Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for:

Polymerization of Silyl Ketenes using Alkoxide Initiators: A Combined Computational and Experimental Study

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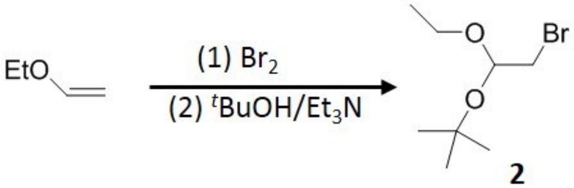
General Considerations. All reagents were purchased from commercial suppliers and used without purification. Unless otherwise noted, all operations were conducted under an inert atmosphere using anhydrous solvents that were obtained by passing commercial grade solvent through a column of activated neutral alumina in a Dow-Grubbs solvent system from Pure Process Technology (Nashua, NH). All ^{1}H, ^{13}C, and ^{29}Si NMR were collected on a Bruker Ascend III HD 500 MHz NMR instrument equipped with prodigy probe and shifts are reported relative to residual solvent peak (of $CDCl_3$). FTIR spectra were acquired using an Aglient Cary 630 FTIR in ATR mode. GPC spectra were acquired with a differential refractive index detector (Optilab T-rEx, Wyatt Technology Corporation) and an 18-angle static light scattering detector (Dawn Heleos II, Wyatt Technology Corporation) in THF or $CHCl_3$ at a flow rate of 1.0 mL/min. ESI spectra were obtained on

THERMO Finnigan LCQ Advantage (or DECA) ion trap mass spectrometer equipped with an external AP ESI ion source. Thermogravimentric analysis (TGA) was performed on a TA Instruments Q500, set at 3 °C min^{-1} under nitrogen gas. Differential Scanning Calorimetry (DSC) was performed using a TA instruments Q100; the temperature was first equilibrated at 40 °C then tramped from -50 °C at 10 °C min^{-1}.

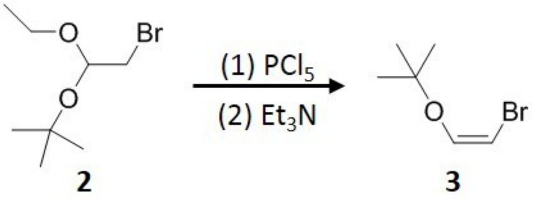
Materials Preparation



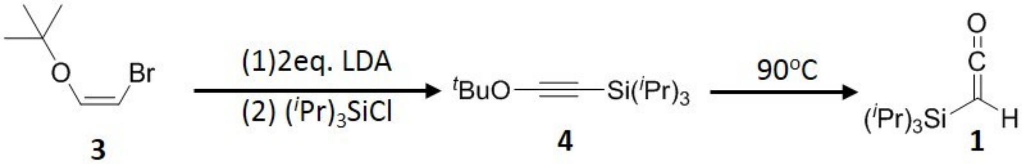
2

Preparation of 2-bromo-1-tert-butoxy-1-ethoxyethane (2).[1] An oven-dried round bottom flask with a magnetic stir bar was charged with ethyl vinyl ether (3.6 g, 0.05 mol) and dry CH_2Cl_2 (15 mL) and placed under an inert atmosphere of nitrogen, then cooled to -78 °C using a dry ice/acetone bath. Bromine (2.6 mL, 0.05 mol) was then added dropwise until persistent colouration was reached. The solution was then decolourized with the addition of ethyl vinyl ether dropwise. An attached addition funnel was loaded with a solution of triethyl amine (8.3 mL, 0.056 mol) and tert-butanol (8.6 mL, 0.056 mol), and this solution was added dropwise over ~20 minutes. After complete addition, dry CH_2Cl_2 (15 mL) was added to the solution and the round bottom flask was allowed to warm to 0 °C by transfer to an ice water bath. After approximately 15 minutes at 0 °C, the mixture was exposed to atmosphere and poured into ice water (20 mL), and the mixture then transferred to a separation funnel. The organic layer was isolated and the aqueous layer was washed with CH_2Cl_2 (1 x 50 mL), then the organic layers were combined and washed with an aqueous solution of HCl (0.05 N, 2 x 7 mL) and an aqueous solution of $NaHCO_3$

(saturated, 1 x 14 mL), then dried over $MgSO_4$. After filtration and removal of solvent under reduced pressure, the title compound was obtained by vacuum distillation as a clear oil (70%, 7 g). ^1H NMR (400 MHz, $CDCl_3$) δ 4.81 (t, *J* = 5.5 Hz, 1H), 3.53 (q, *J* = 7.0 Hz, 2H), 3.34 (dd, *J* = 10.5, 5.7 Hz, 1H), 3.24 (dd, *J* = 10.5, 5.4 Hz, 1H), 1.23 (s, 9H), 1.17 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 96.25, 75.02, 59.86, 33.43, 28.80, 15.47.

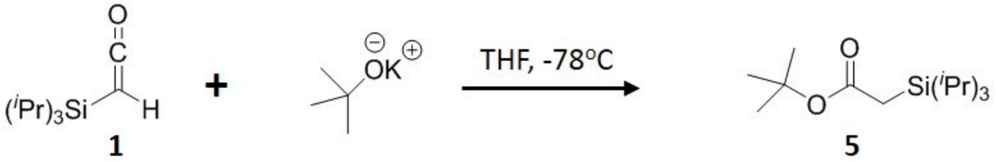


Preparation of (Z)-1-bromo-2-tert-butoxylethene (3)[1]: An oven-dried round bottom flask was charged with a magnetic stir bar and PCl_5 (18.5 g, 0.089 mol), then dry CH_2Cl_2 (74 mL) was added and the reaction mixture was placed under an inert nitrogen environment, and cooled to 0 °C in an ice-water bath. The flask was equipped with an addition funnel loaded with a solution of compound 2 (16.6 g, 0.074 mol) in CH_2Cl_2 (37 mL) which was added dropwise over the course of ~30 minutes. The reaction mixture was stirred at 0 °C for 45 minutes or until full consumption of 2 was observed (by TLC in Hex: EA, 9.9:0.1), after which triethyl amine (51 mL, 0.37 mol) was added dropwise. The reaction mixture was stirred for 35 minutes at 0 °C, then warmed to room temperature and finally heated to reflux for 2 hours. This reaction mixture was then carefully poured onto crushed ice (~80 g) and the entire mixture was transferred to a separatory funnel and the organic layer was isolated. The aqueous layer was washed with CH_2Cl_2 (2 x 30 mL) and the combined organic phases were washed with aqueous HCl (0.5 N, 2 x 35 mL) and saturated aqueous $NaHCO_3$ (2 x 35 mL), then dried over $MgSO_4$. The solution was filtered and the solvent removed under reduced pressure; the title compound was obtained by vacuum distillation as a transparent oil (75%, 10.1 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 4.2 Hz, 1H), 5.08 (d, *J* = 4.2 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.28, 83.10, 78.15, 28.27.



Preparation of Triisopropylsilylketene (TIPS ketene, 1)[2]**.** A solution of LDA in THF (2.0 M, 48 mL, 0.096 mol LDA) was added to dry THF (48 mL) in an oven-dried round bottom flask which was cooled to -78 °C in a dry ice/acetone bath and placed under N_2. A mixture of compound 3 (7.08 g, 0.04 moL) and dry THF (16 mL) was then prepared in an attached addition funnel and added dropwise to the solution of LDA. After addition, the reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction vessel was cooled to about -20 °C using a salt water ice bath and triisopropylsilyl chloride (10.2 mL, 0.048 mol) was then added and the resulting solution was 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 resulting organic layer was isolated and the aqueous layer washed with hexane (2 x 20 mL). The organic layers were combined and washed with an aqueous HCl soluiton (5 N, 2 x 80 mL), water (1 x 120 mL) and an aqueous solution of saturated NaCl (1 x 120 mL); the organic phase was then dried over Na_2SO_4 overnight, then filtered and the solvent removed under reduced pressure. The isolated crude product 4 was then run through a plug column of silica gel, with eluent of 2.5 vol% NEt_3 in hexanes. A pale yellow oil was obtained and then heated to 90 °C for ~2 hours under nitrogen gas (or until disappearance of the alkyne stretching frequency in the FTIR spectrum). The title compound 1 was isolated by vacuum distillation

(58%, 4.6 g, 0.023 mol).^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66(s, 1H), 1.08~1.03(m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.32, 18.66, 12.36, -6.97. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 10.69.



Preparation of ^{t}Butyl triisopropylsilylacetate (5). A solution of ^{t}BuOK in THF (3 mL, 0.003 mol) was loaded into an oven dried round bottom flask equipped with a magnetic stire bar, which was placed under nitrogen gas and cooled to -78 °C using a dry ice/acetone mixture. A mixture of THF (2 mL) and TIPS ketene (0.5 g, 0.0025 mol) was then added. After the addition was complete, the mixture was kept at -78 °C for one minute and then poured into an aqueous solution of saturated $NaHCO_3$ (15 mL). The aqueous phase was extracted with hexanes (2 x 20 mL). The combined organic phases were washed with aqueous HCl (5 N, 2 x 4 mL) and dried over Na_2SO_4 for 30 minutes. After filtration, the solvent was removed under reduced pressure and the residue was loaded onto a silica gel column using an eluent of hexanes:ethyl acetate (15:1) to obtained the final product as transparent light yellow oil (44%, 0.3 g, 0.001 mol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.81 (s, 2H), 1.40 (s, 9H), 1.08~1.02 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.54, 28.54, 20.73, 18.80, 11.65. ^{29}Si NMR (99 MHz, $CDCl_3$) δ 7.95.

Polymerization of TIPS ketene by ^{t}BuOM. A solution of alkoxide in THF was added to an oven dried round bottom flask and placed under nitrogen; then, the desired amount of TIPS ketene was added and the reaction was heated to the desired temperature. At different time points, an aliquot of the reaction was removed using a gas tight syringe and this solution was directly loaded onto ATR-FTIR to determine the extent of monomer consumption. At the desired extent of reaction, the crude mixture was quenched by adding the reaction mixture into methanol, which led to a yellow-orange precipitate. The product was obtained after centrifuging for 10 minutes (5,000 rpm) and isolation of the pellet.

To determine the percent conversion, the following relationship was used, using values for the area of integration under the peaks in FTIR spectra.

Equation 1: Convert B_{tx} to a standard of A_{tx} with respect to A_{t0}

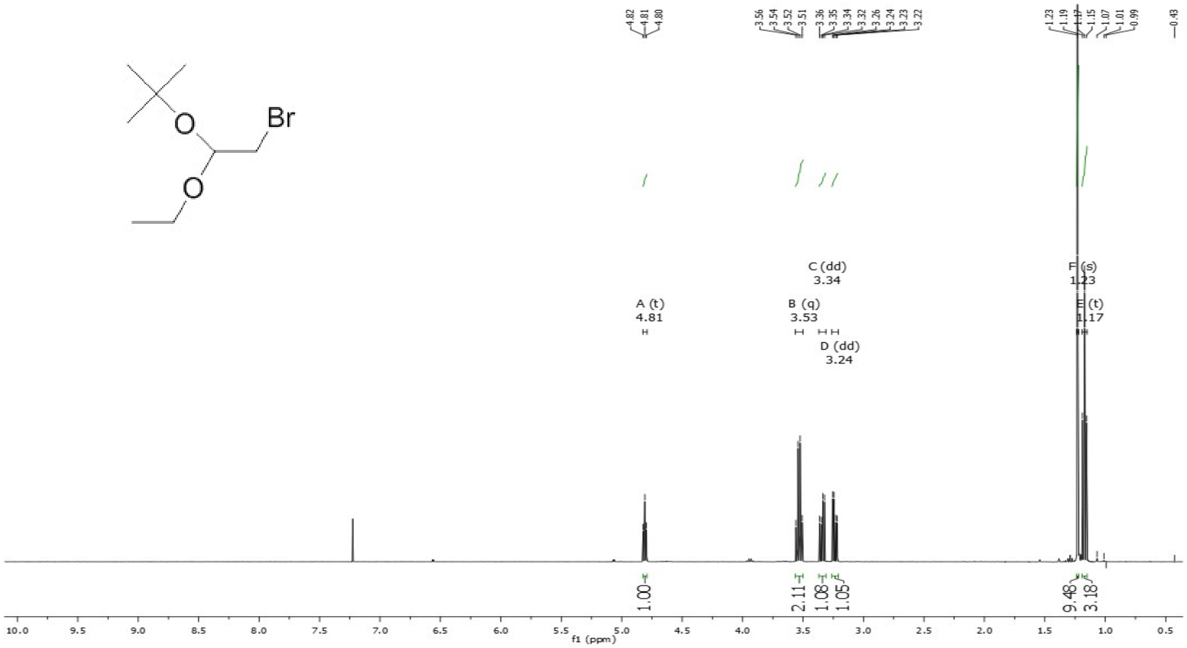
$$S_{Btx} = \frac{B_{t0}A_{t0}}{A_{tx}}$$

Equation 2: Determine % conversion using the area of A and B at t_x compared to t_0.

$$Percent\ Conversion = \left[1 - \left(\frac{S_{Btx}}{B_{t0}}\right)\right] x\ 100$$

Figure S1: Characterization of **Compound 2**: A) ^{1}H NMR; B) ^{13}C NMR. NMR spectra were collected in $CDCl_3$

A)



B)

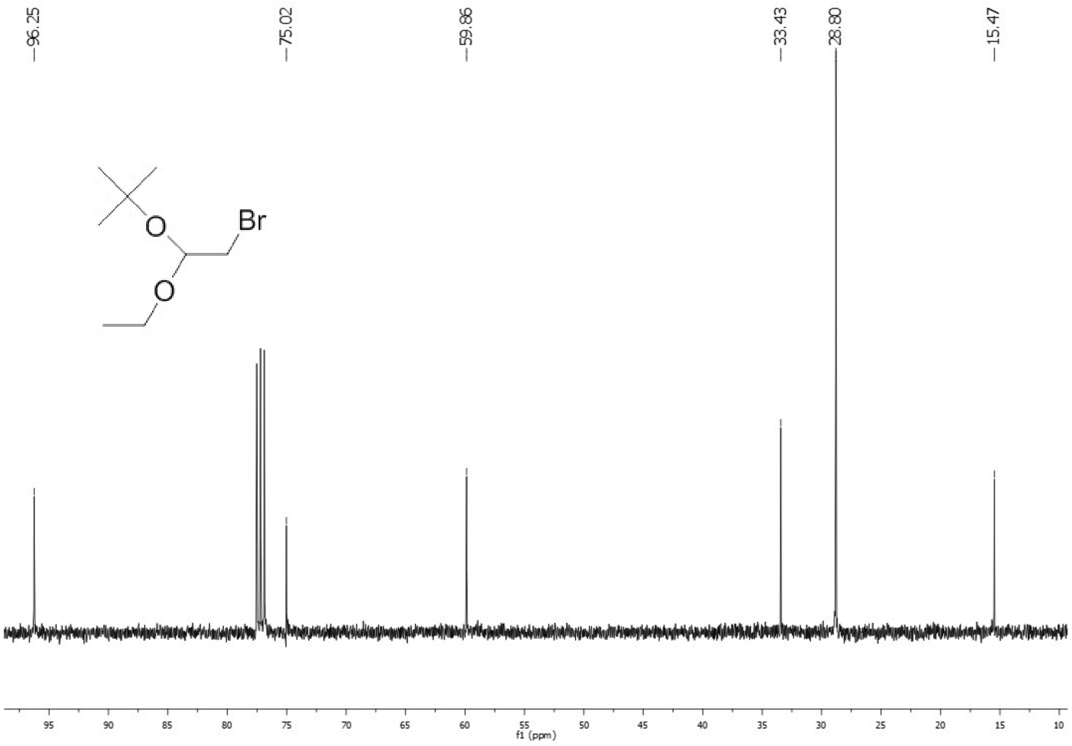
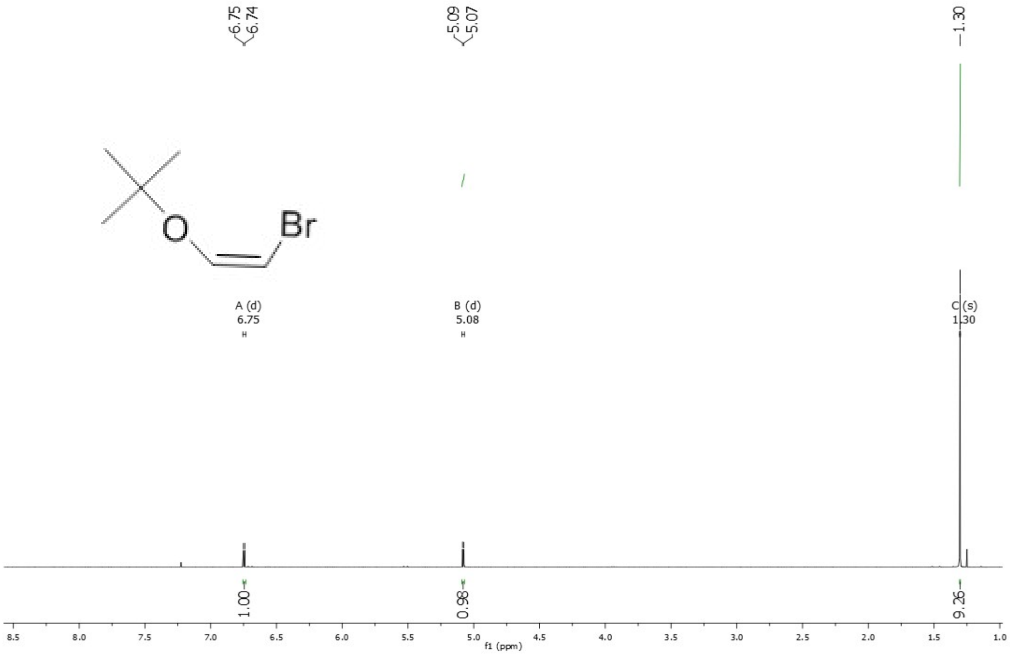


Figure S2: Characterization of **Compound 3**: A) ^{1}H NMR; B) ^{13}C NMR. NMR spectra were collected in $CDCl_3$.

A)



B)

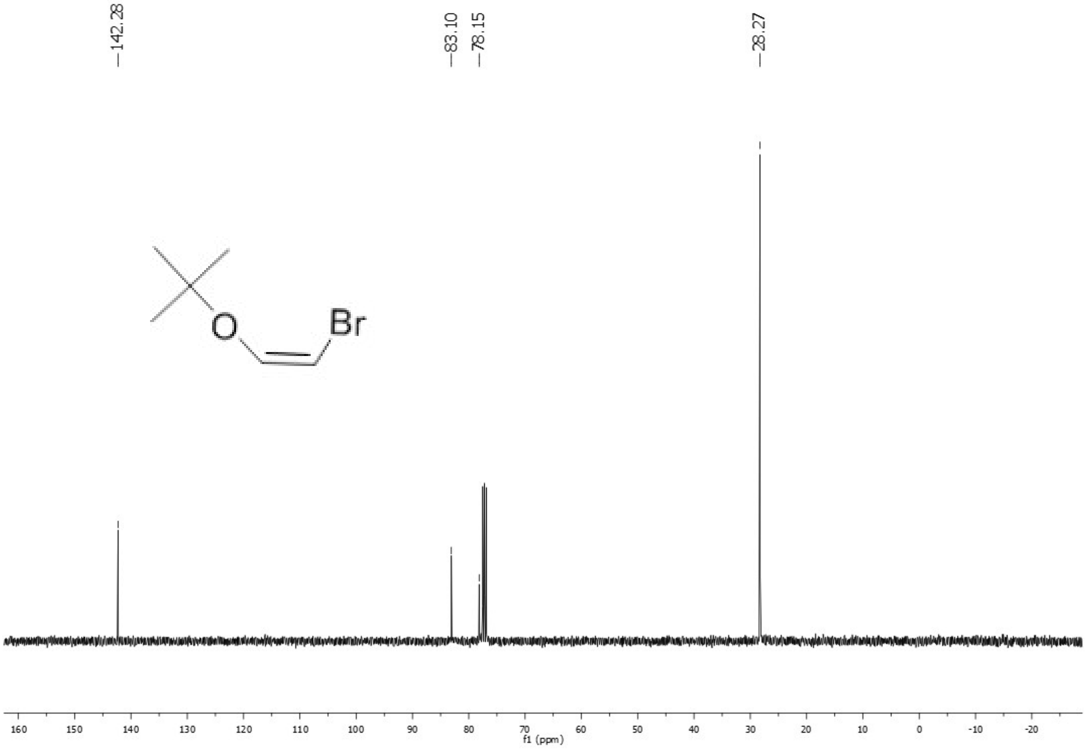
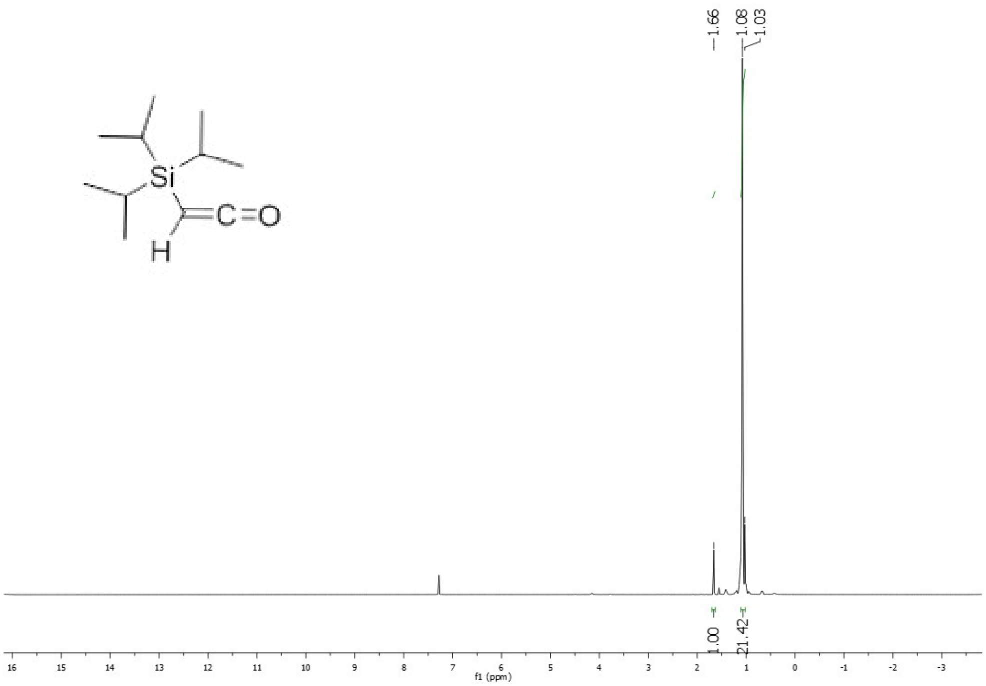
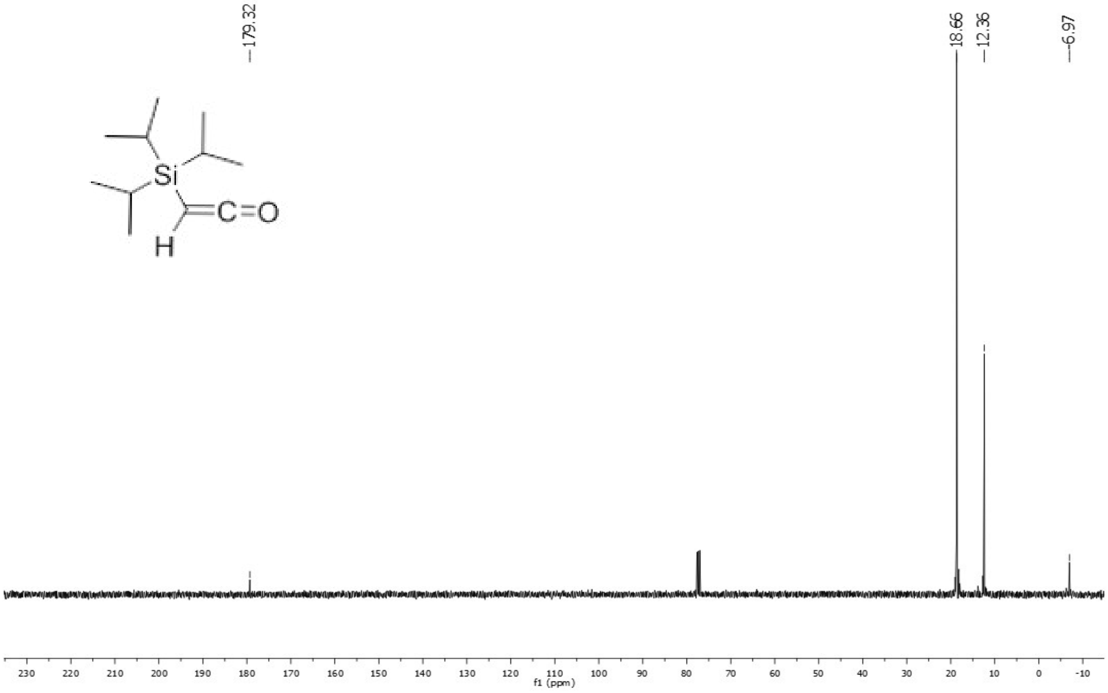


Figure S3: Characterization of **Compound 1**: A) ^1H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) FTIR; E) Gas chromotograph; F) Mass spectrum from GC-MS.

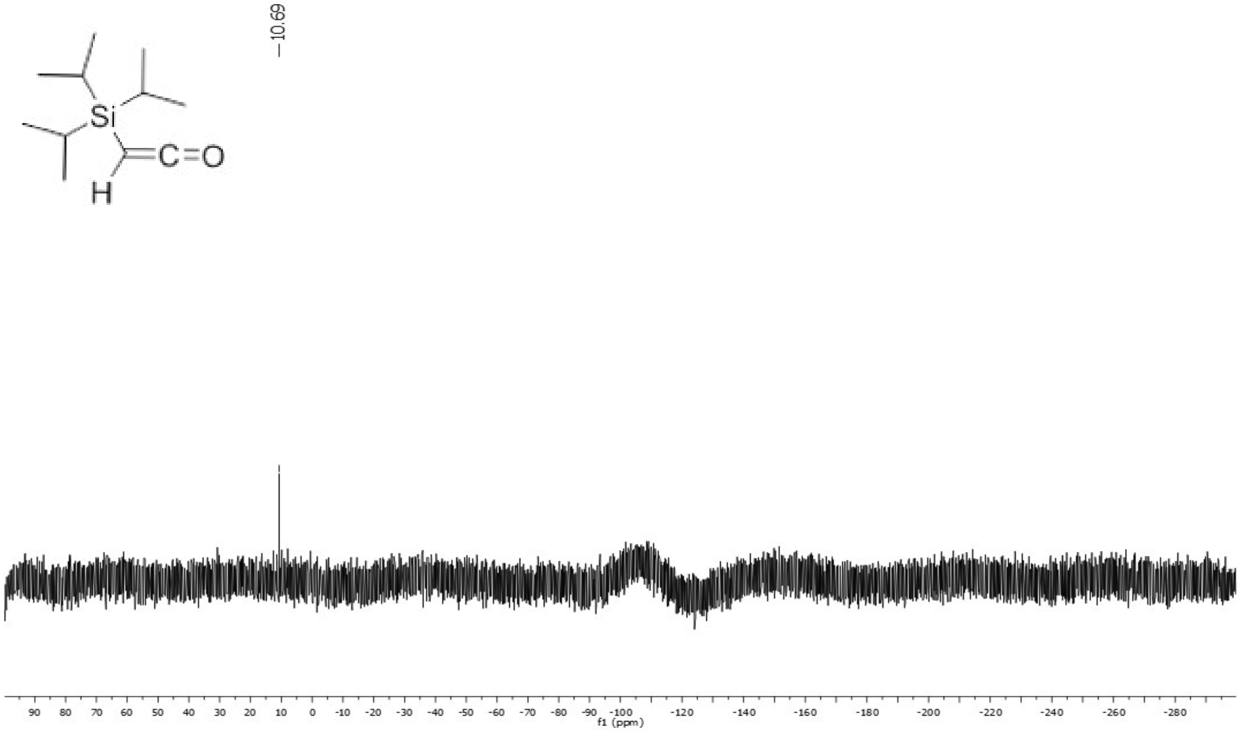
A)



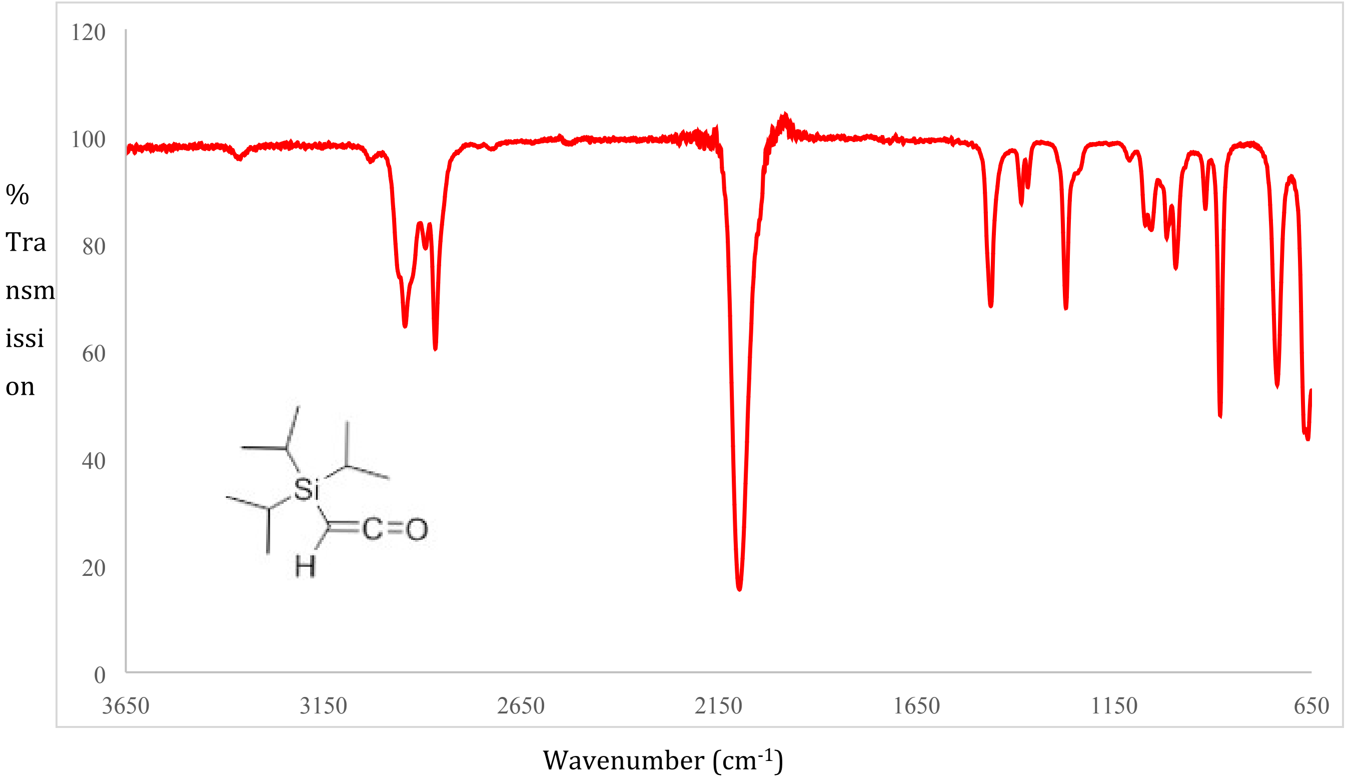
B)



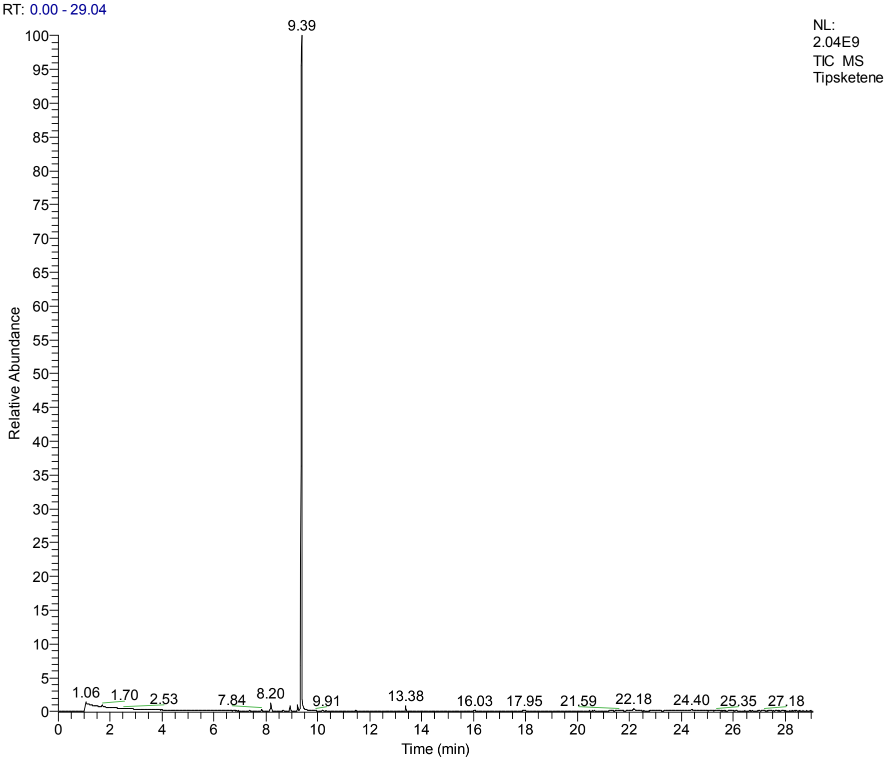
C)


Si
C=O
H
—10.69
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)

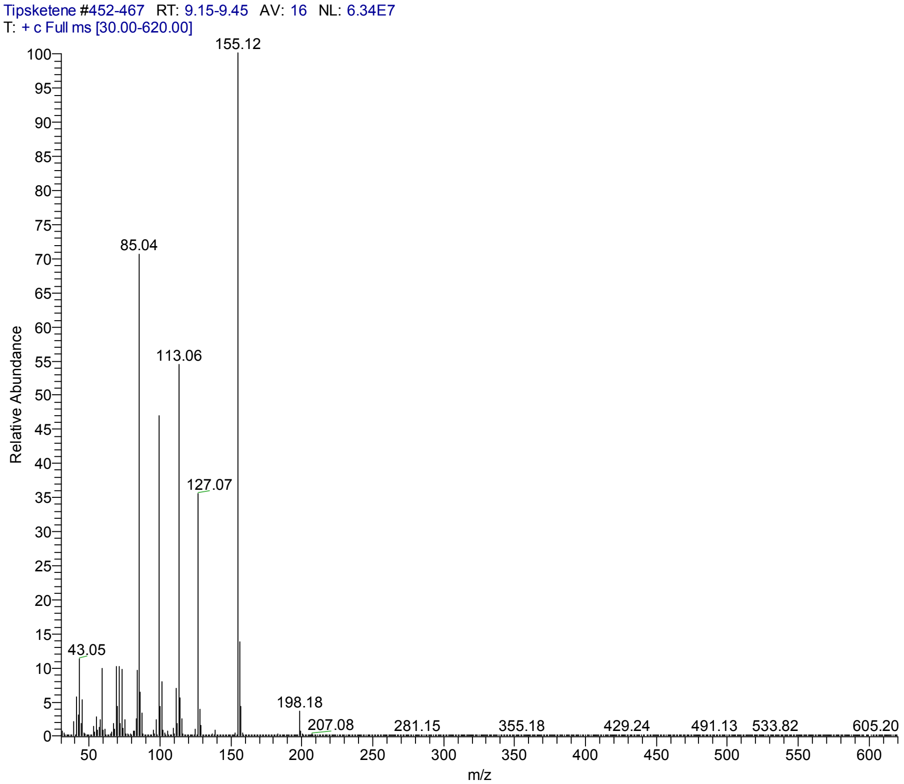

120
100
80
60
40
20
0
% Transmission
Si
C=O
H
3650
3150
2650
2150
1650
1150
650
Wavenumber (cm-1)

E)



RT: 0.00 - 29.04
NL:
2.04E9
TIC MS
Tipsketene
9.39
1.06
1.70
2.53
7.84
8.20
9.91
13.38
16.03
17.95
21.59
22.18
24.40
25.35
27.18
Relative Abundance
Time (min)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

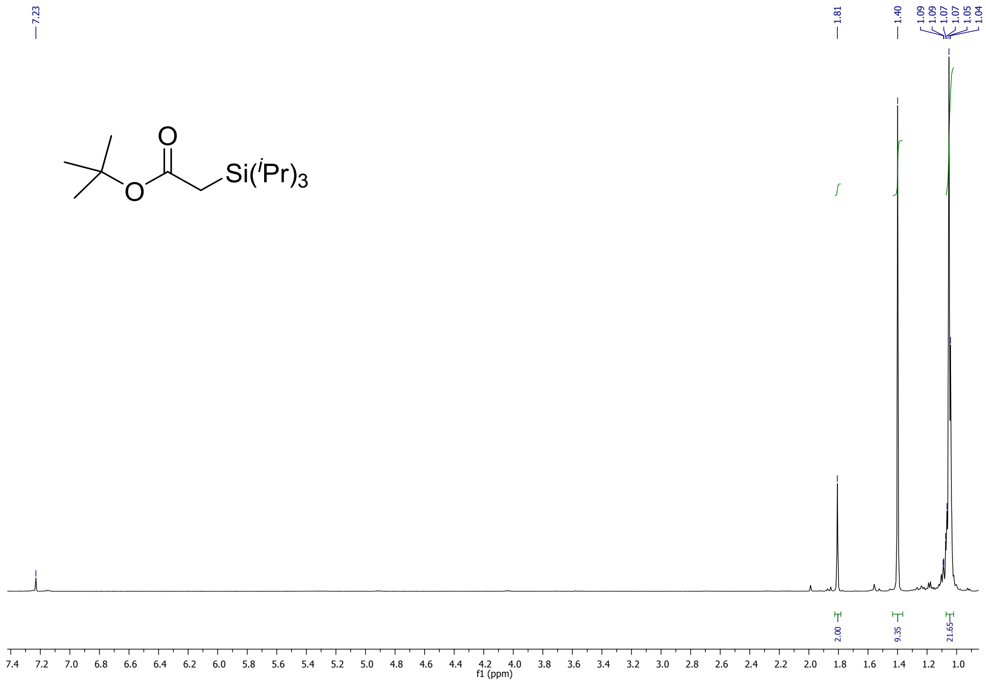
F)



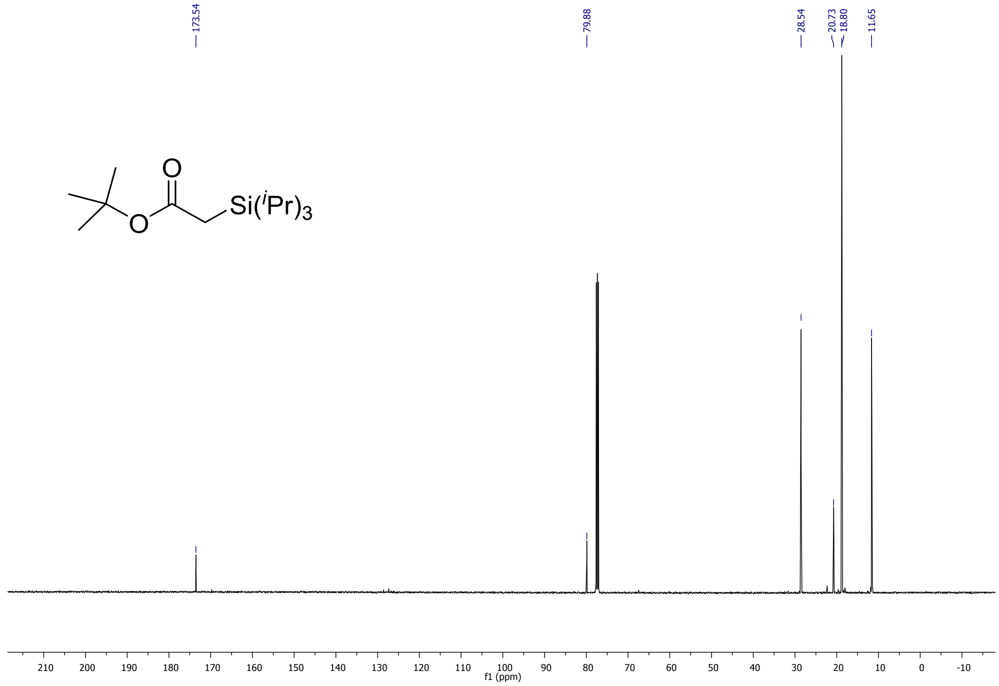
Tipsketene #452-467 RT: 9.15-9.45 AV: 16 NL: 6.34E7
T: + c Full ms [30.00-620.00]
155.12
85.04
113.06
127.07
43.05
198.18
207.08
281.15
355.18
429.24
491.13
533.82
605.20
Relative Abundance
m/z
50
100
150
200
250
300
350
400
450
500
550
600
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100

Figure S4: Characterization of **Compound 5**: A) ^{1}H NMR; B) ^{13}C NMR; C) ^{29}Si NMR; D) FTIR; E) Gas chromotograph; F) Mass spectrum from GC-MS.

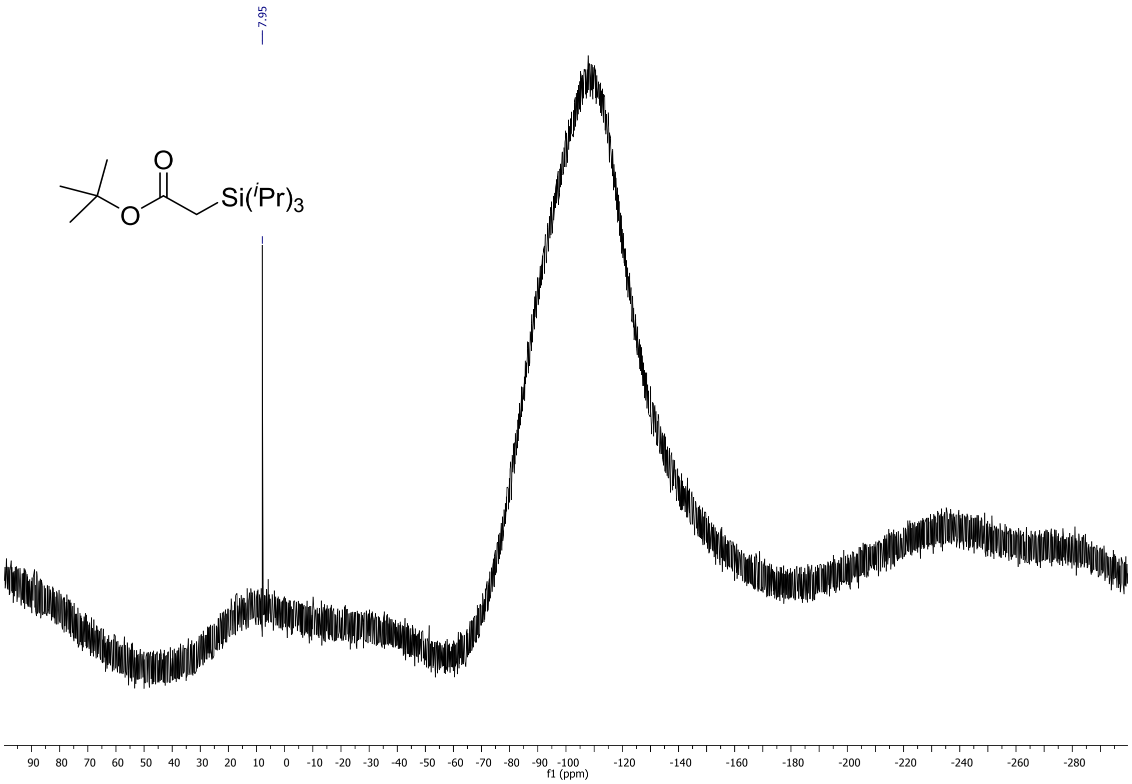
A)



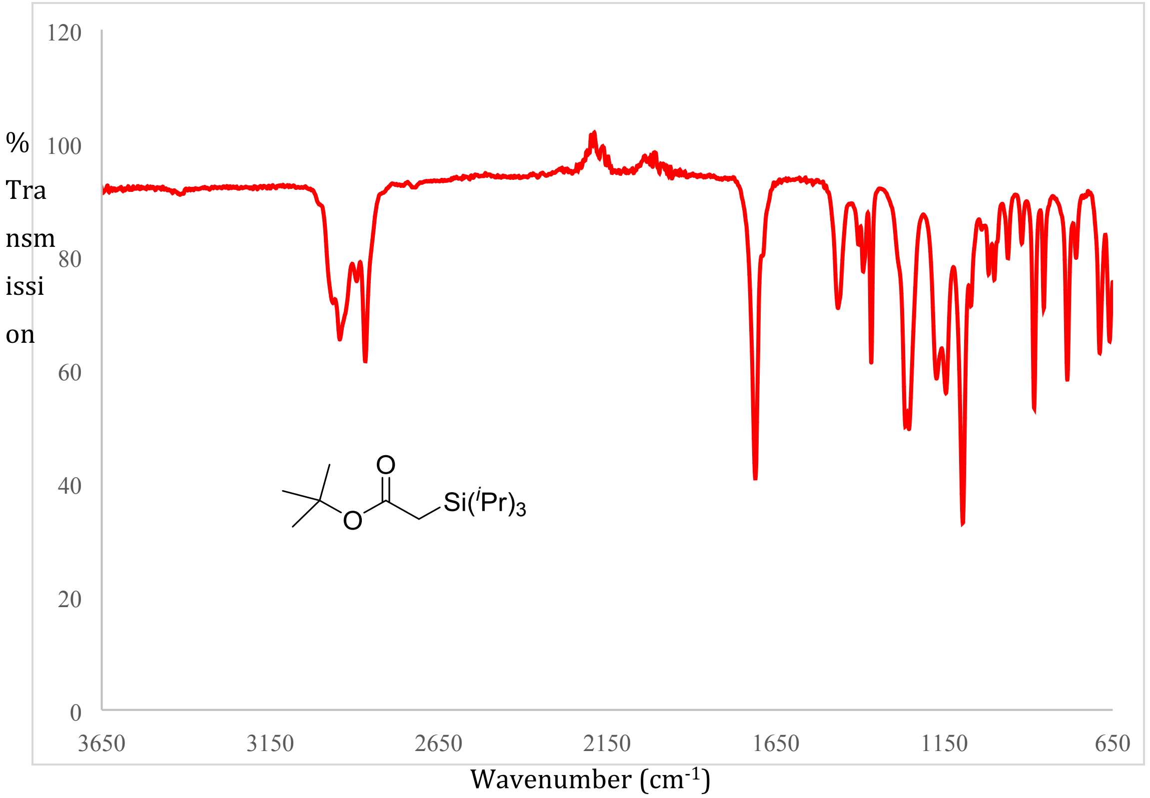
B)



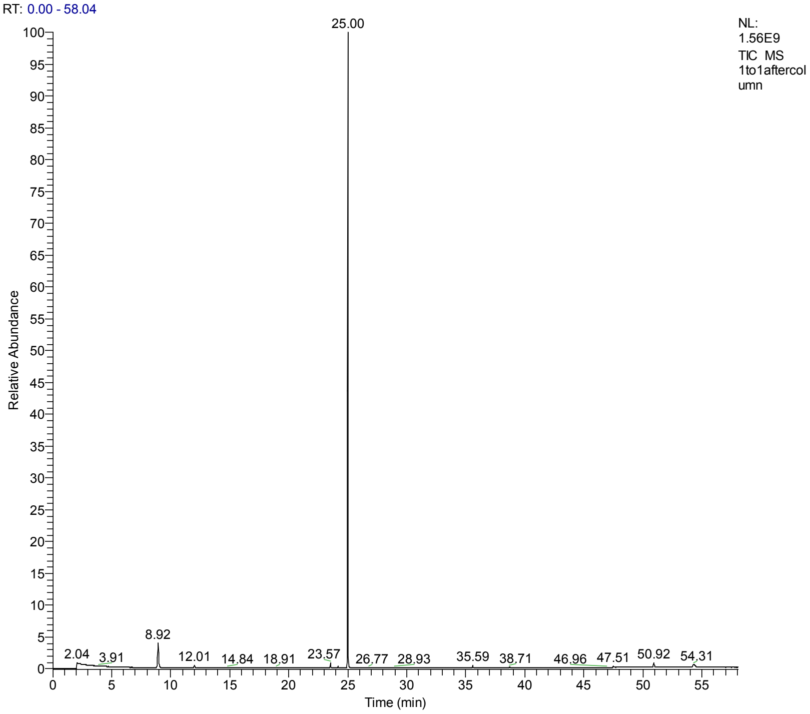
C)


7.95
O
O
Si(iPr)3
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)

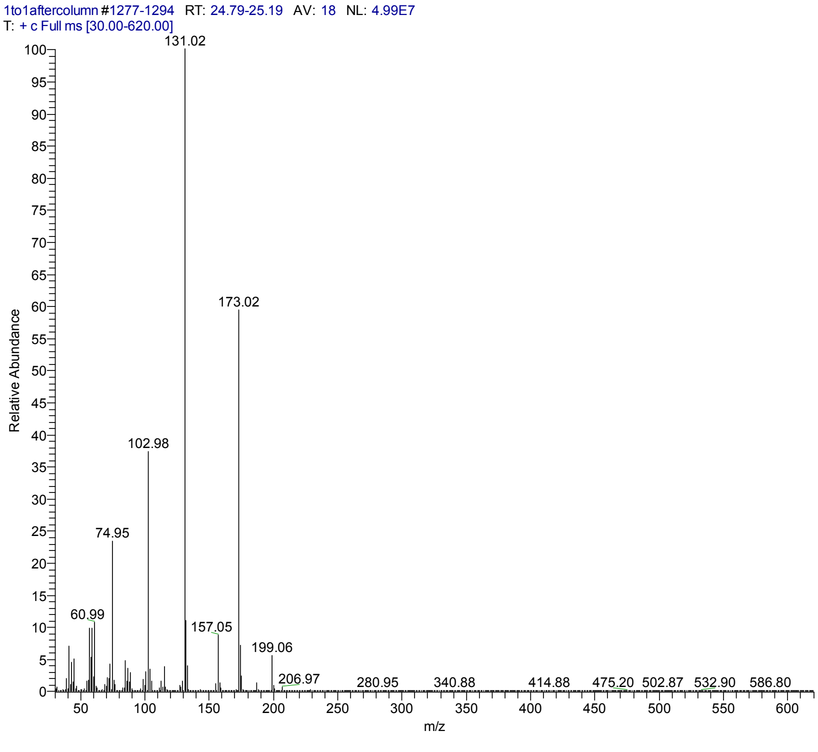

120
100
80
60
40
20
0
% Transmission
O
O
Si(iPr)3
3650
3150
2650
2150
1650
1150
650
Wavenumber (cm-1)

E)



RT: 0.00 - 58.04
NL:
1.56E9
TIC MS
1to1aftercol
umn
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
25.00
2.04
3.91
8.92
12.01
14.84
18.91
23.57
26.77
28.93
35.59
38.71
46.96
47.51
50.92
54.31
0
5
10
15
20
25
30
35
40
45
50
55
Time (min)

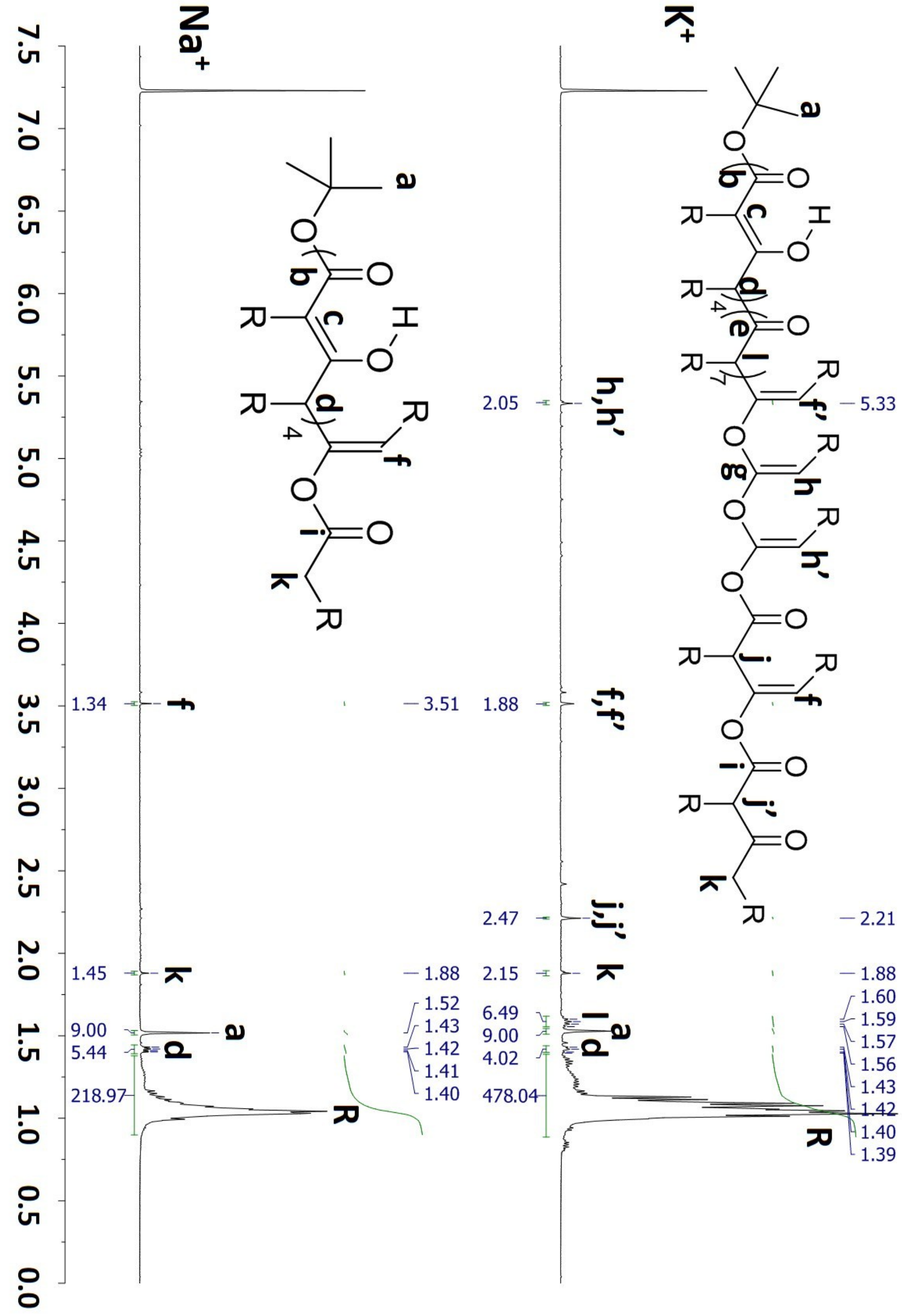
F)



1to1aftercolumn #1277-1294 RT: 24.79-25.19 AV: 18 NL: 4.99E7
T: + c Full ms [30.00-620.00]
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
131.02
173.02
102.98
74.95
60.99
157.05
199.06
206.97
280.95
340.88
414.88
475.20
502.87
532.90
586.80
50
100
150
200
250
300
350
400
450
500
550
600
m/z

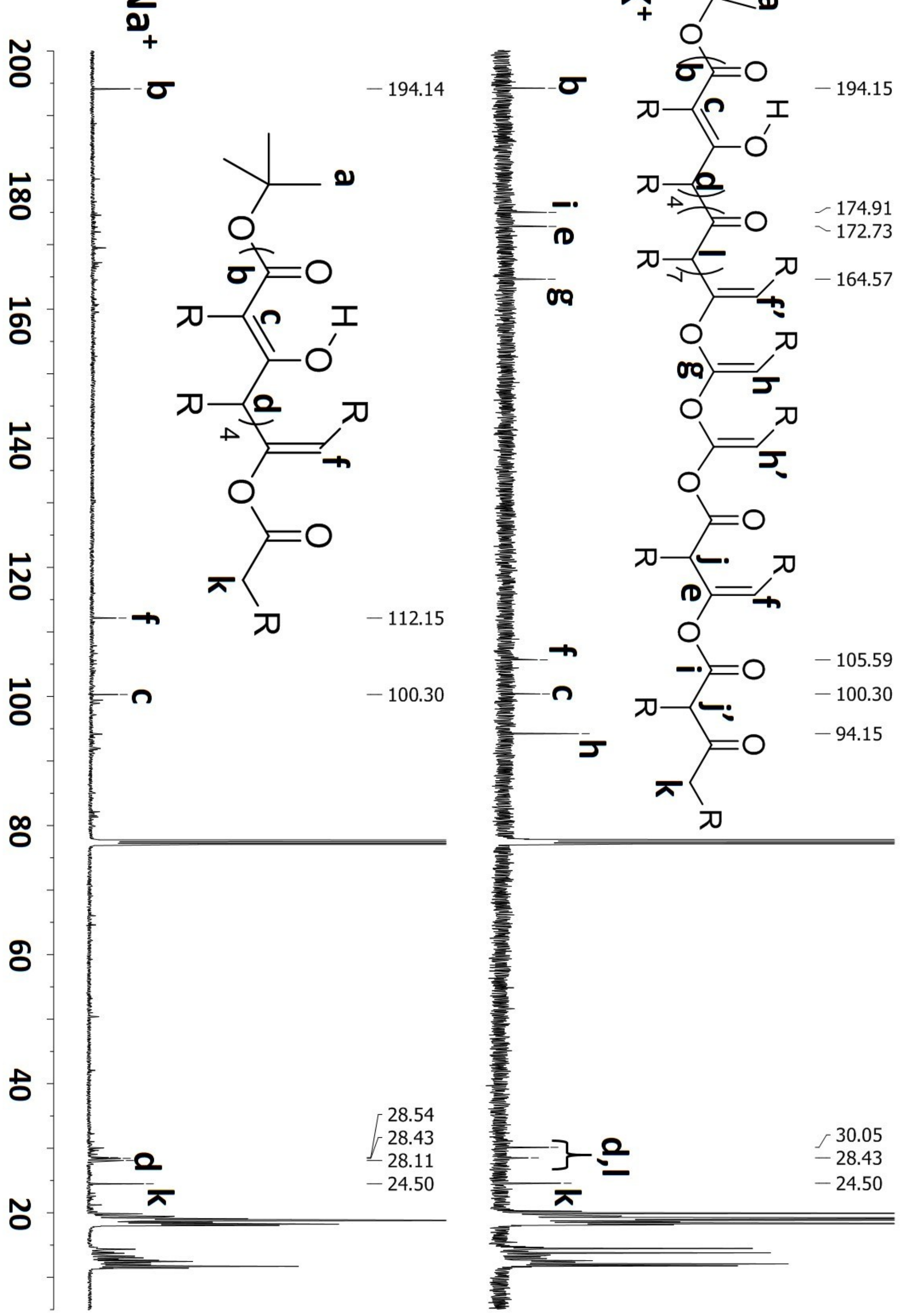
Figure S5: Characterization of the products isolated from the polymerizaiton of TIPS ketene with ^{t}Bu(B) ^{13}C NMR; C) FTIR.

A)



B)

C)



194.15
174.91
172.73
164.57
105.59
100.30
94.15
30.05
28.43
24.50
b
i e
g
f
c
h
d,l
k
194.14
112.15
100.30
28.54
28.43
28.11
24.50
a
b
c
d
f
k
R
4
7
200
180
160
140
120
100
80
60
40
20

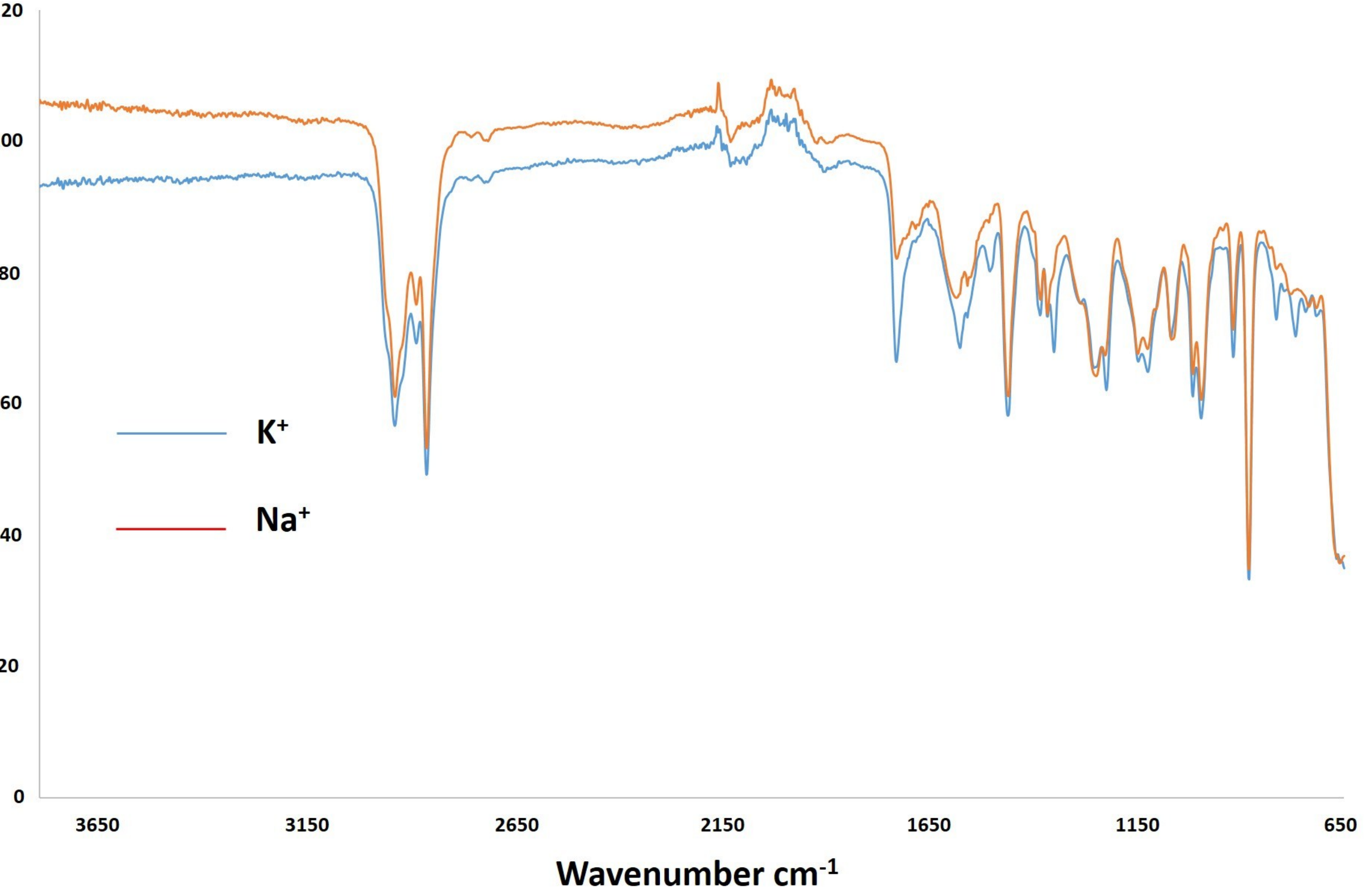
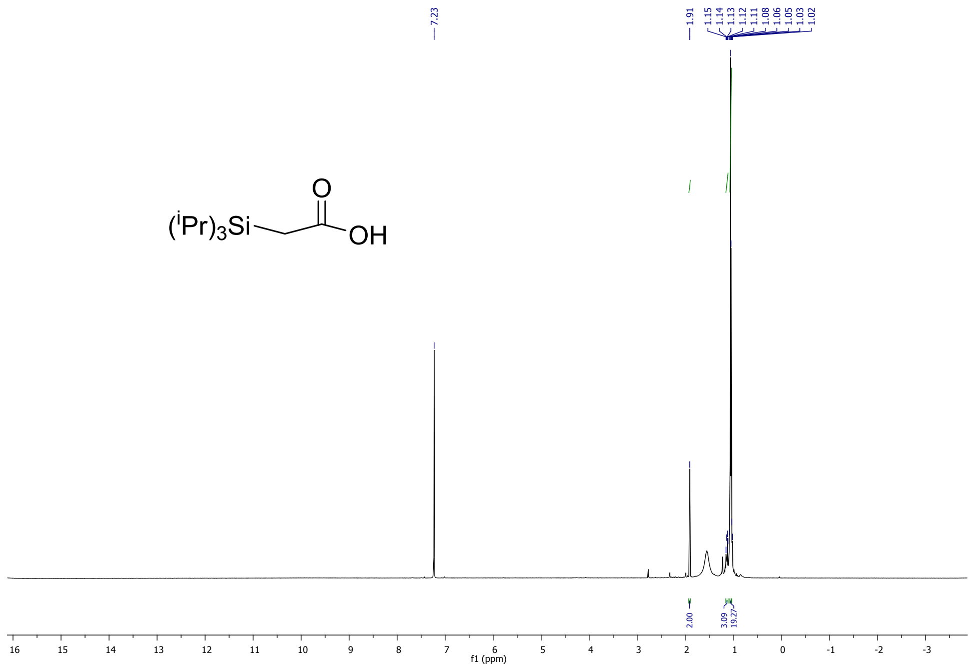
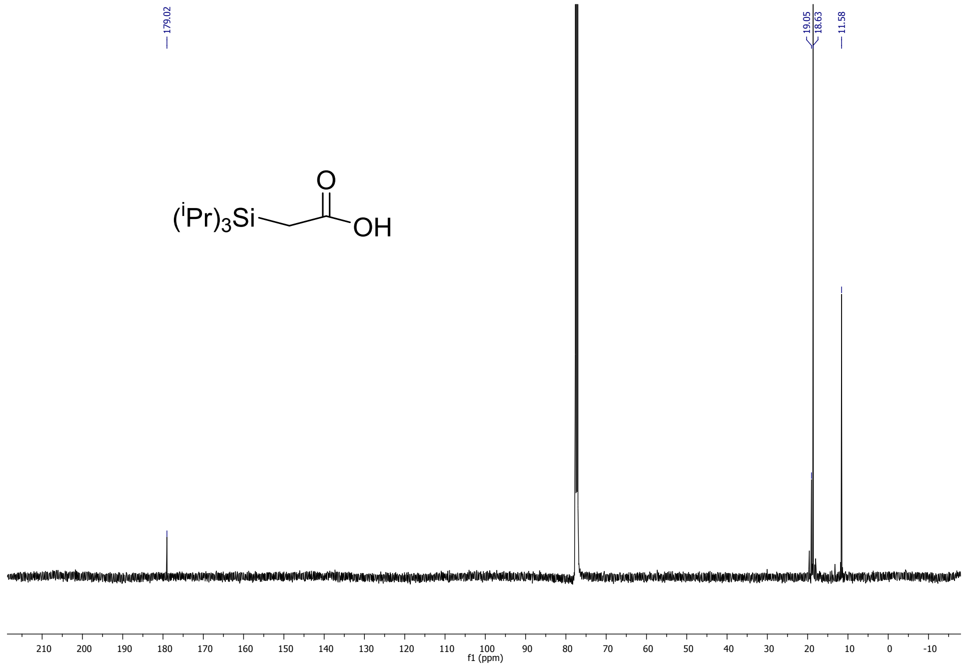

20
00
80
60
40
20
0
K+
Na+
3650
3150
2650
2150
1650
1150
650
Wavenumber cm-1

Figure S6: Characterization of ^{t}Butyl triisopropylacetic acid obtained from the attempted polymerization of TIPS ketene with ^{t}BuOLi. A) ^{1}H NMR; B) ^{13}C NMR; C)^{29}Si NMR; D) ESI-MS.

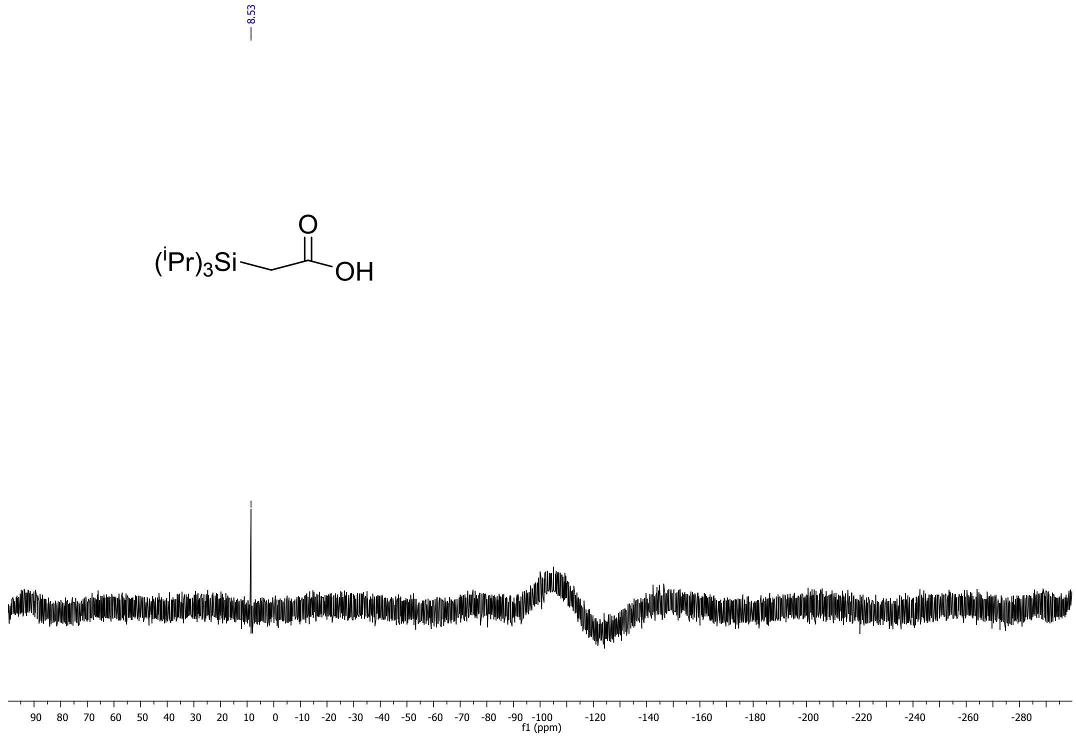
A)



B)



C)


8.53
$(^{i}Pr)_3Si$
O
OH
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)

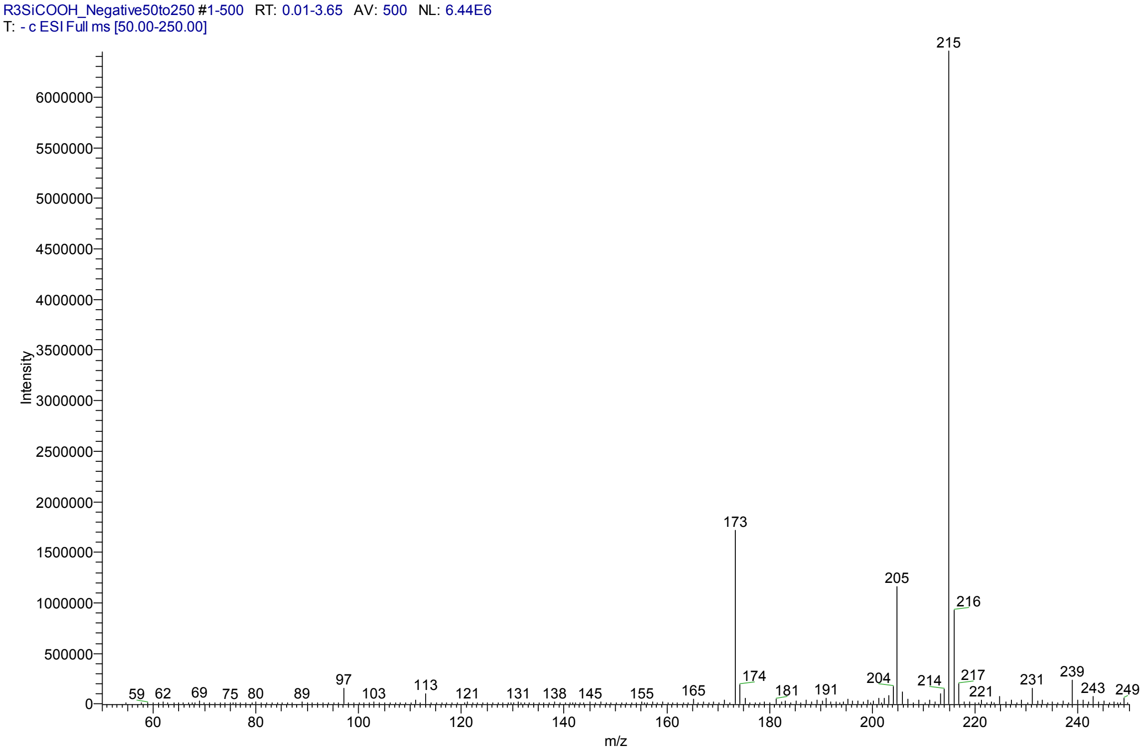
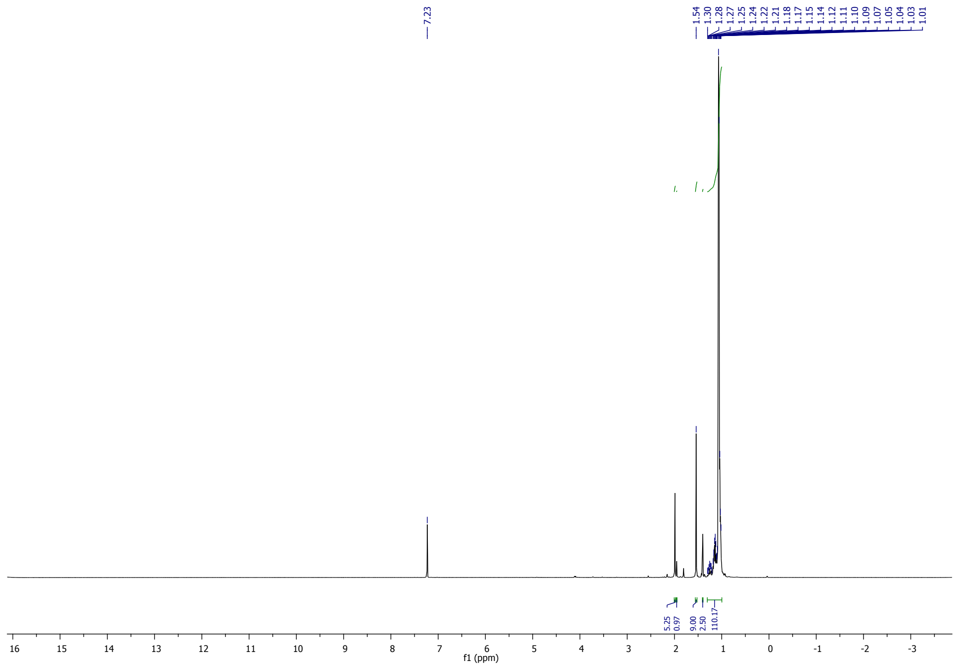
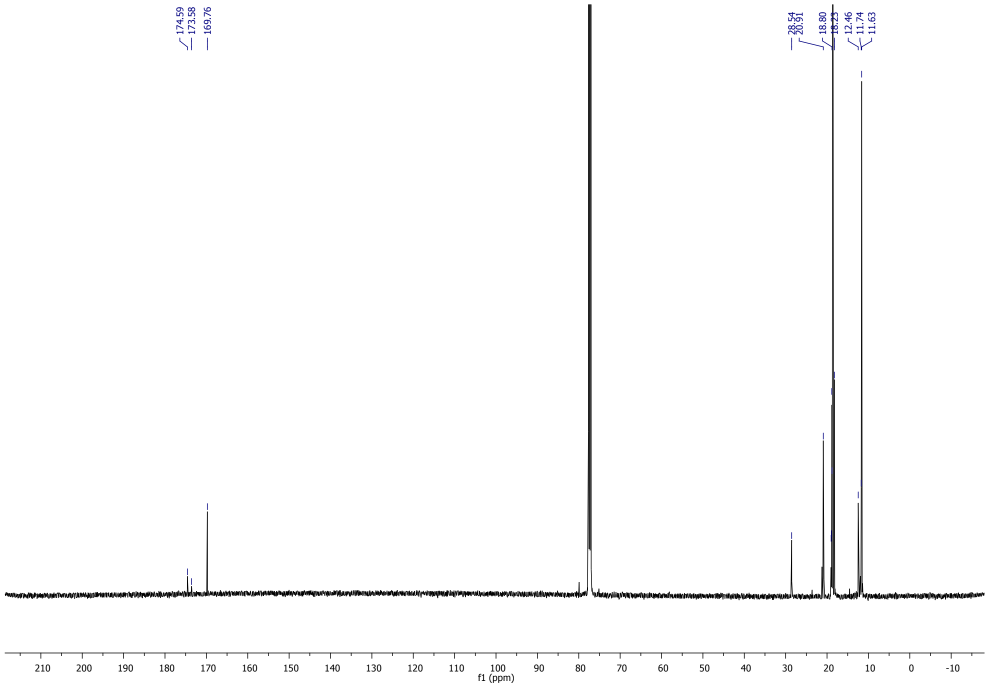

R3SiCOOH_Negative50to250 #1-500 RT: 0.01-3.65 AV: 500 NL: 6.44E6
T: - c ESI Full ms [50.00-250.00]
Intensity
m/z
0
500000
1000000
1500000
2000000
2500000
3000000
3500000
4000000
4500000
5000000
5500000
6000000
60 80 100 120 140 160 180 200 220 240
215
173
205
216
59 62 69 75 80 89 97 103 113 121 131 138 145 155 165 174 181 191 204 214 217 221 231 239 243 249

Figure S7: Characterization of the product of the attempted polymerization of TIPS ketene initiated by ^{t}BuOLi. A) ^{1}H NMR; B) ^{13}C NMR; C)^{29}Si NMR; D) FTIR; E) ESI-MS.

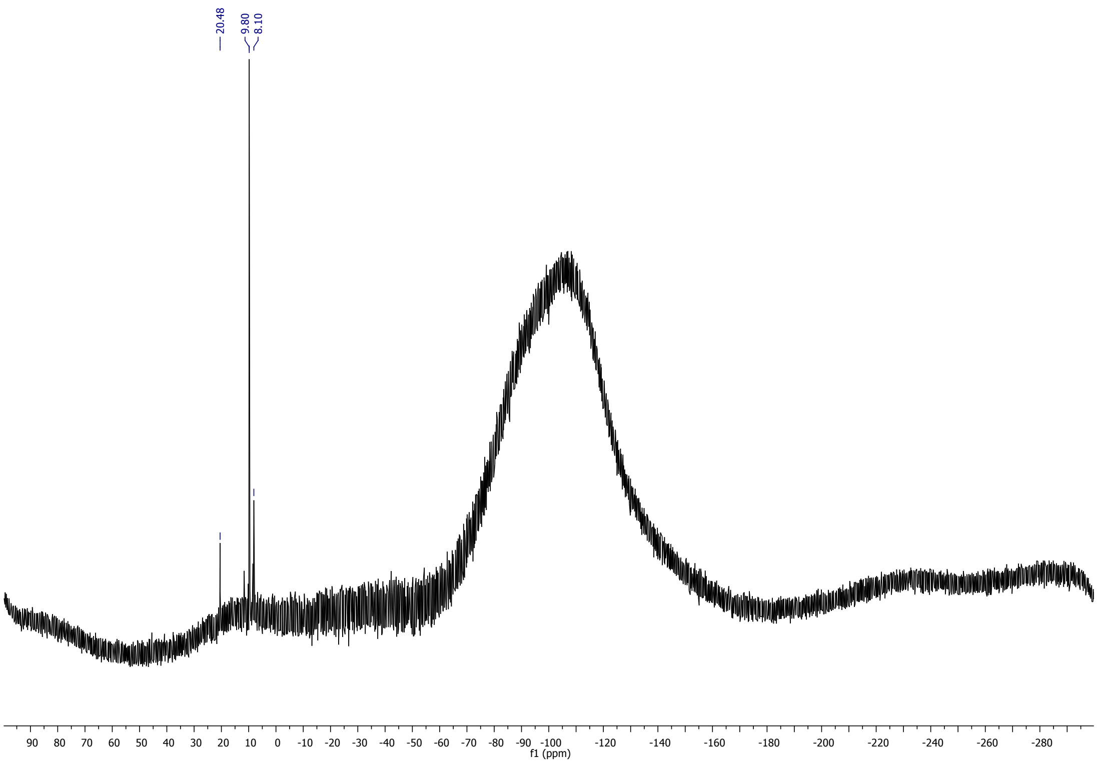
A)



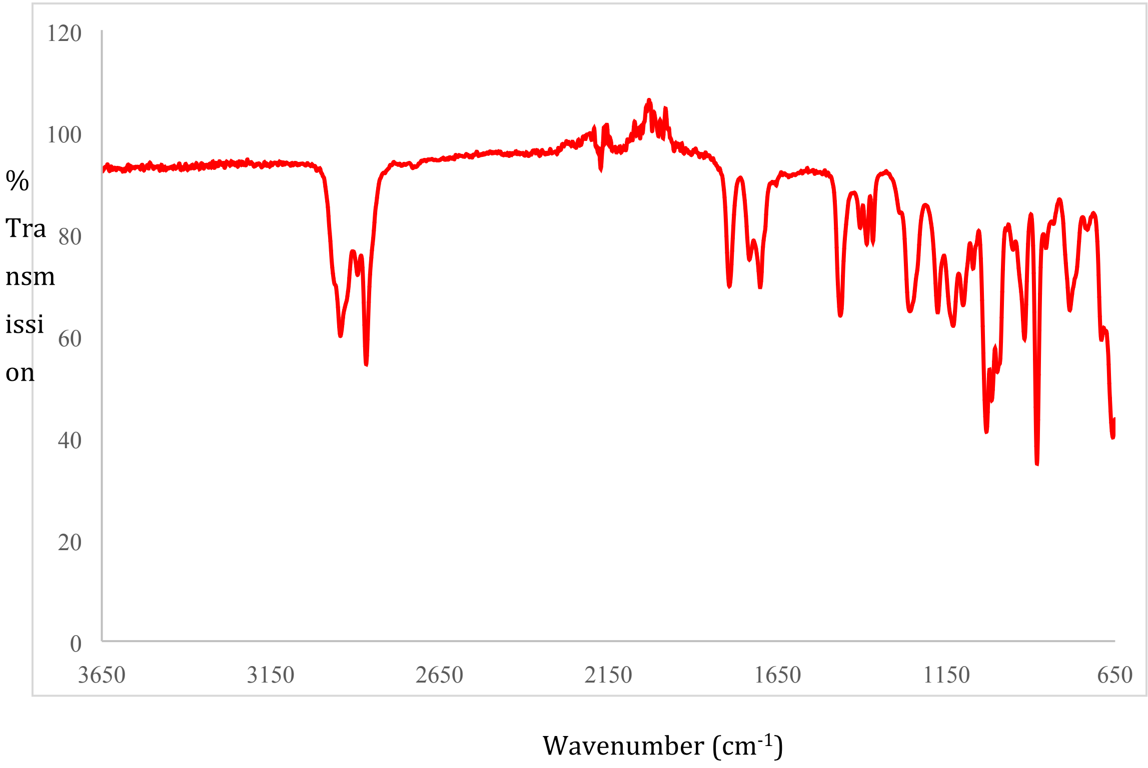
B)



C)


20.48
9.80
8.10
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)


120
100
80
60
40
20
0
% Transmission
3650
3150
2650
2150
1650
1150
650
Wavenumber (cm-1)

E)

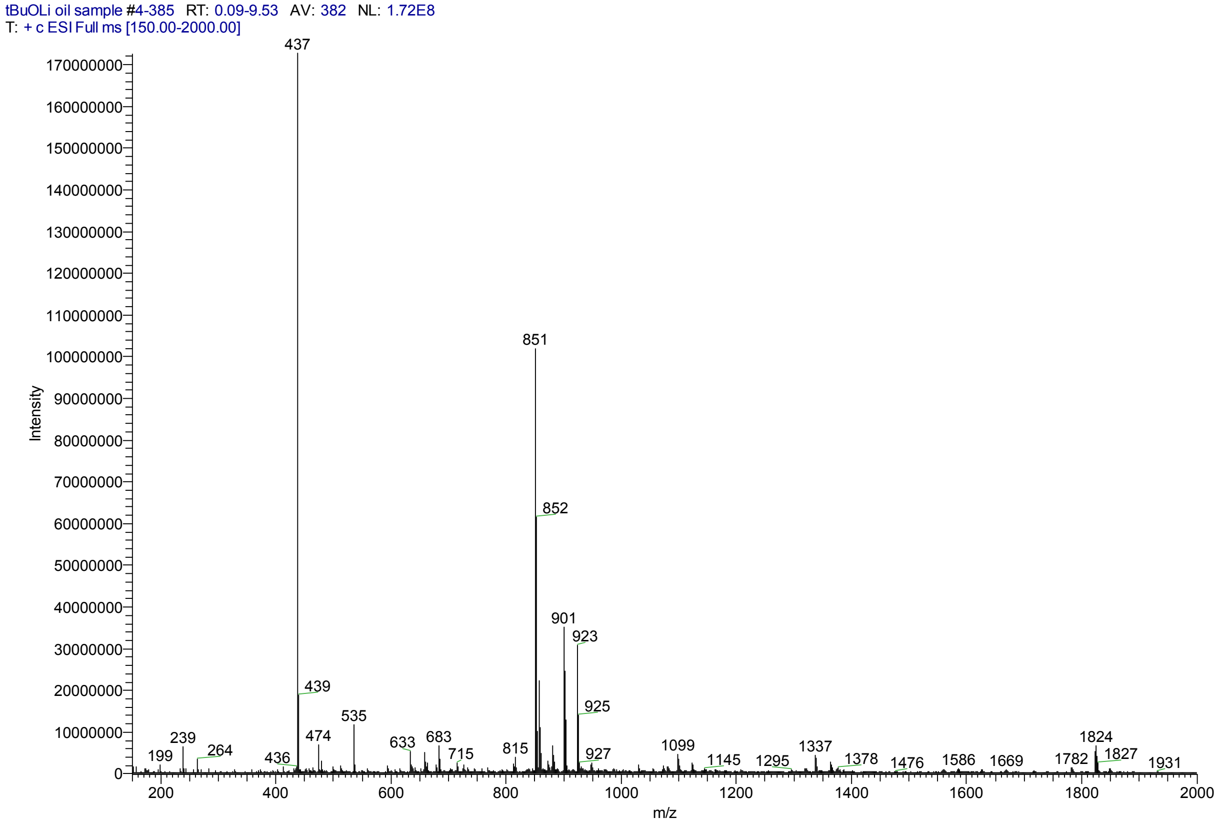
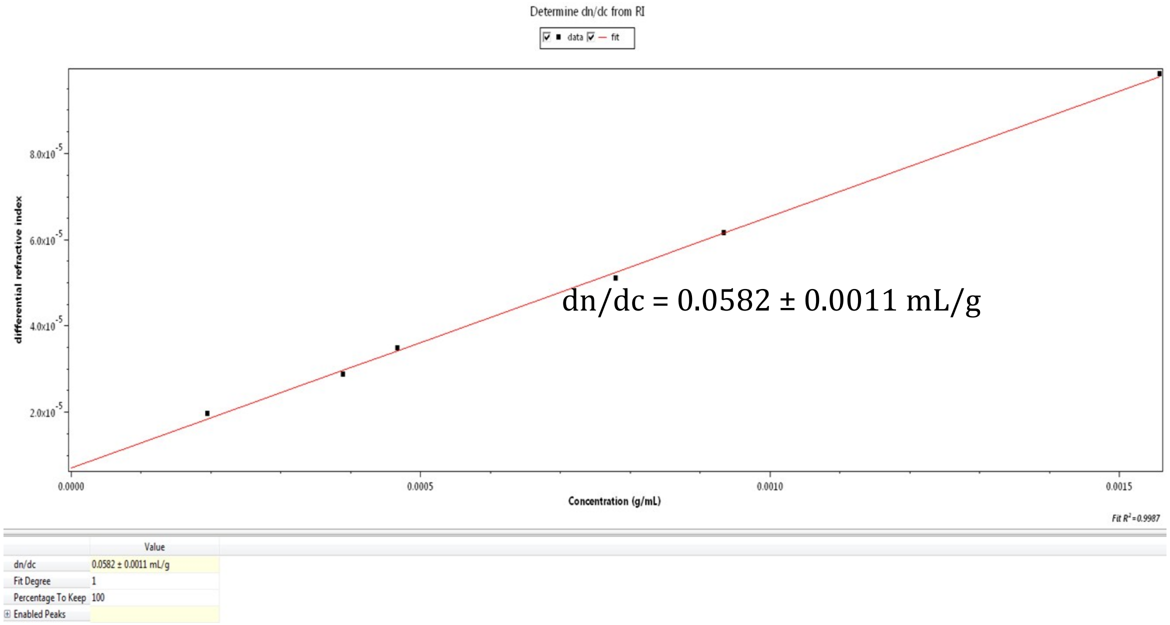

tBuOLi oil sample #4-385 RT: 0.09-9.53 AV: 382 NL: 1.72E8
T: + c ESI Full ms [150.00-2000.00]
Intensity
m/z
437
851
852
901
923
925
439
535
474
239
264
199
436
633
683
715
815
927
1099
1145
1295
1337
1378
1476
1586
1669
1782
1824
1827
1931
0
10000000
20000000
30000000
40000000
50000000
60000000
70000000
80000000
90000000
100000000
110000000
120000000
130000000
140000000
150000000
160000000
170000000
200
400
600
800
1000
1200
1400
1600
1800
2000

Figure S8. Measurement of the dn/dc of the polymer initiated by ^{t}BuOK A) in $CHCl_3$; B) in THF; Measurement of the dn/dc of the polymer initiated by ^{t}BuONa (C) in $CHCl_3$.

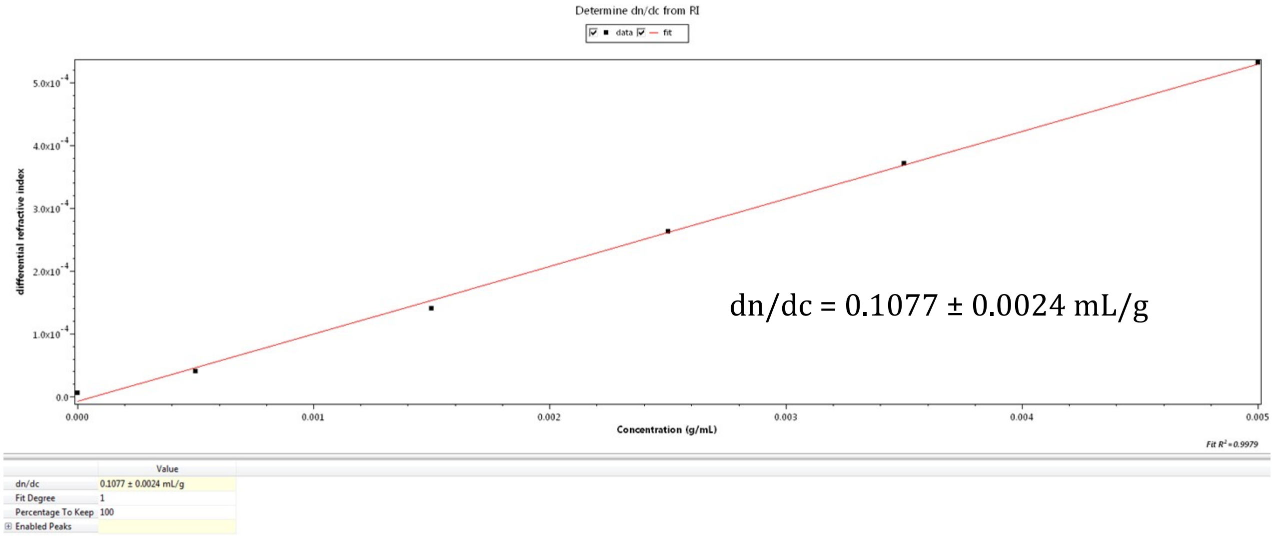
Polymer dn/dc values were measured using the OptiLab T-rEx RI detector and Astra software dn/dc template in a batch mode. Six solutions of polymer in $CHCl_3$ with precisely known concentrations (0.1 mg/mL to 2 mg/mL) were prepared by diluting a stock solution using volumetric flasks, and injected to the RI detector using a syringe pump. The dn/dc value was determined from the linear fit to a plot of differential RI versus concentration.

A)



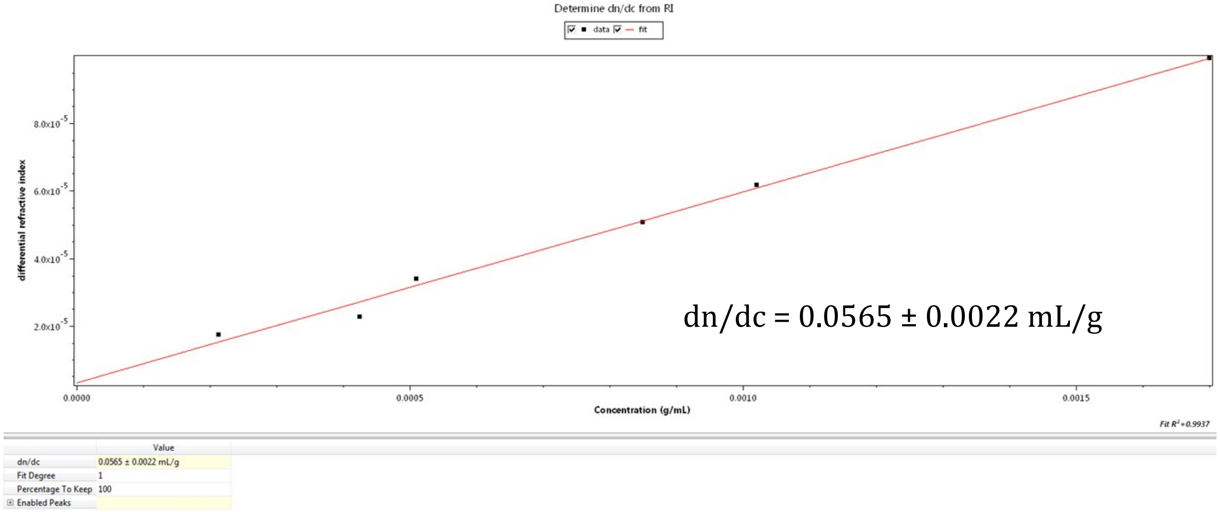
	Value
dn/dc	0.0582 ± 0.0011 mL/g
Fit Degree	1
Percentage To Keep	100
⊞ Enabled Peaks	

B)



	Value
dn/dc	0.1077 ± 0.0024 mL/g
Fit Degree	1
Percentage To Keep	100
⊞ Enabled Peaks	

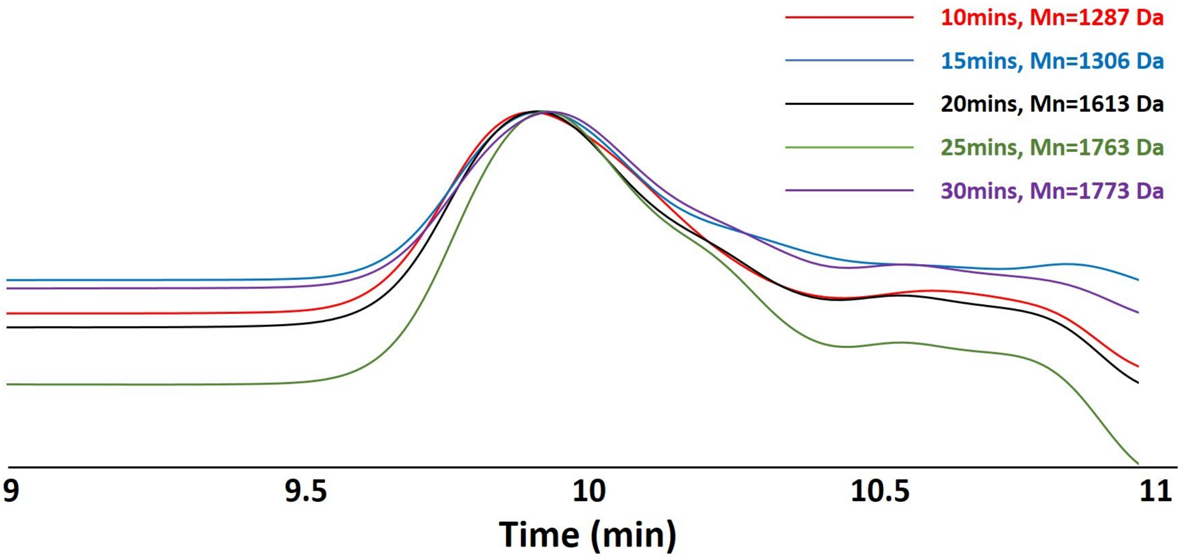
C)



	Value
dn/dc	0.0565 ± 0.0022 mL/g
Fit Degree	1
Percentage To Keep	100
⊞ Enabled Peaks	

Figure S9. GPC traces of product of the polymerization of TIPS ketene initiated by ^{t}BuOK with M:I=20:1: A) RI traces at different time points; B) MALS traces at different time points.

A)



B)

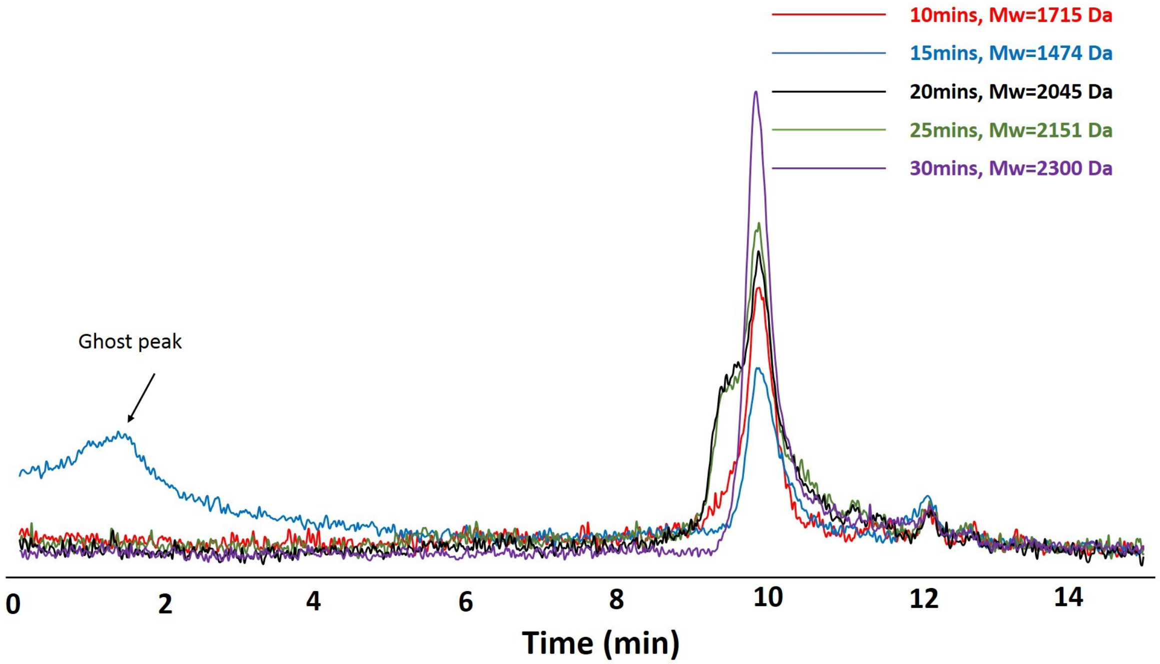
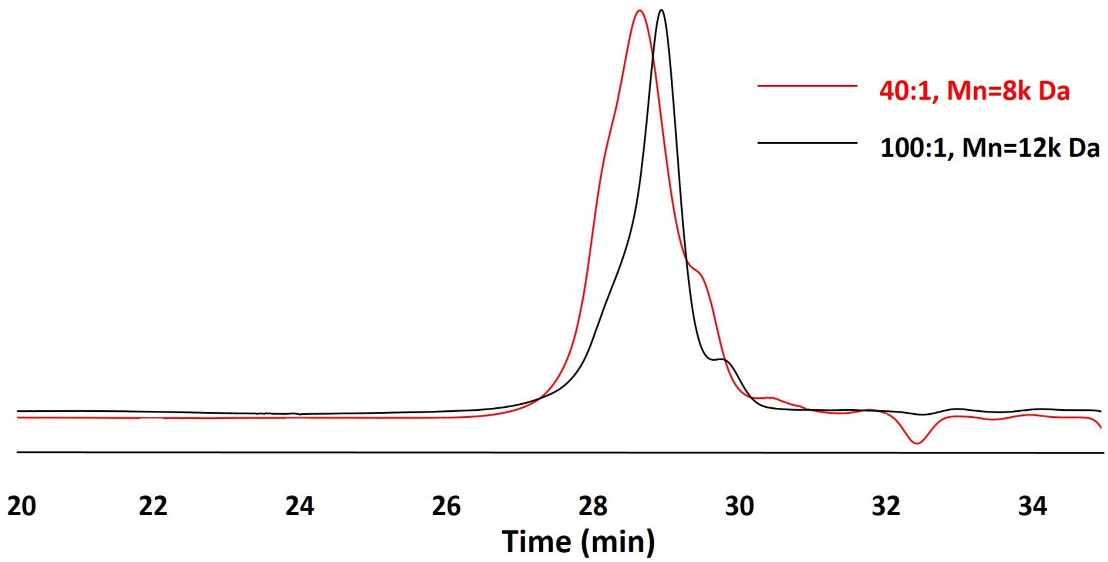


Figure S10. GPC traces of product of the polymerization of TIPS ketene initiated by ^{t}BuOK at 40:1 and 100:1 M:I: A) RI traces; B) MALS traces.

A)



B)

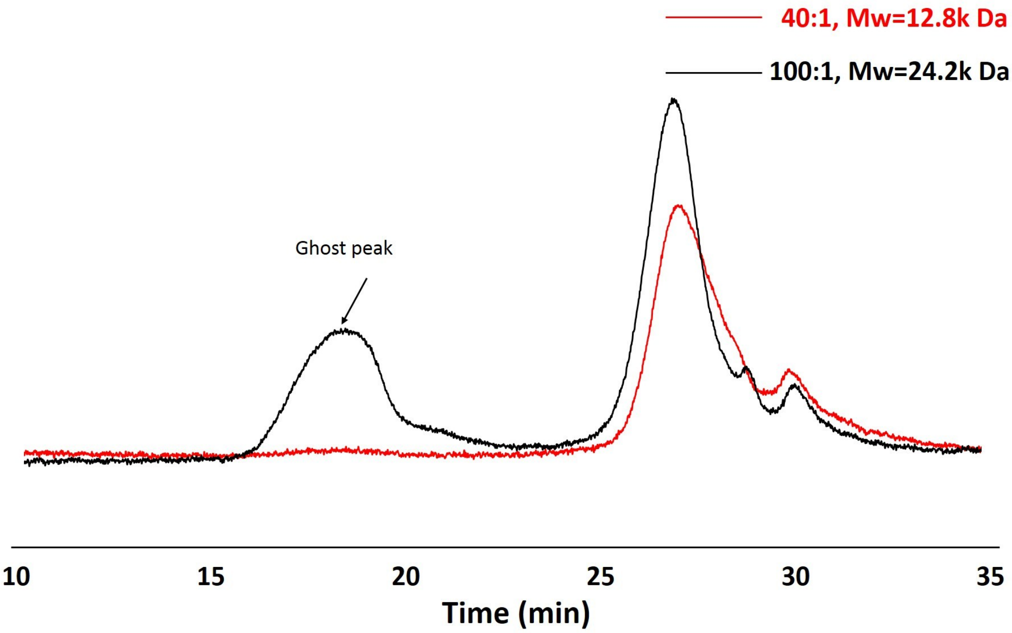
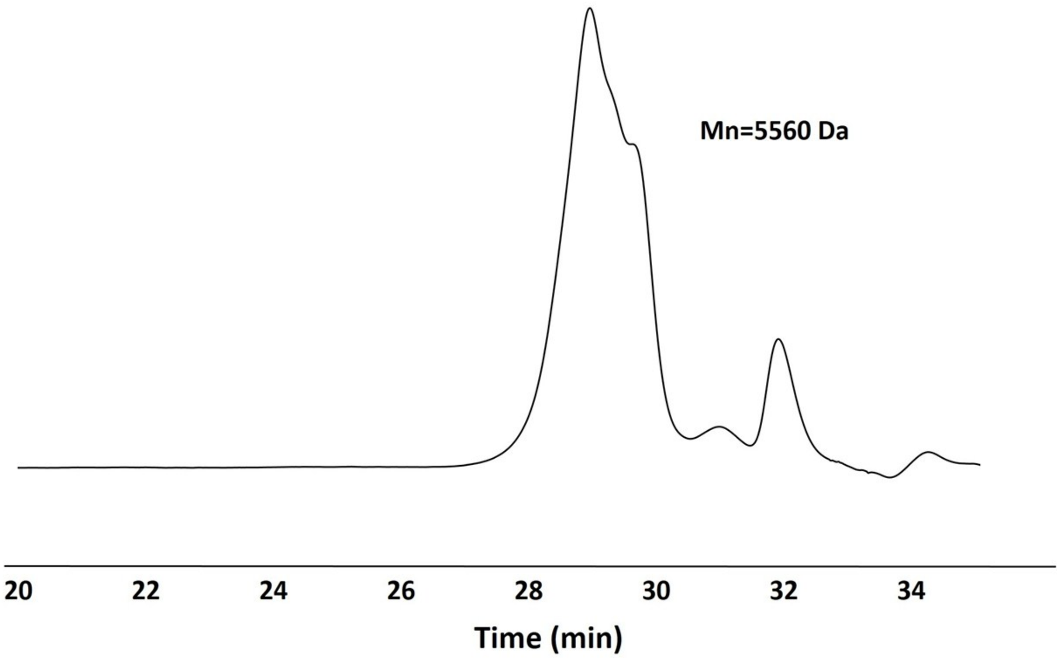


Figure S11. GPC for polymers initiated by ^tBuONa with M:I=20:1 using A) RI detector B) MALS detector.

A)



B)

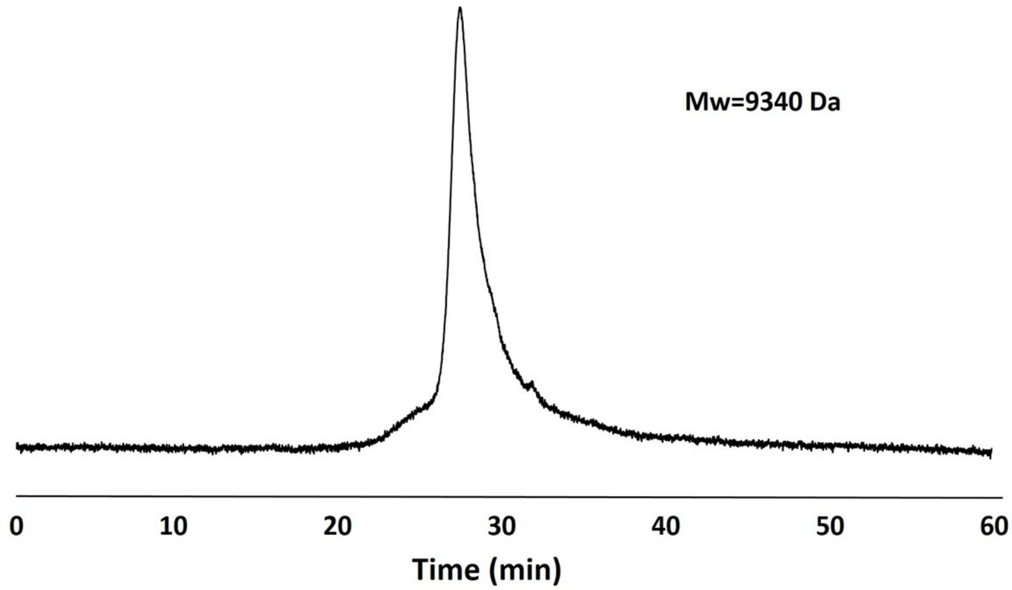
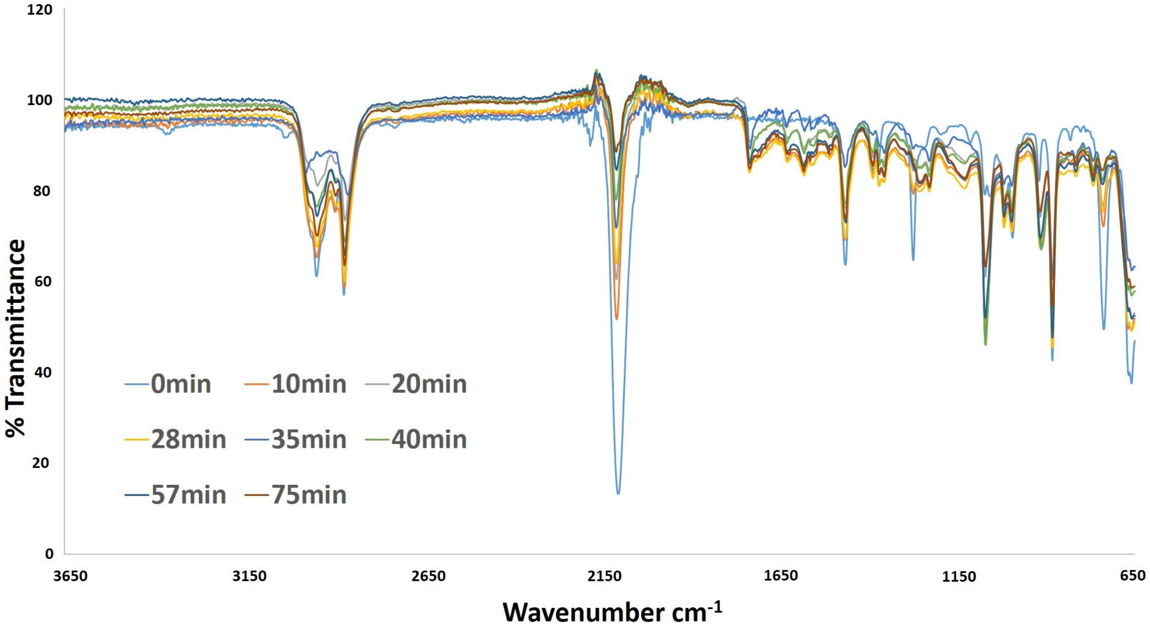


Figure S12. FTIR spectra of the reaction of TIPS ketene with ^{t}BuOK in THF at different time points at A) 30°C; B) 40°C.

A)



B)

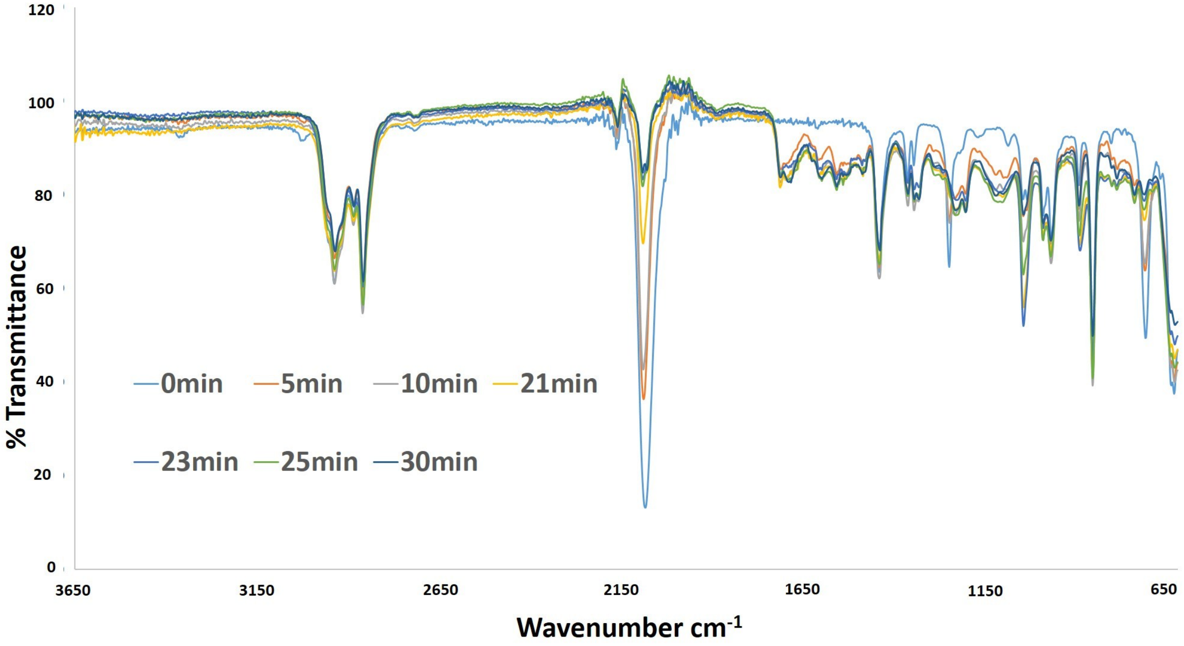
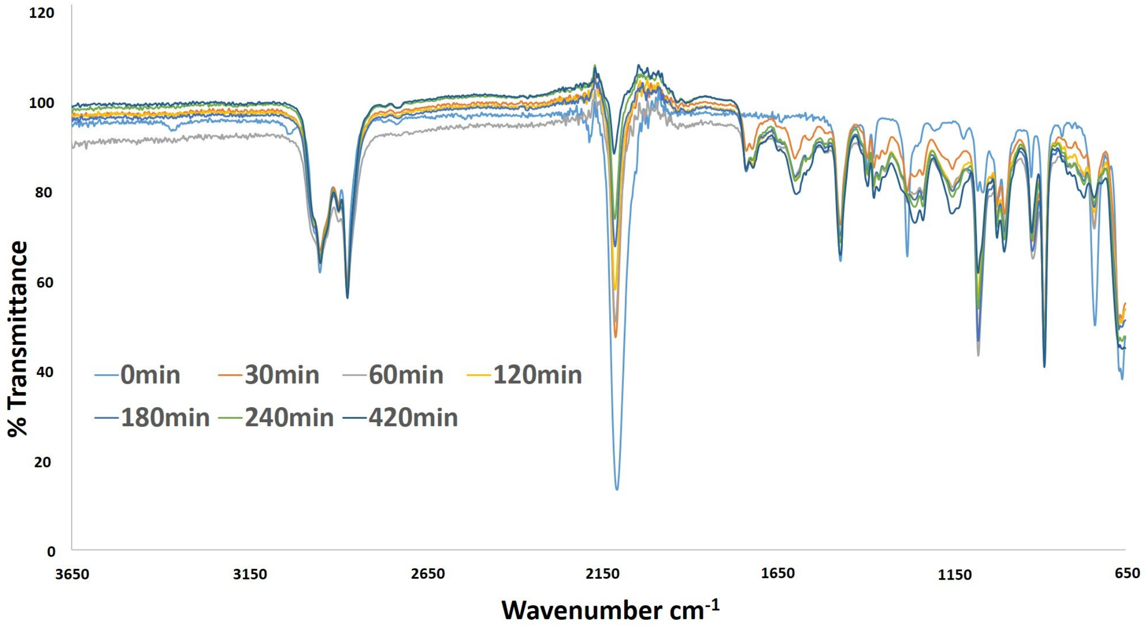
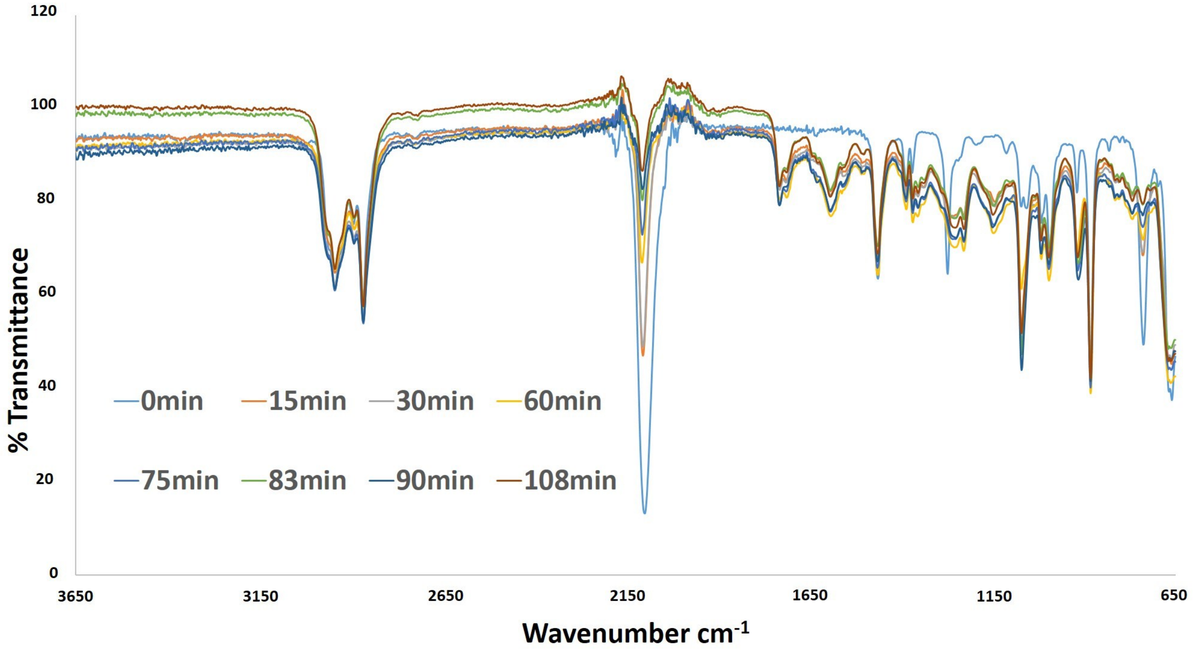


Figure S13 FTIR spectra of the reaction of TIPS ketene with ^{t}BuONa in THF at different time points at A) 40°C; B) 60°C.

A)

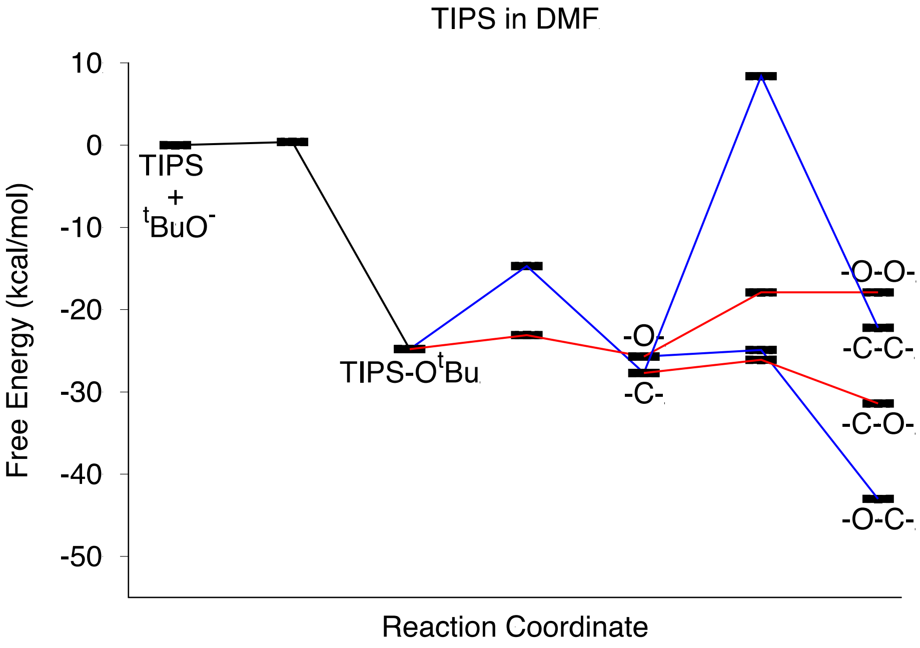


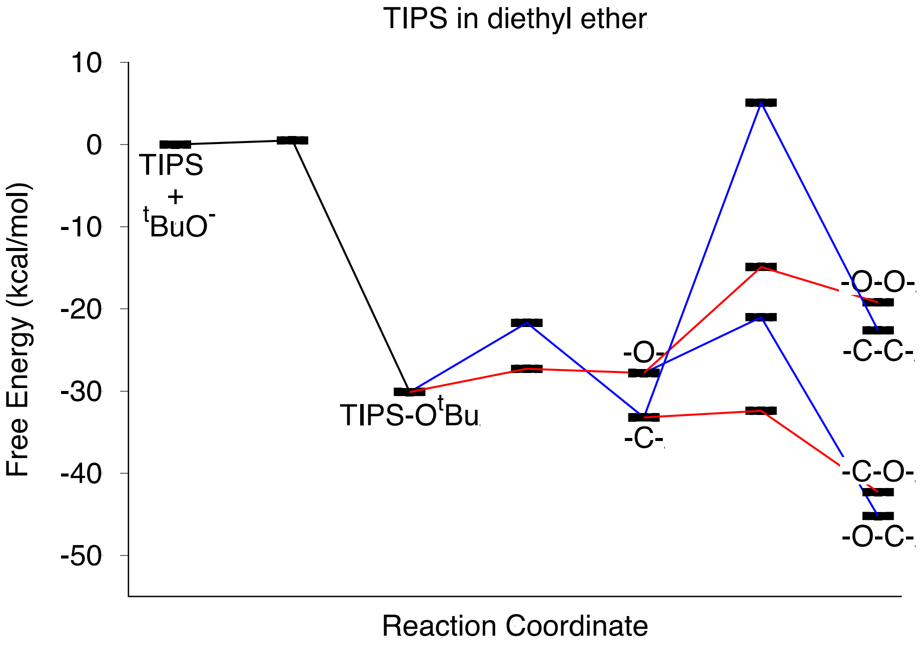
B)

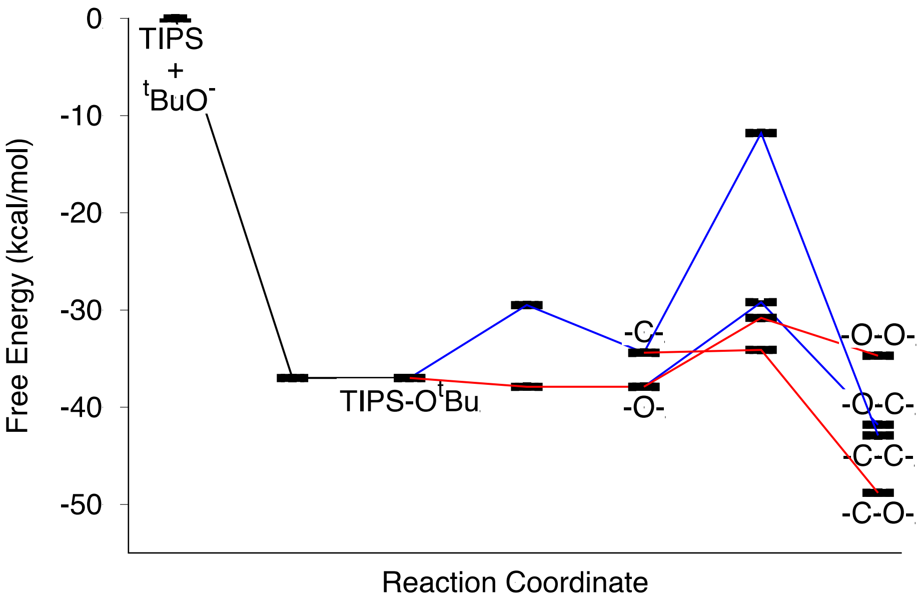


Computationally predicted reaction pathways

Figure S14. Predicted reaction pathways for different dielectric environments (e.g., in DMF, diethyl ether, dioxane, and vacuum, see Table 2 for an overview of resulting preferences for thermodynamic and kinetic products).






TIPS in dioxane

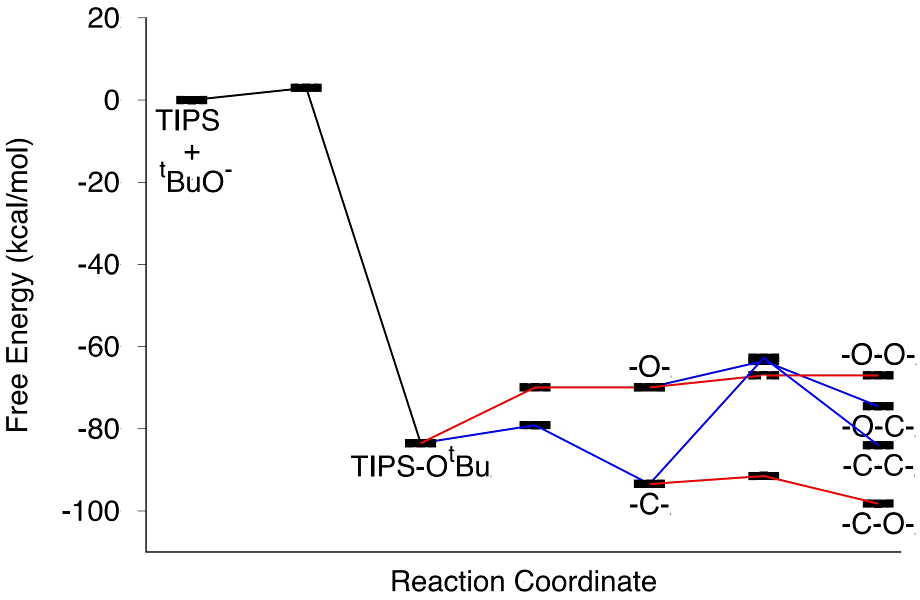

TIPS in Vacuum

Figure S15. Thermal characterization of polymer from Entry 12 of Table 1 in the manuscript A) thermogravimentric weight loss profile; B) differential scanning calorimetry isotherm (three heating and cooling cycles)**.**

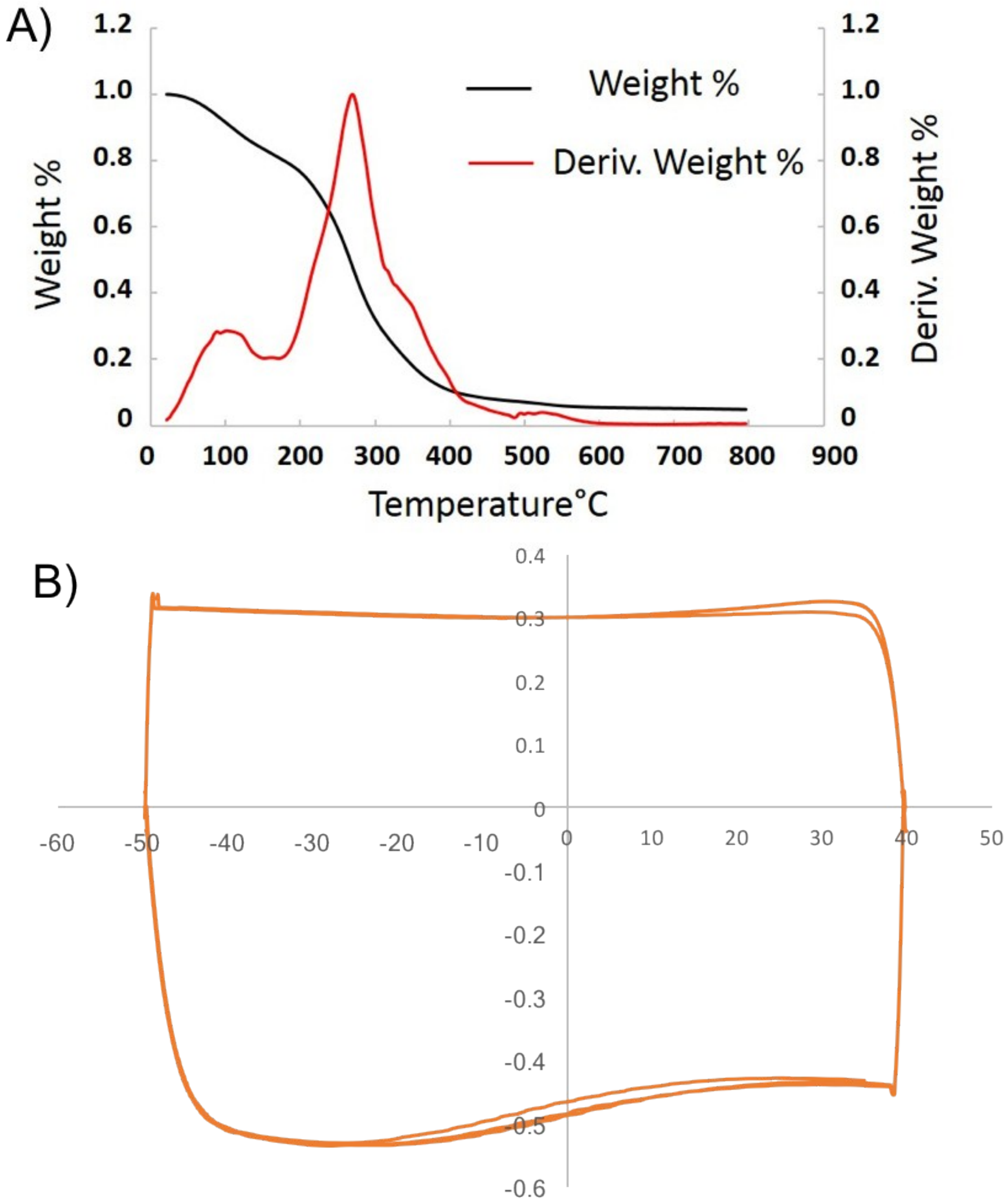
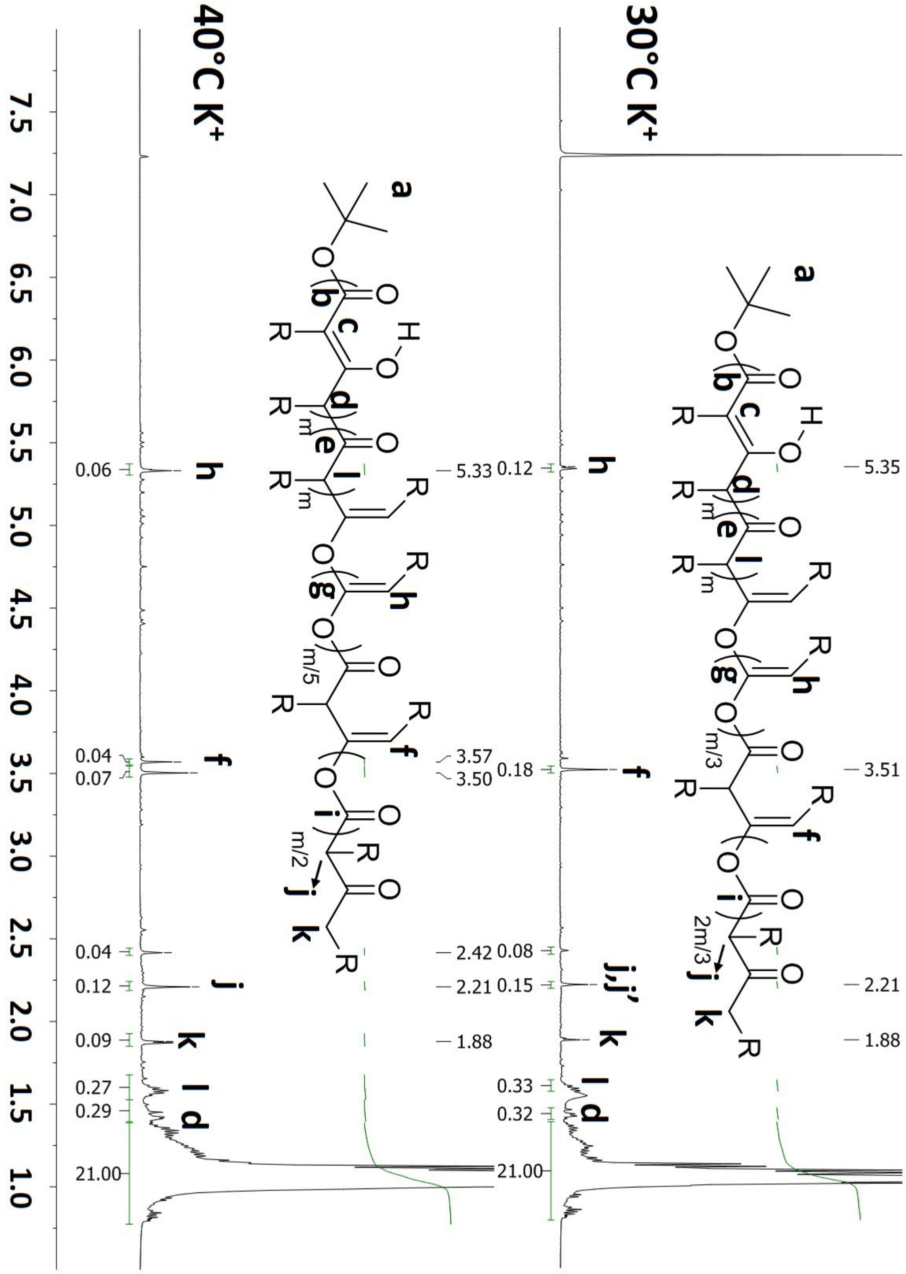


Figure S16. Characterization of the products isolated from the polymerizaiton of TIPS ketene: A) ^{1}H nd 40°C.

A)



B)

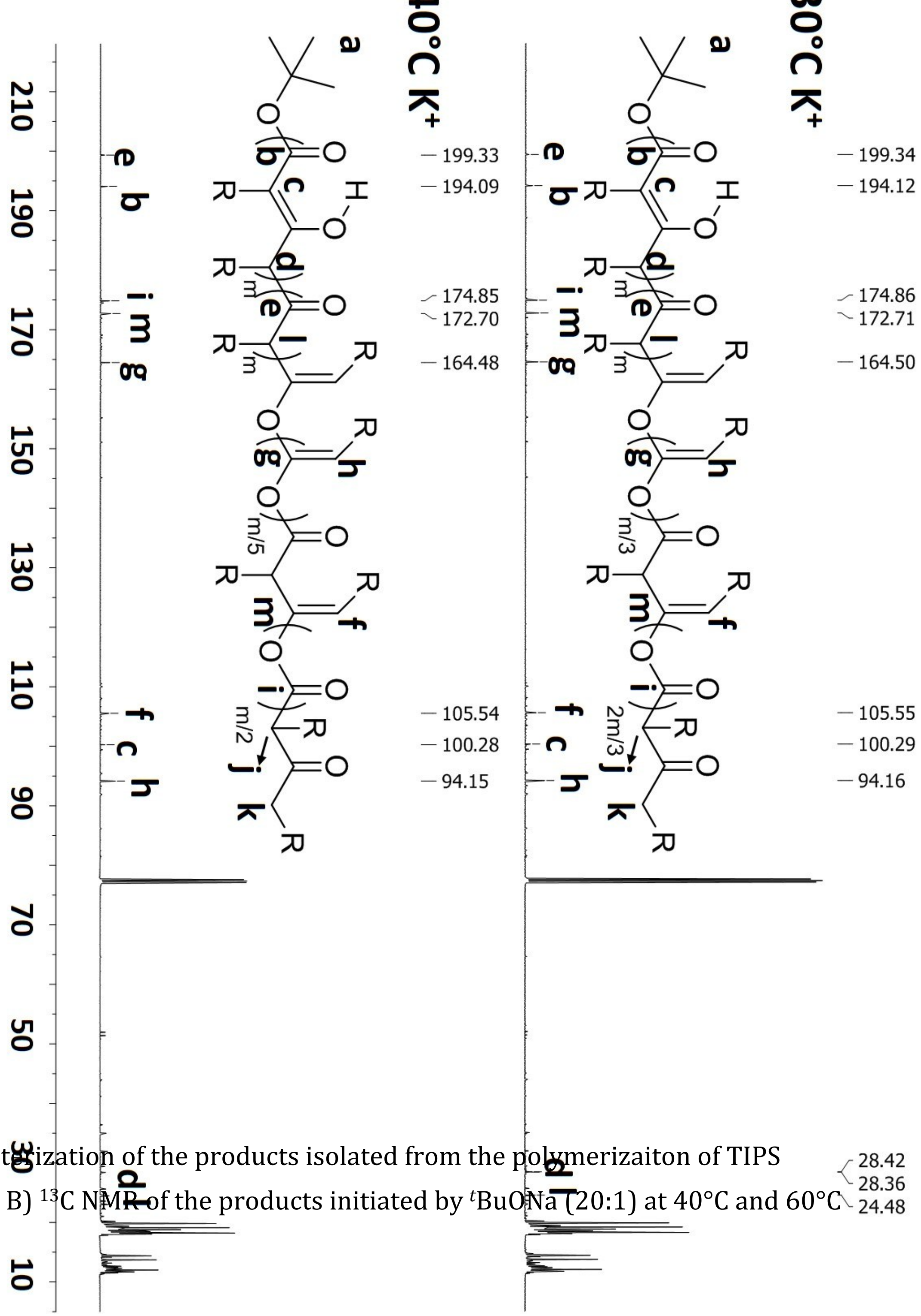
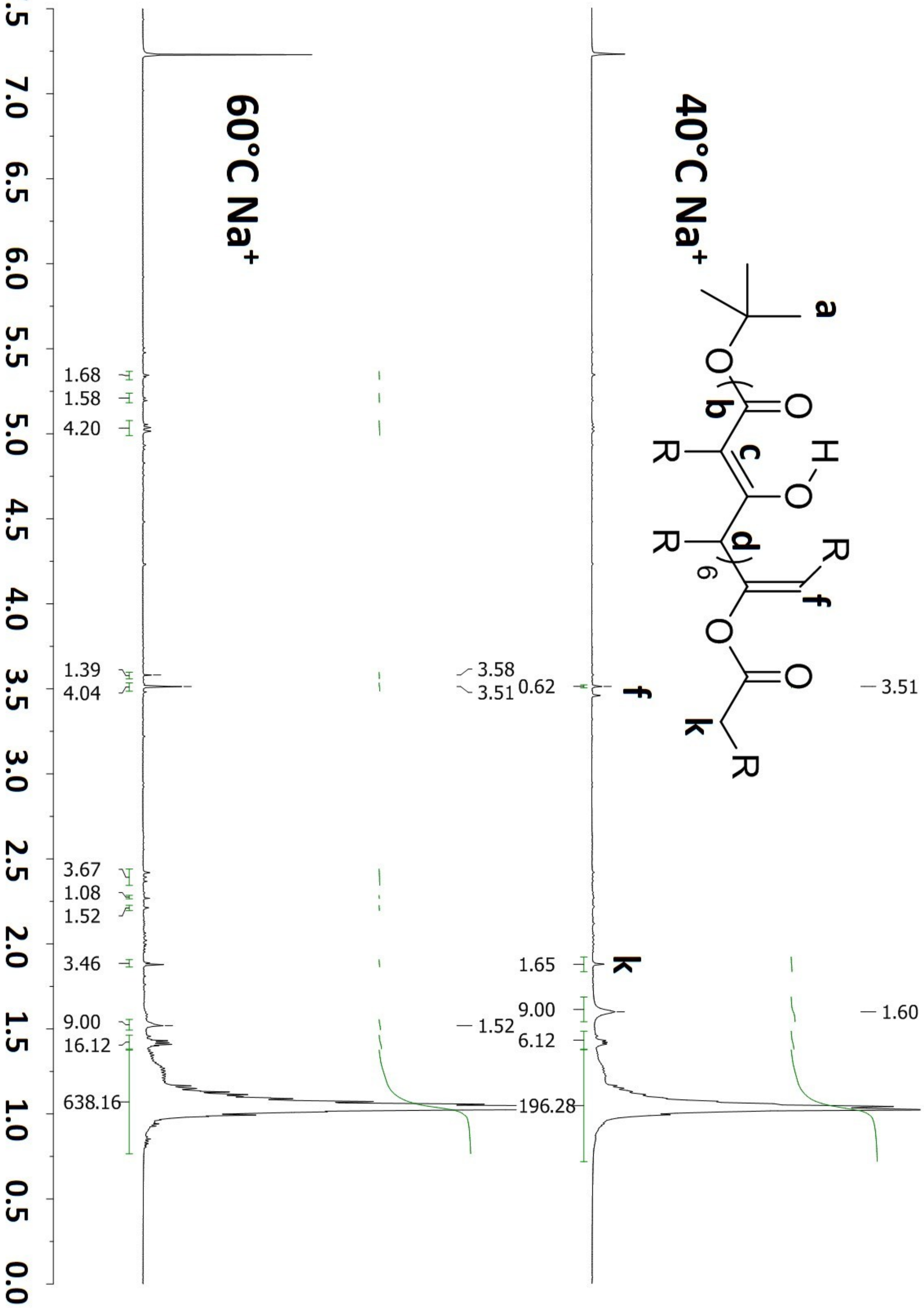


Figure S17. Characterization of the products isolated from the polymerizaiton of TIPS ketene: A) ^{1}H NMR; B) ^{13}C NMR of the products initiated by ^{t}BuONa (20:1) at 40°C and 60°C

A)

B)



60°C Na+
40°C Na+
a
b
c
d
f
k
R
O
H
6
1.68
1.58
4.20
1.39
4.04
3.67
1.08
1.52
3.46
9.00
16.12
638.16
3.58
3.51
1.52
196.28
0.62
1.65
9.00
6.12
3.51
1.60
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

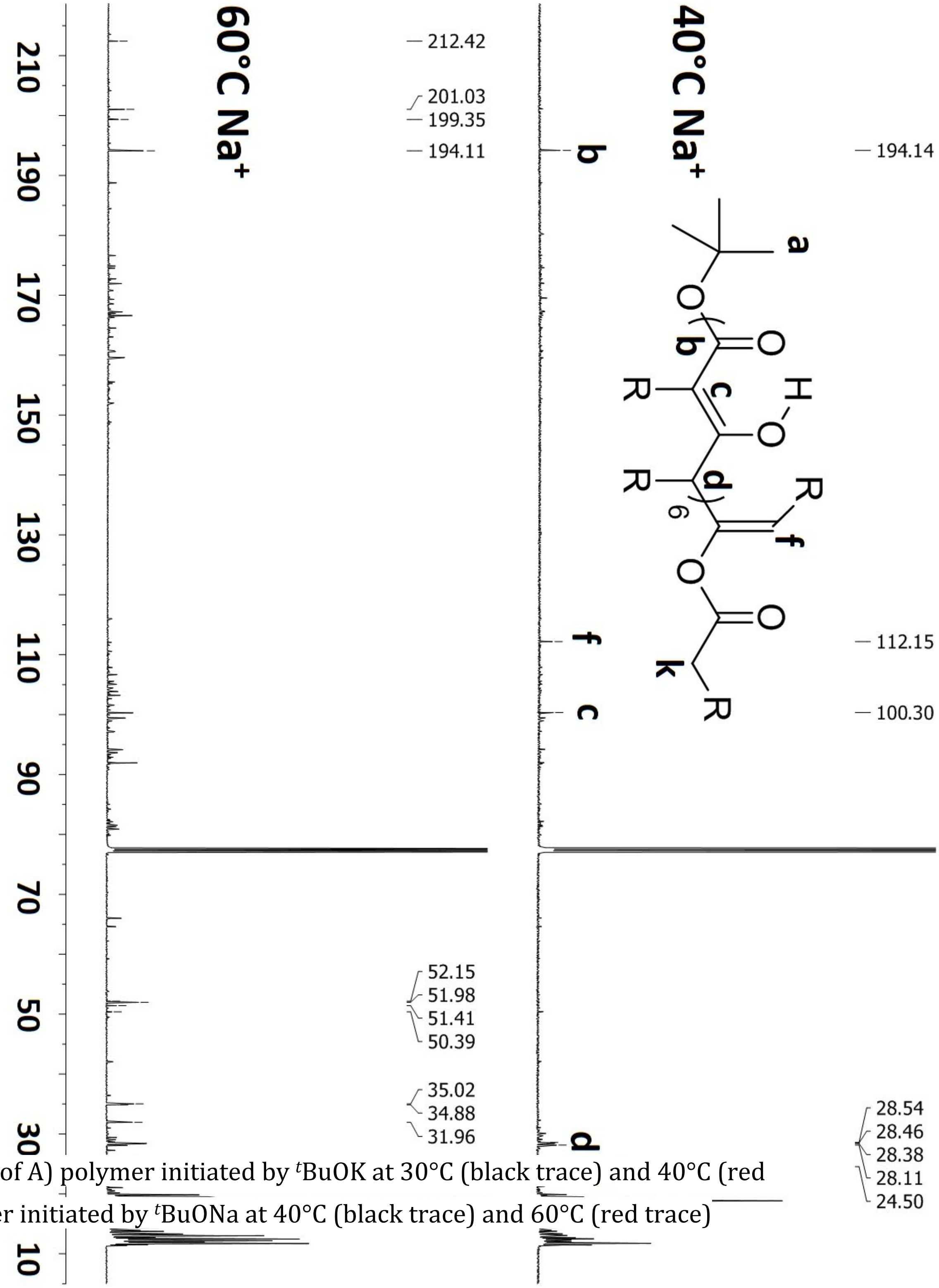
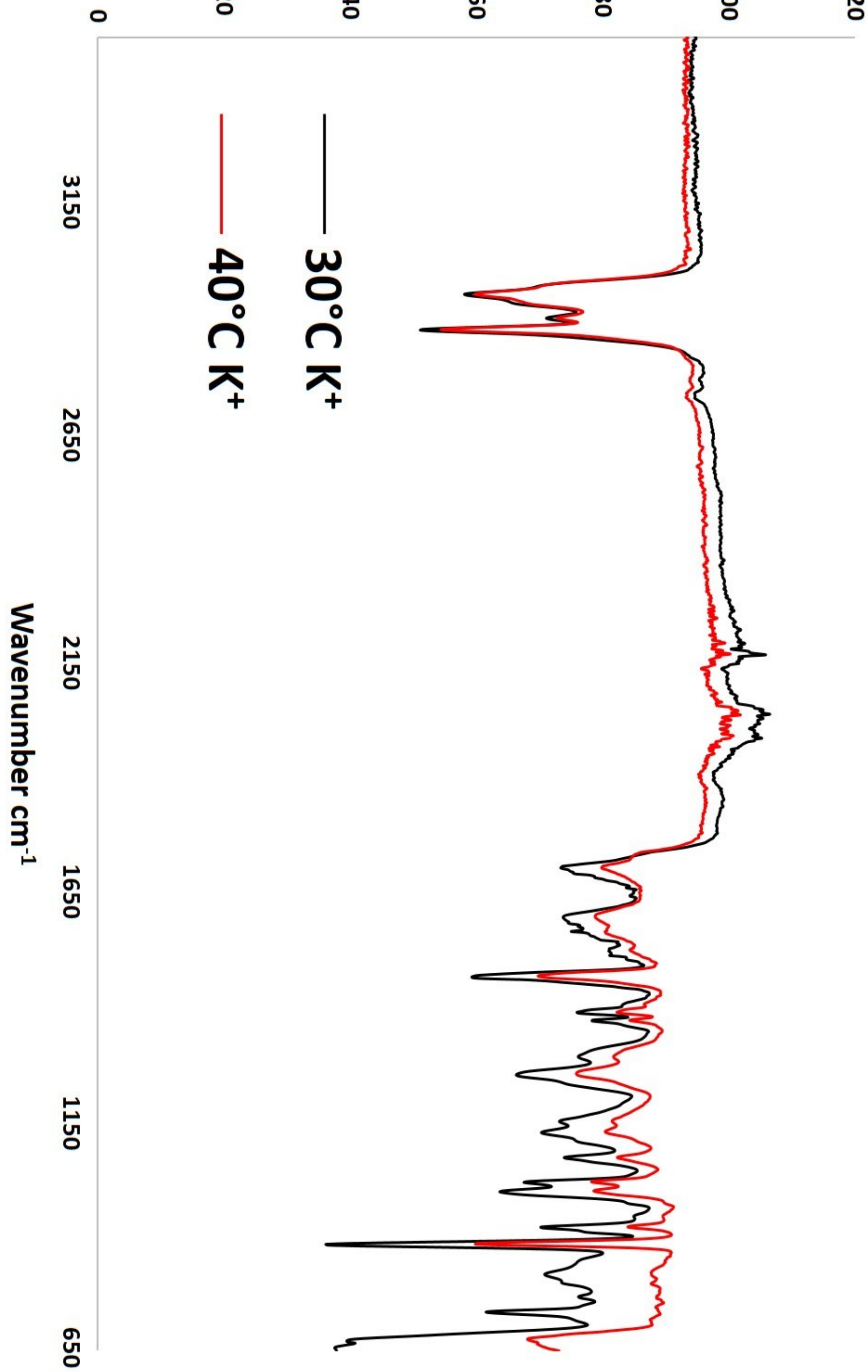


Figure S18. FTIR of A) polymer initiated by ${}^tBuOK$ at 30°C (black trace) and 40°C (red trace); B) polymer initiated by ${}^tBuONa$ at 40°C (black trace) and 60°C (red trace)

A)

B)



0
0
40
60
80
00
20
30°C K+
40°C K+
3150
2650
2150
1650
1150
650
Wavenumber cm-1

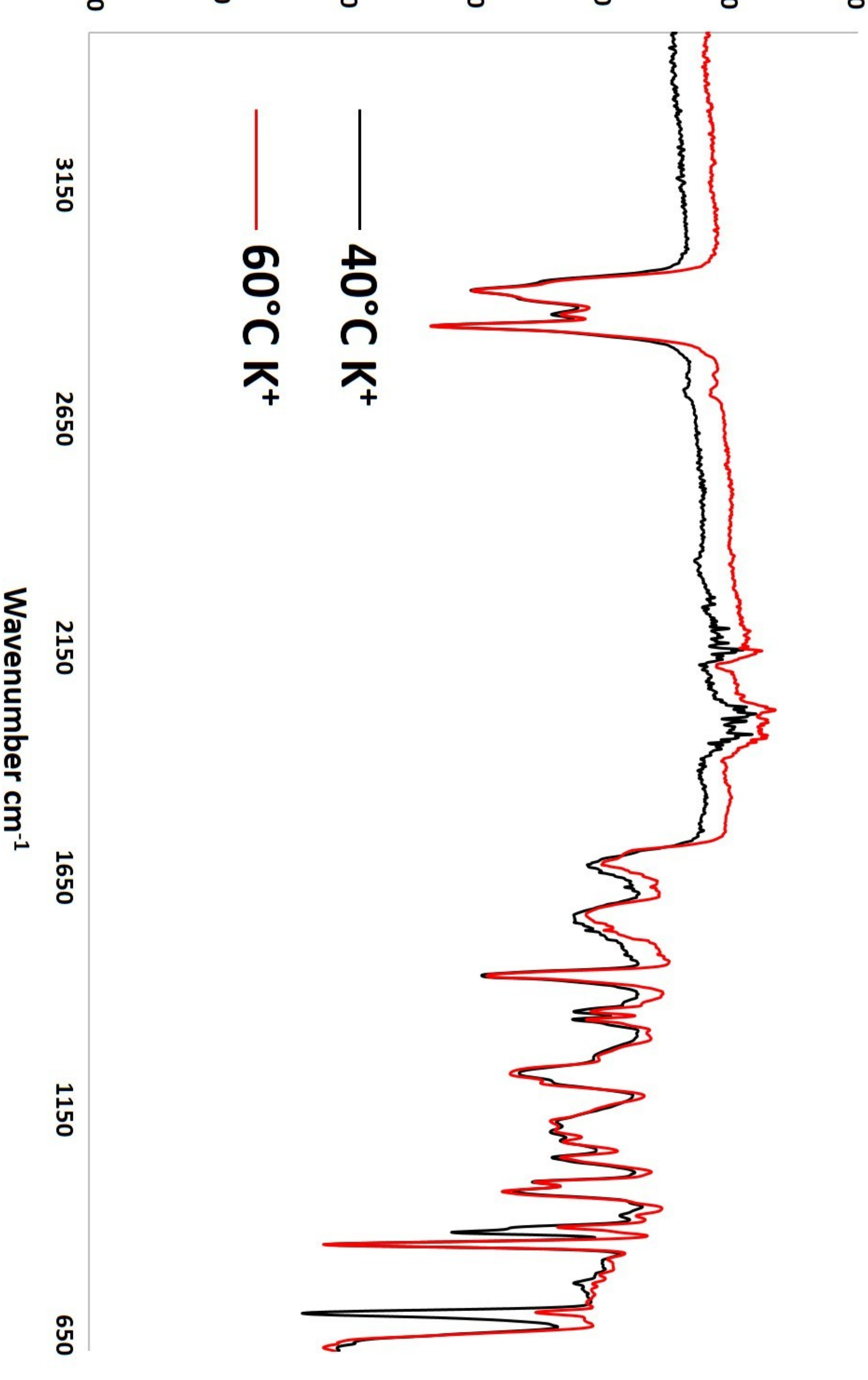
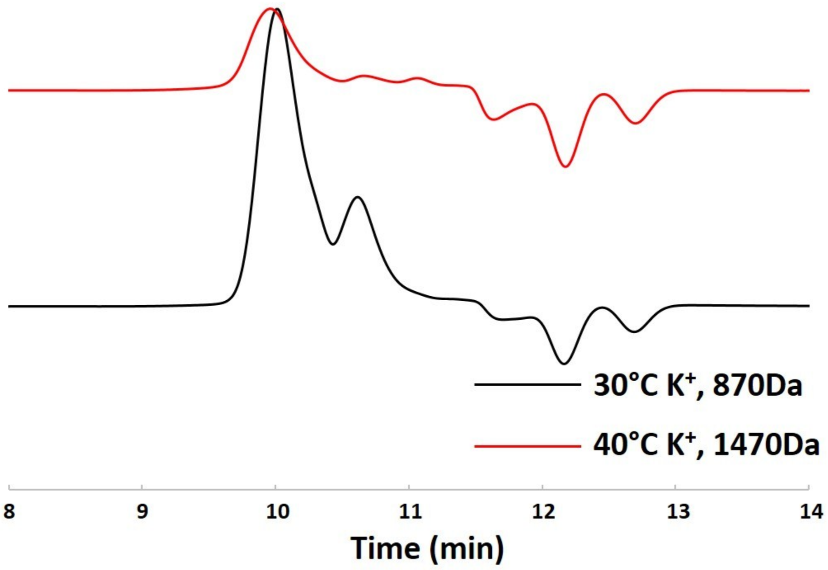

40°C K+
60°C K+
3150
2650
2150
1650
1150
650
Wavenumber cm-1

Figure S19. GPC traces of product of the polymerization of TIPS ketene initiated by tBuOK with M:I=20:1 at 30°C(black trace) and 40°C (red trace): A) RI traces; B) MALS traces.

A)



B)

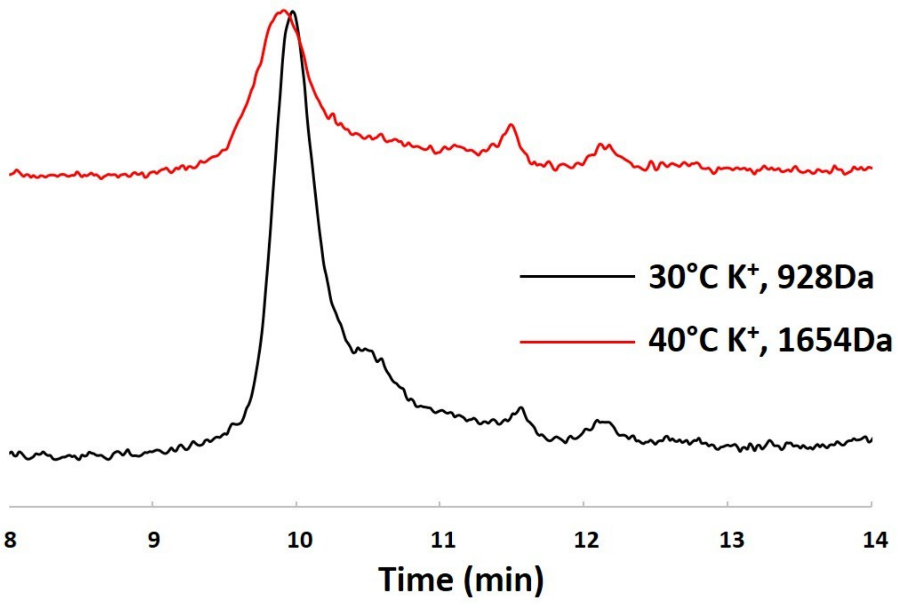
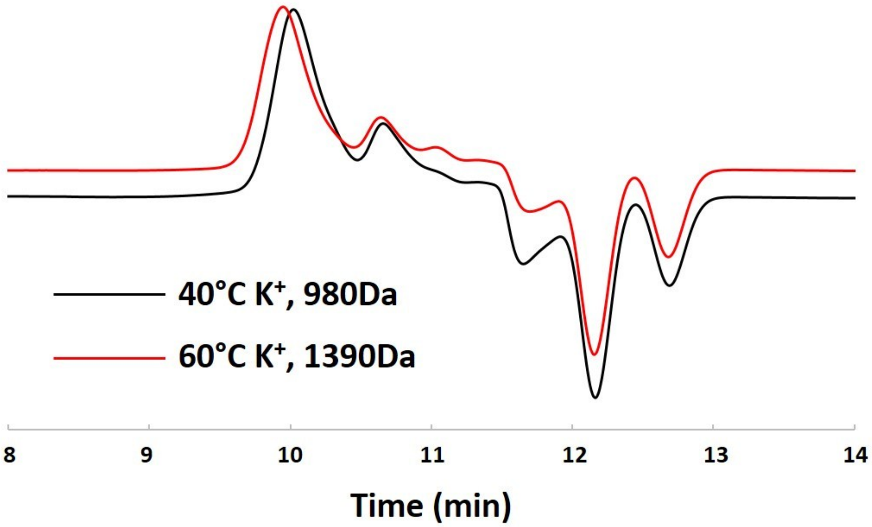
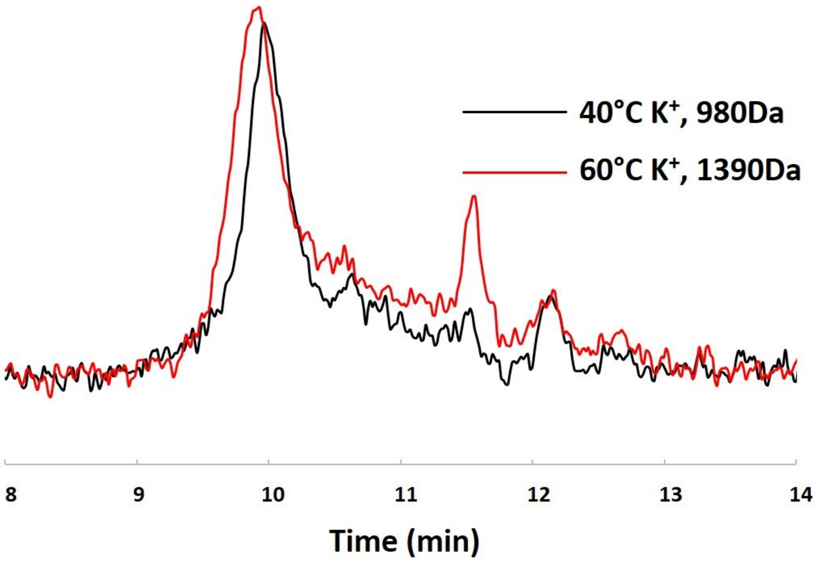


Figure S20. GPC traces of product of the polymerization of TIPS ketene initiated by ^{t}BuONa with M:I=20:1 at 40°C(black trace) and 60°C (red trace): A) RI traces; B) MALS traces.

A)



B)



References

(1) HIQUEL A. PERICAS.; FELIX SERRATOSA.; EDUARD VALENTf. *Tetrahedron.* **1987**, *43*, 2311.

(2) Eduard Valenti.; Miquel A. Pericas.; Felix Serratosa. *J.Org.Chem.* **1990**, 55, 395.