1129(2)	32(1)
C(46)	3299(2)	-824(2)	3164(2)	31(1)
C(8)	4453(2)	9494(2)	1115(2)	29(1)
C(9)	3661(2)	10544(2)	957(2)	31(1)
C(49)	1096(2)	256(2)	3111(2)	35(1)
C(15)	-805(2)	7137(2)	1064(2)	34(1)
C(48)	1425(2)	-820(2)	3012(2)	41(1)
C(20)	1807(3)	8838(2)	-1281(2)	49(1)
C(21)	3883(3)	8375(3)	-1079(2)	56(1)

Table S8. Bond lengths [Å] and angles [°] for compound **3**.

Si(2)-C(22)	1.875(2)
Si(2)-C(2)	1.909(2)
Si(2)-C(34)	1.932(2)
Si(2)-C(28)	1.8941(19)
Si(3)-O(3)	1.6951(13)
Si(3)-C(38)	1.871(2)
Si(3)-C(44)	1.864(2)
Si(3)-C(50)	1.900(2)
Si(1)-C(6)	1.877(2)
Si(1)-C(54)	1.907(2)
Si(1)-C(12)	1.880(2)
Si(1)-C(18)	1.903(2)
O(1)-C(1)	1.375(2)
O(1)-C(5)	1.392(2)
O(3)-C(3)	1.357(2)
O(2)-C(5)	1.214(2)
C(22)-C(23)	1.400(3)
C(22)-C(27)	1.401(3)
C(3)-C(4)	1.357(3)
C(3)-C(2)	1.456(3)
C(38)-C(39)	1.396(3)
C(38)-C(43)	1.406(3)
C(39)-H(39)	0.9500
C(39)-C(40)	1.385(3)
C(6)-C(11)	1.404(3)
C(6)-C(7)	1.403(3)
C(23)-H(23)	0.9500
C(23)-C(24)	1.389(3)
C(4)-H(4)	0.9500
C(4)-C(5)	1.422(3)
C(1)-C(2)	1.361(3)
C(1)-C(54)	1.485(3)
C(27)-H(27)	0.9500
C(27)-C(26)	1.390(3)

C(33)-H(33)	0.9500
C(33)-C(32)	1.382(3)
C(33)-C(28)	1.409(3)
C(44)-C(45)	1.391(3)
C(44)-C(49)	1.394(3)
C(31)-H(31)	0.9500
C(31)-C(32)	1.392(3)
C(31)-C(30)	1.379(3)
C(54)-H(54A)	0.9900
C(54)-H(54B)	0.9900
C(34)-C(37)	1.535(3)
C(34)-C(35)	1.538(3)
C(34)-C(36)	1.543(3)
C(29)-H(29)	0.9500
C(29)-C(28)	1.396(3)
C(29)-C(30)	1.393(3)
C(32)-H(32)	0.9500
C(25)-H(25)	0.9500
C(25)-C(26)	1.380(3)
C(25)-C(24)	1.388(3)
C(40)-H(40)	0.9500
C(40)-C(41)	1.387(3)
C(43)-H(43)	0.9500
C(43)-C(42)	1.383(3)
C(26)-H(26)	0.9500
C(11)-H(11)	0.9500
C(11)-C(10)	1.384(3)
C(41)-H(41)	0.9500
C(41)-C(42)	1.384(3)
C(12)-C(17)	1.404(3)
C(12)-C(13)	1.399(3)
C(7)-H(7)	0.9500
C(7)-C(8)	1.388(3)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800

C(42)-H(42)	0.9500
C(30)-H(30)	0.9500
C(45)-H(45)	0.9500
C(45)-C(46)	1.382(3)
C(50)-C(53)	1.548(3)
C(50)-C(51)	1.536(3)
C(50)-C(52)	1.535(3)
C(24)-H(24)	0.9500
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(17)-H(17)	0.9500
C(17)-C(16)	1.386(3)
C(18)-C(19)	1.525(3)
C(18)-C(20)	1.545(4)
C(18)-C(21)	1.532(3)
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(16)-H(16)	0.9500
C(16)-C(15)	1.374(4)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(10)-H(10)	0.9500
C(10)-C(9)	1.378(3)
C(47)-H(47)	0.9500
C(47)-C(46)	1.378(3)
C(47)-C(48)	1.365(3)
C(13)-H(13)	0.9500
C(13)-C(14)	1.394(3)
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800

C(52)-H(52C)	0.9800
C(14)-H(14)	0.9500
C(14)-C(15)	1.387(4)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(46)-H(46)	0.9500
C(8)-H(8)	0.9500
C(8)-C(9)	1.378(3)
C(9)-H(9)	0.9500
C(49)-H(49)	0.9500
C(49)-C(48)	1.385(3)
C(15)-H(15)	0.9500
C(48)-H(48)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(22)-Si(2)-C(2)	107.77(9)
C(22)-Si(2)-C(34)	114.51(9)
C(22)-Si(2)-C(28)	106.87(9)
C(2)-Si(2)-C(34)	111.42(9)
C(28)-Si(2)-C(2)	110.68(9)
C(28)-Si(2)-C(34)	105.50(8)
O(3)-Si(3)-C(38)	101.68(8)
O(3)-Si(3)-C(44)	108.41(8)
O(3)-Si(3)-C(50)	112.08(8)
C(38)-Si(3)-C(50)	110.11(9)
C(44)-Si(3)-C(38)	109.51(9)
C(44)-Si(3)-C(50)	114.28(9)
C(6)-Si(1)-C(54)	105.35(9)
C(6)-Si(1)-C(12)	110.85(10)
C(6)-Si(1)-C(18)	106.93(9)

C(12)-Si(1)-C(54)	111.13(9)
C(12)-Si(1)-C(18)	110.73(10)
C(18)-Si(1)-C(54)	111.66(10)
C(1)-O(1)-C(5)	123.13(15)
C(3)-O(3)-Si(3)	130.74(12)
C(23)-C(22)-Si(2)	123.44(15)
C(23)-C(22)-C(27)	117.16(18)
C(27)-C(22)-Si(2)	119.38(15)
O(3)-C(3)-C(4)	121.99(17)
O(3)-C(3)-C(2)	115.46(17)
C(4)-C(3)-C(2)	122.55(18)
C(39)-C(38)-Si(3)	122.16(15)
C(39)-C(38)-C(43)	117.45(19)
C(43)-C(38)-Si(3)	120.38(15)
C(38)-C(39)-H(39)	119.2
C(40)-C(39)-C(38)	121.59(18)
C(40)-C(39)-H(39)	119.2
C(11)-C(6)-Si(1)	122.82(16)
C(7)-C(6)-Si(1)	119.96(16)
C(7)-C(6)-C(11)	116.93(19)
C(22)-C(23)-H(23)	119.2
C(24)-C(23)-C(22)	121.65(19)
C(24)-C(23)-H(23)	119.2
C(3)-C(4)-H(4)	119.8
C(3)-C(4)-C(5)	120.48(18)
C(5)-C(4)-H(4)	119.8
O(1)-C(1)-C(54)	108.14(16)
C(2)-C(1)-O(1)	122.44(17)
C(2)-C(1)-C(54)	129.24(18)
C(22)-C(27)-H(27)	119.3
C(26)-C(27)-C(22)	121.42(19)
C(26)-C(27)-H(27)	119.3
C(32)-C(33)-H(33)	118.8
C(32)-C(33)-C(28)	122.42(19)
C(28)-C(33)-H(33)	118.8
C(45)-C(44)-Si(3)	119.97(15)

C(45)-C(44)-C(49)	116.6(2)
C(49)-C(44)-Si(3)	123.38(17)
C(3)-C(2)-Si(2)	119.80(14)
C(1)-C(2)-Si(2)	125.76(14)
C(1)-C(2)-C(3)	114.32(17)
O(1)-C(5)-C(4)	115.51(17)
O(2)-C(5)-O(1)	116.07(18)
O(2)-C(5)-C(4)	128.34(18)
C(32)-C(31)-H(31)	120.1
C(30)-C(31)-H(31)	120.1
C(30)-C(31)-C(32)	119.84(18)
Si(1)-C(54)-H(54A)	108.4
Si(1)-C(54)-H(54B)	108.4
C(1)-C(54)-Si(1)	115.32(14)
C(1)-C(54)-H(54A)	108.4
C(1)-C(54)-H(54B)	108.4
H(54A)-C(54)-H(54B)	107.5
C(37)-C(34)-Si(2)	109.74(14)
C(37)-C(34)-C(35)	108.40(17)
C(37)-C(34)-C(36)	108.06(17)
C(35)-C(34)-Si(2)	114.21(13)
C(35)-C(34)-C(36)	107.03(17)
C(36)-C(34)-Si(2)	109.21(14)
C(28)-C(29)-H(29)	119.2
C(30)-C(29)-H(29)	119.2
C(30)-C(29)-C(28)	121.64(19)
C(33)-C(32)-C(31)	119.36(19)
C(33)-C(32)-H(32)	120.3
C(31)-C(32)-H(32)	120.3
C(26)-C(25)-H(25)	120.1
C(26)-C(25)-C(24)	119.89(19)
C(24)-C(25)-H(25)	120.1
C(39)-C(40)-H(40)	120.1
C(39)-C(40)-C(41)	119.9(2)
C(41)-C(40)-H(40)	120.1
C(38)-C(43)-H(43)	119.5

C(42)-C(43)-C(38)	121.0(2)
C(42)-C(43)-H(43)	119.5
C(27)-C(26)-H(26)	120.0
C(25)-C(26)-C(27)	120.09(19)
C(25)-C(26)-H(26)	120.0
C(6)-C(11)-H(11)	119.3
C(10)-C(11)-C(6)	121.4(2)
C(10)-C(11)-H(11)	119.3
C(40)-C(41)-H(41)	120.2
C(42)-C(41)-C(40)	119.6(2)
C(42)-C(41)-H(41)	120.2
C(17)-C(12)-Si(1)	121.70(17)
C(13)-C(12)-Si(1)	121.55(16)
C(13)-C(12)-C(17)	116.6(2)
C(6)-C(7)-H(7)	119.3
C(8)-C(7)-C(6)	121.4(2)
C(8)-C(7)-H(7)	119.3
C(34)-C(37)-H(37A)	109.5
C(34)-C(37)-H(37B)	109.5
C(34)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(33)-C(28)-Si(2)	121.99(15)
C(29)-C(28)-Si(2)	121.53(15)
C(29)-C(28)-C(33)	116.47(17)
C(43)-C(42)-C(41)	120.4(2)
C(43)-C(42)-H(42)	119.8
C(41)-C(42)-H(42)	119.8
C(31)-C(30)-C(29)	120.24(19)
C(31)-C(30)-H(30)	119.9
C(29)-C(30)-H(30)	119.9
C(44)-C(45)-H(45)	119.2
C(46)-C(45)-C(44)	121.6(2)
C(46)-C(45)-H(45)	119.2
C(53)-C(50)-Si(3)	108.59(14)

C(51)-C(50)-Si(3)	109.02(13)
C(51)-C(50)-C(53)	107.74(17)
C(52)-C(50)-Si(3)	114.43(15)
C(52)-C(50)-C(53)	108.81(17)
C(52)-C(50)-C(51)	108.05(17)
C(23)-C(24)-H(24)	120.1
C(25)-C(24)-C(23)	119.76(19)
C(25)-C(24)-H(24)	120.1
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(12)-C(17)-H(17)	118.9
C(16)-C(17)-C(12)	122.1(2)
C(16)-C(17)-H(17)	118.9
C(19)-C(18)-Si(1)	114.41(15)
C(19)-C(18)-C(20)	108.0(2)
C(19)-C(18)-C(21)	107.9(2)
C(20)-C(18)-Si(1)	108.01(17)
C(21)-C(18)-Si(1)	108.76(16)
C(21)-C(18)-C(20)	109.7(2)
C(50)-C(53)-H(53A)	109.5
C(50)-C(53)-H(53B)	109.5
C(50)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-C(17)	119.8(2)
C(15)-C(16)-H(16)	120.1
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36B)	109.5

H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-C(11)	120.3(2)
C(9)-C(10)-H(10)	119.8
C(46)-C(47)-H(47)	120.6
C(48)-C(47)-H(47)	120.6
C(48)-C(47)-C(46)	118.9(2)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-C(12)	121.4(2)
C(14)-C(13)-H(13)	119.3
C(50)-C(51)-H(51A)	109.5
C(50)-C(51)-H(51B)	109.5
C(50)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(50)-C(52)-H(52A)	109.5
C(50)-C(52)-H(52B)	109.5
C(50)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-C(13)	120.0(2)
C(15)-C(14)-H(14)	120.0
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(45)-C(46)-H(46)	119.7
C(47)-C(46)-C(45)	120.6(2)
C(47)-C(46)-H(46)	119.7
C(7)-C(8)-H(8)	119.9

C(9)-C(8)-C(7)	120.2(2)
C(9)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	119.8(2)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(44)-C(49)-H(49)	119.3
C(48)-C(49)-C(44)	121.5(2)
C(48)-C(49)-H(49)	119.3
C(16)-C(15)-C(14)	119.9(2)
C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(47)-C(48)-C(49)	120.9(2)
C(47)-C(48)-H(48)	119.6
C(49)-C(48)-H(48)	119.6
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(2)	11(1)	14(1)	15(1)	-7(1)	2(1)	-4(1)
Si(3)	14(1)	14(1)	15(1)	-6(1)	3(1)	-7(1)
Si(1)	24(1)	14(1)	12(1)	-5(1)	1(1)	-7(1)
O(1)	24(1)	14(1)	14(1)	-5(1)	2(1)	-8(1)
O(3)	16(1)	18(1)	13(1)	-6(1)	4(1)	-8(1)
O(2)	40(1)	27(1)	17(1)	-11(1)	3(1)	-16(1)
C(22)	15(1)	14(1)	17(1)	-7(1)	3(1)	-7(1)
C(3)	12(1)	11(1)	16(1)	-3(1)	2(1)	-1(1)
C(38)	10(1)	17(1)	17(1)	-6(1)	4(1)	-4(1)
C(39)	14(1)	16(1)	18(1)	-5(1)	3(1)	-4(1)
C(6)	32(1)	15(1)	14(1)	-5(1)	-1(1)	-7(1)
C(23)	16(1)	19(1)	19(1)	-8(1)	0(1)	-5(1)
C(4)	18(1)	13(1)	19(1)	-7(1)	2(1)	-7(1)
C(1)	13(1)	13(1)	18(1)	-8(1)	2(1)	-2(1)
C(27)	18(1)	16(1)	17(1)	-7(1)	3(1)	-7(1)
C(33)	16(1)	17(1)	24(1)	-12(1)	2(1)	-3(1)
C(44)	23(1)	16(1)	15(1)	-6(1)	4(1)	-7(1)
C(2)	12(1)	12(1)	18(1)	-8(1)	2(1)	-2(1)
C(5)	19(1)	15(1)	19(1)	-8(1)	2(1)	-6(1)
C(31)	18(1)	21(1)	26(1)	-5(1)	1(1)	-10(1)
C(54)	20(1)	15(1)	19(1)	-6(1)	5(1)	-8(1)
C(34)	14(1)	17(1)	19(1)	-6(1)	2(1)	-5(1)
C(29)	13(1)	19(1)	16(1)	-7(1)	0(1)	-3(1)
C(32)	15(1)	24(1)	22(1)	-8(1)	4(1)	-5(1)
C(25)	18(1)	23(1)	27(1)	-16(1)	9(1)	-5(1)
C(40)	18(1)	24(1)	20(1)	-12(1)	3(1)	-6(1)
C(43)	25(1)	19(1)	20(1)	-7(1)	6(1)	-10(1)
C(26)	15(1)	19(1)	24(1)	-10(1)	1(1)	-2(1)
C(11)	32(1)	18(1)	22(1)	-7(1)	-7(1)	-4(1)
C(41)	28(1)	29(1)	16(1)	-6(1)	5(1)	-10(1)
C(12)	23(1)	17(1)	15(1)	-2(1)	-3(1)	-2(1)

C(7)	29(1)	17(1)	22(1)	-7(1)	1(1)	-7(1)
C(37)	23(1)	19(1)	28(1)	-8(1)	5(1)	0(1)
C(28)	12(1)	15(1)	16(1)	-4(1)	-1(1)	-2(1)
C(42)	35(1)	20(1)	22(1)	-3(1)	6(1)	-11(1)
C(30)	20(1)	16(1)	22(1)	-9(1)	0(1)	-6(1)
C(45)	22(1)	18(1)	32(1)	-8(1)	2(1)	-6(1)
C(50)	16(1)	20(1)	20(1)	-10(1)	1(1)	-7(1)
C(24)	25(1)	24(1)	18(1)	-12(1)	5(1)	-11(1)
C(35)	19(1)	18(1)	20(1)	-3(1)	0(1)	-4(1)
C(17)	25(1)	22(1)	22(1)	-4(1)	-2(1)	-5(1)
C(18)	51(2)	22(1)	16(1)	-7(1)	7(1)	-19(1)
C(53)	18(1)	25(1)	35(1)	-16(1)	5(1)	-8(1)
C(16)	25(1)	30(1)	28(1)	1(1)	-5(1)	-9(1)
C(36)	18(1)	26(1)	27(1)	-5(1)	-4(1)	-5(1)
C(10)	45(2)	14(1)	28(1)	-7(1)	-8(1)	0(1)
C(47)	39(1)	18(1)	32(1)	-14(1)	1(1)	-2(1)
C(13)	32(1)	24(1)	19(1)	-5(1)	1(1)	-3(1)
C(51)	19(1)	19(1)	29(1)	-7(1)	-5(1)	-4(1)
C(52)	22(1)	37(1)	26(1)	-15(1)	-4(1)	-5(1)
C(14)	32(1)	30(1)	22(1)	-1(1)	9(1)	5(1)
C(19)	55(2)	32(1)	17(1)	-12(1)	11(1)	-23(1)
C(46)	28(1)	22(1)	39(2)	-11(1)	6(1)	0(1)
C(8)	32(1)	23(1)	34(1)	-10(1)	-2(1)	-10(1)
C(9)	48(2)	18(1)	33(1)	-11(1)	-4(1)	-13(1)
C(49)	22(1)	32(1)	65(2)	-33(1)	6(1)	-9(1)
C(15)	23(1)	32(1)	29(1)	6(1)	1(1)	-4(1)
C(48)	35(1)	33(1)	69(2)	-34(1)	2(1)	-12(1)
C(20)	95(2)	26(1)	17(1)	-3(1)	-11(1)	-6(2)
C(21)	101(3)	67(2)	31(2)	-26(2)	36(2)	-67(2)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **3**.

	x	y	z	U(eq)
H(39)	1582	3527	4594	19
H(23)	3907	4441	4997	21
H(4)	2184	2555	1721	20
H(27)	1913	5745	2762	19
H(33)	6103	4425	2187	22
H(31)	7216	7088	2354	26
H(54A)	4535	5972	671	21
H(54B)	4231	6184	1551	21
H(29)	4565	6270	3616	20
H(32)	7327	5607	1790	24
H(25)	780	6416	4873	25
H(40)	1724	3077	6090	23
H(43)	1582	145	5031	25
H(26)	497	6624	3427	23
H(11)	1574	9850	330	30
H(41)	1820	1153	7063	29
H(7)	4728	7841	1107	27
H(37A)	4861	1907	3094	37
H(37B)	5947	1221	3757	37
H(37C)	5923	2427	2958	37
H(42)	1751	-305	6525	32
H(30)	5851	7392	3279	22
H(45)	3530	602	3358	29
H(24)	2495	5331	5657	24
H(35A)	4103	2427	5044	31
H(35B)	4899	1225	5028	31
H(35C)	3784	1856	4392	31
H(17)	1228	6246	31	29
H(53A)	-817	1930	3423	36
H(53B)	-1567	3234	3253	36

H(53C)	-682	2558	4085	36
H(16)	-580	6159	309	37
H(36A)	6504	3186	4011	38
H(36B)	6458	2021	4825	38
H(36C)	5765	3292	4791	38
H(10)	2048	11393	559	37
H(47)	2742	-2104	2971	35
H(13)	1136	8194	1517	32
H(51A)	96	4356	3564	35
H(51B)	-820	4932	2752	35
H(51C)	461	4820	2591	35
H(52A)	321	3809	1609	42
H(52B)	-948	3837	1772	42
H(52C)	-58	2607	1928	42
H(14)	-674	8089	1804	40
H(19A)	3699	6280	-896	47
H(19B)	2939	7164	-1768	47
H(19C)	2384	6479	-924	47
H(46)	4065	-1190	3178	37
H(8)	5191	9408	1311	35
H(9)	3851	11179	1049	38
H(49)	329	621	3085	42
H(15)	-1550	7118	1166	41
H(48)	880	-1185	2926	49
H(20A)	1164	8517	-1112	74
H(20B)	1840	9090	-1914	74
H(20C)	1738	9519	-1110	74
H(21A)	3805	9069	-924	84
H(21B)	3930	8604	-1710	84
H(21C)	4557	7770	-771	84

Appendix 2.

Caculation of the compounds' concentration at different time points:

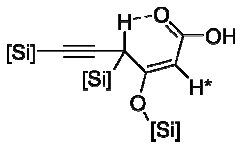
Concentration of compound **2** at 0 hour is 0.17M.

Integral of **2** (Proton attached to sp2 hybridized carbon) at 0 hour is 15.89 compared to the internal standard Et_2O.

Integral of **2** (Proton attached to sp2 hybridized carbon) at X hour is I_2 compared to Et_2O.

Then the concentration of **2** at X hour is

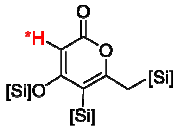
$$C_2=\frac{I2}{15.89}*0.17$$



Integral of **3** (Proton attached to sp2 hybridized carbon) at X hour is I_3 compared to Et_2O.

Then the concentration of **3** at X hour is

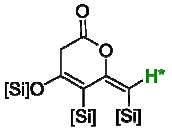
$$C_3=\frac{I3}{15.89}*0.17$$



Integral of **6** (Proton attached to sp2 hybridized carbon) at X hour is I_6 compared to Et_2O.

Then the concentration of **6** at X hour is

$$C_6=\frac{I6}{15.89}*0.17$$



Integral of **10** (Proton attached to sp2 hybridized carbon) at X hour is I_{10} compared to Et_2O.

Then the concentration of **10** at X hour is

$$C_{10}=\frac{I10}{15.89}*0.17$$

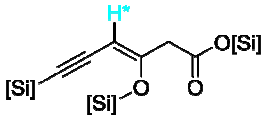


Table S11. Concentration of compound 2, 3, 10 and total concentration of 3&6 at different time points

Time (h)	Compound **2** integral	Compound **2** concentration (M)	Compound **6** integral	Cmpound **6** concentration (M)	Compound **3** integral	Compound **3** concentration (M)	Compound **10** integral	Compound **10** concentration (M)	Total concentration (M) of **3** and **6**
0	15.89	0.17	0	0	0	0	0	0	0
1	15.11	0.161655129	0.18	0.001925739	0	0	0	0	0.001925739
2	14.39	0.153952171	0.55	0.005884204	0.02	0.000213971	0.03	0.000320957	0.006098175
3	13.88	0.148495909	0.87	0.009307741	0.08	0.000855884	0.14	0.001497797	0.010163625
4	13.46	0.144002517	1.16	0.012410321	0.15	0.001604783	0.21	0.002246696	0.014015104
5	12.97	0.138760227	1.54	0.016475771	0.25	0.002674638	0.3	0.003209566	0.019150409
6	12.37	0.132341095	1.8	0.019257395	0.34	0.003637508	0.37	0.003958464	0.022894902
7	12.01	0.128489616	2.16	0.023108874	0.46	0.004921334	0.47	0.00502832	0.028030208
8	11.5	0.123033354	2.39	0.025569541	0.56	0.005991189	0.53	0.005670233	0.03156073
9	11.06	0.118325991	2.67	0.028565135	0.71	0.007595972	0.67	0.00716803	0.036161108
10	10.49	0.112227816	2.88	0.030811831	0.81	0.008665828	0.72	0.007702958	0.039477659
11	10.26	0.109767149	3.18	0.034021397	0.94	0.010056639	0.8	0.008558842	0.044078037
12	9.89	0.105808685	3.4	0.036375079	1.07	0.011447451	0.88	0.009414726	0.04782253
13	9.46	0.101208307	3.6	0.038514789	1.19	0.012731278	0.95	0.010163625	0.051246067
19	6.39	0.068363751	4.74	0.050711139	2.04	0.021825047	1.43	0.01529893	0.072536186
26	4.11	0.043971051	5.43	0.05809314	3.15	0.033700441	1.81	0.01936438	0.091793581
32	2.71	0.028993077	5.44	0.058200126	4.37	0.046752675	2.09	0.022359975	0.104952801
37	1.88	0.020113279	5.04	0.053920705	5.39	0.057665198	2.24	0.023964758	0.111585903
42	1.38	0.014764003	4.46	0.047715544	6.33	0.067721838	2.35	0.025141598	0.115437382
48	0.87	0.009307741	3.65	0.039049717	7.58	0.081095028	2.45	0.026211454	0.120144745
54	0.54	0.005777218	2.74	0.029314034	8.74	0.093505349	2.57	0.02749528	0.122819383
60	0.29	0.00310258	1.82	0.019471366	10.12	0.108269352	2.64	0.028244179	0.127740717
66	0.12	0.001283826	0.99	0.010591567	11.08	0.118539962	2.72	0.029100063	0.129131529
72	0.06	0.000641913	0.4	0.004279421	11.6	0.12410321	2.74	0.029314034	0.128382631
78	0	0	0	0	12.16	0.130094399	2.74	0.029314034	0.130094399

Appendix 3.

Rate law derivation.

Consumption rate of **2** = -(k_1+k_5)[**2**]

The rate law of compound **2** can be described as:

$$\frac{d[\mathbf{2}]}{dt} = -(k_1+k_5)[\mathbf{2}] \quad \text{(Eq. 1)}$$

Based on (Eq 1)

$$[\mathbf{2}] = 0.17 * e^{-(k1+k5)t}. \quad \text{(Eq. 2)}$$

To obtain the rate law of **6**+**3**:

Production rate of **4**=k_1[**2**]
Consumption rate of **4**=k_2[**4**]

Production rate of **5**=k_2[**4**]
Consumption rate of **5**=k_3[**5**]

With stead-state approximation:

$$k_1[\mathbf{2}]=k_2[\mathbf{4}]=k_3[\mathbf{5}] \quad \text{(Eq. 3)}$$

Since compound **6** can be observed, the rate of its generation and consumption cannot be treated as equal based SSA. Thus the rate law of compound **6** can be expressed as:

$$\frac{d[\mathbf{6}]}{dt}=k_3[\mathbf{5}]-k_4[\mathbf{6}]^{\alpha} \quad \text{(Eq. 4)}$$

The rate law of compound **3** can be expressed as:

$$\frac{d[\mathbf{3}]}{dt}=k_4[\mathbf{6}]^{\alpha} \quad \text{(Eq. 5)}$$

Combination of (Eq. 3), (Eq. 4) and (Eq. 5)

$$[\mathbf{3}]+[\mathbf{6}]=-\frac{0.17k1}{k1+k5}e^{-(k1+k5)t}+\frac{0.17k1}{k1+k5} \quad \text{(Eq. 6)}$$

To obtain the rate law of compound **10:**

Production rate of **7**=k_5[**2**]
Consumption rate of **7**=k_6[**7**]

Production rate of **8**=k_6[**7**]
Consumption rate of **8**=k_7[**8**]

Production rate of **9**=k_7[**8**]
Consumption rate of **9**=k_8[**9**]

With stead-state approximation:

$$k_5[\mathbf{2}]=k_6[\mathbf{7}]=k_7[\mathbf{8}]=k_8[\mathbf{9}] \quad \text{(Eq. 7)}$$

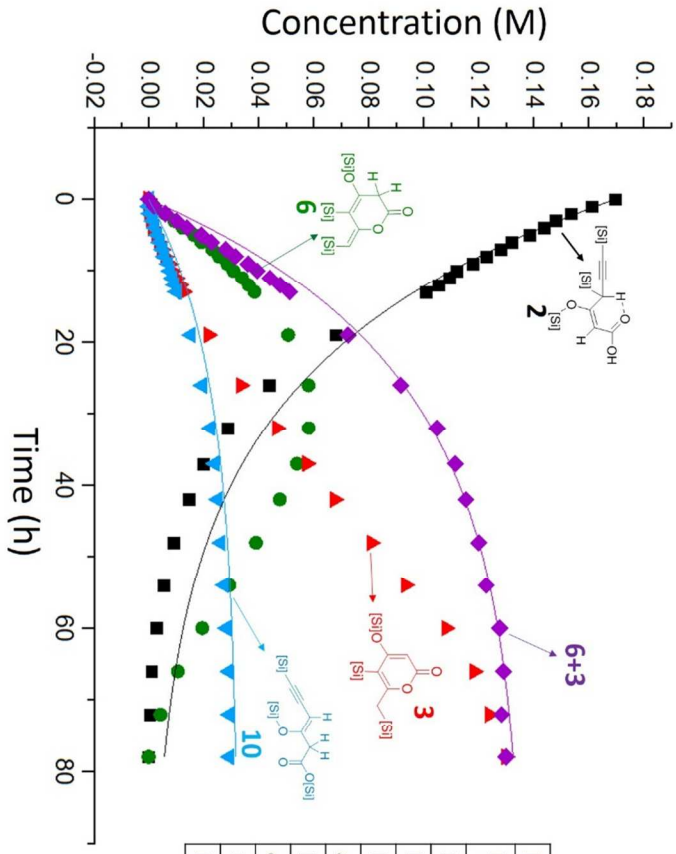
The rate law of compound 10 can be described as:

$$\frac{d[\mathbf{10}]}{dt}=k_8[\mathbf{9}] \quad \text{(Eq. 8)}$$

Combine (Eq 7) and (Eq 8)

$$[\mathbf{10}]=-\frac{0.17k5}{k1+k5}e^{-(k1+k5)t}+\frac{0.17k5}{k1+k5} \quad \text{(Eq. 9)}$$

Figure S7. Fitting result of the kinetic data with the derived rate law.



Model	GlobalFitting concentration of compound **2**, **6+3** and **10**		
Equation	$a*(0.17*\exp(-(k_1+k_5)*t)+b*(-0.17*k_1/(k_1+k_5)*\exp(-(k_1+k_5)*t)+0.17*k_5/(k_1+k_5))+c*(-0.17*k_5/(k_1+k_5)*\exp(-(k_1+k_5)*t)+0.17*k_5/(k_1+k_5))$		
Plot	Compound **2**	Compound **6+3**	Compound **10**
k_1*	0.03505±5.554478E-4	0.03505±5.554478E-4	0.03505±5.554478E-4
k_5*	0.00836±4.4391E-4	0.00836±4.4391E-4	0.00836±4.4391E-4
a	1	0	0
b	0	1	0
c	0	0	1
R-Square(COD)	0.98578	0.98563	0.93049
R-Square(COD)*	0.98917		

Reference:

1 Y. Xiang, D. J. Burrill, K. K. Bullard, B. J. Albrecht, L. E. Tragesser, J. McCaffrey, D. S. Lambrecht and E. Pentzer, *Polym. Chem.*, 2017, **8**, 5381–5387.