Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Investigating the Effect of α-Pinene on the ROMP of δ-Pinene

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I. Materials

All chemicals were used as received unless otherwise noted. Grubbs Catalyst M204 (Grubbs 2nd generation/G2) (99.95%) was obtained from Umicore. Hoveyda-Grubbs catalyst 2nd generation (HG2) (97%), Sodium hydroxide (≥85%), boron trifluoride diethyl etherate (98%), and 3-bromopyridine (99%) were obtained from Sigma-Aldrich. Hexane (≥98.5%), dichloromethane (DCM) (≥99.5%), tetrahydrofuran (THF) (≥99.5%), diethyl ether (DEE) (≥99.0%), and methanol (≥99.8 %) were obtained from EMD Millipore. Potassium *tert*-butoxide (99%), 4-toluenesulfonyl chloride (tosyl chloride) (99%), sodium borohydride (98%), pyridine (99.9%), (-)-alpha-pinene (98%), hydrogen peroxide (35%), chlorosulfonyl isocyanate (CSI) (99%), and anhydrous sodium sulfite (99%) were obtained from Oakwood Chemical. 4-dimethylaminopyridine (DMAP) (99%) was obtained from Acros. Basic aluminum oxide Brockman Grade I (99%) was obtained from Alfa-Aesar. Neutral aluminum oxide Brockman Grade I (99%) was obtained from BeanTown Chemical. THF and DCM were purified with a SG Water USA Company solvent still by filtration through two columns of neutral alumina and an in-line 2 µm filter. Hydrochloric acid (HCl, 36.5-38%) was obtained from VWR. Sodium sulfate (>99%), sodium chloride (>99%), sodium bicarbonate (≥99.7%) were obtained from BDH. Silica gel, SiliaFlash P60 (40-63 µm), was obtained from SiliCycle. Chloroform-*d* ($CDCl_3$) (99.8%, Sigma-Aldrich) was stored over 4 Å molecular sieves. Grubbs' 3rd generation catalyst (G3) was synthesized from G2 following previous procedures.[1, 2]

II. Monomer Synthesis, Purification, and Characterization

δ-pinene [(1R, 4R, 5S)-4,6,6-trimethylbicyclo[3.1.1]hept-2-ene] was synthesized according to our previously reported procedure[3] and modified as described in the main manuscript.

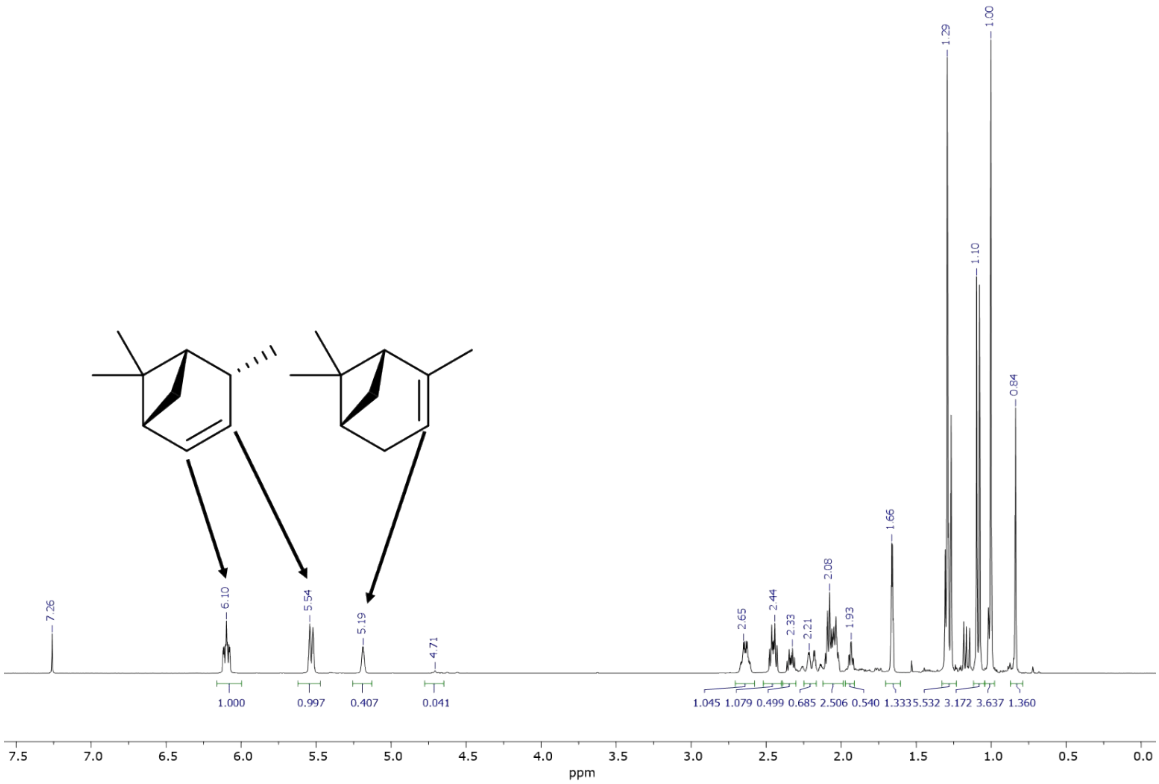


Figure S1. ^{1}H NMR of δ-pinene only purified through a hexane/silica gel plug and subsequent vacuum transfer with no attempt to remove excess α-pinene (~ 28.9 mol % relative to δ-pinene).

III. Additional Characterizations and Instrumentation

Nuclear magnetic resonance (NMR) samples were all prepared by dissolution in $CDCl_3$. Both ^1H and ^{13}C NMR spectra were obtained on either a Bruker Advance III 600 MHz or 400 MHz NMR with a 1 s pulse delay for both small molecules and polymerization aliquots.

Size exclusion chromatography (SEC) samples were prepared by dissolution of between 3 - 10 mg of polymer in 1 mL of THF, followed by filtration through a 0.45 μm polytetrafluoroethylene (PTFE) filter prior to analysis with an Agilent-Wyatt combination triple detection SEC equipped with three successive Agilent PL-gel Mixed C columns (THF mobile phase, 25 °C), an Agilent 1260 infinity series pump, degasser, autosampler and thermostatted column chamber. The triple detection unit consists of a MiniDawn TREOS 3-angle light scattering detector, Optilab TrEX refractive index detector and a Viscostar II differential viscometer in successive order. A previously determined *dn/dc* value (0.1187 mL g^{-1})[3] was utilized for all PδP samples.

A. α-Pinene Homopolymerization ^1H-NMR

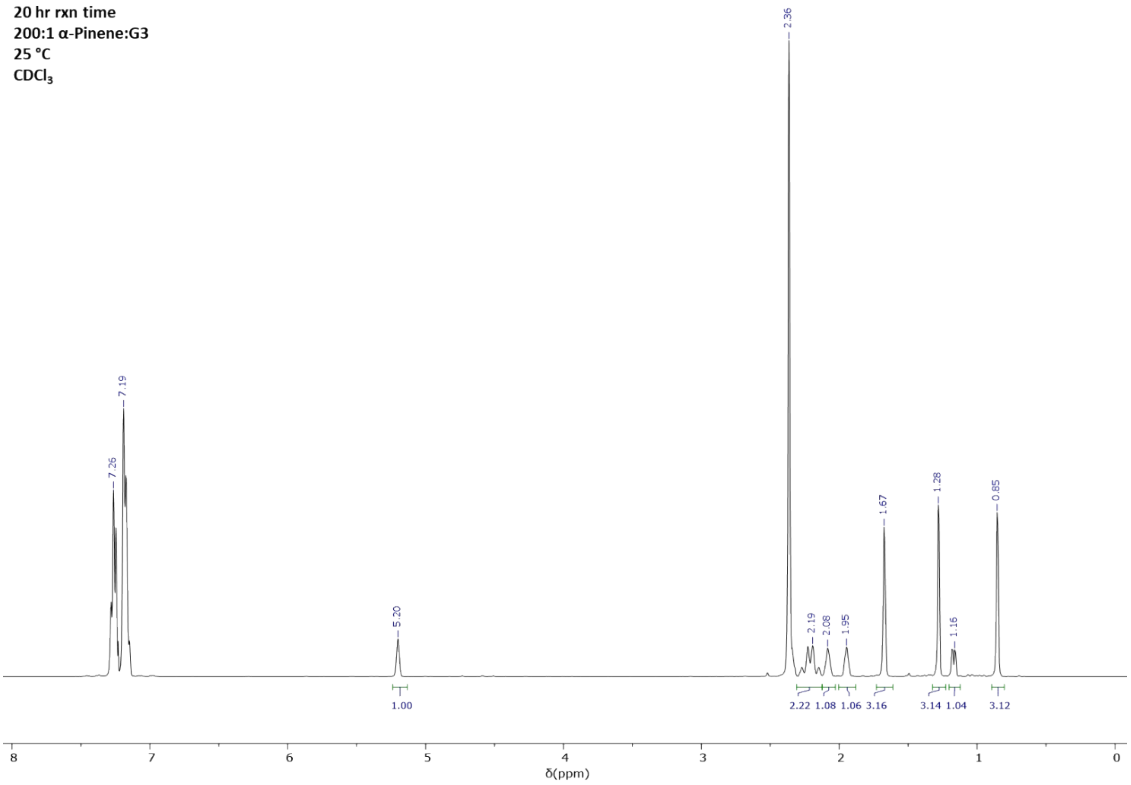


Figure S2. ^1H-NMR (400 MHz, $CDCl_3$) of 200:1 α-pinene:G3 polymerization in tol. after 20 hr.

B. Stacked Crude 1H-NMR of δ-Pinene ROMPs with Varying α-Pinene Content

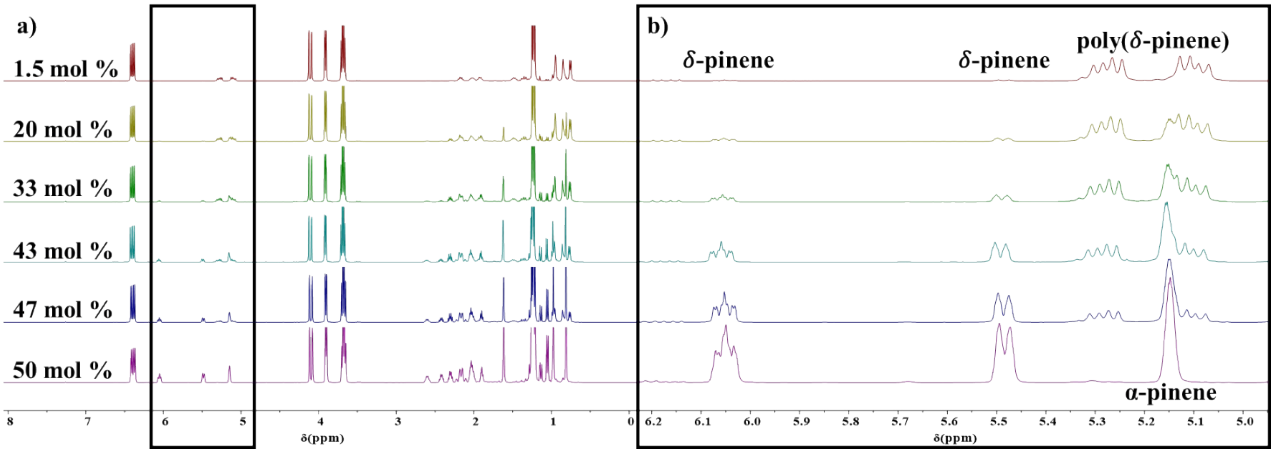


Figure S3. a) Stacked ^{1}H-NMR's (400 MHz, $CDCl_3$, 25 °C) following ROMP of δ-pinene with varying molar ratios of α-pinene (1.5 – 50 mol %) for 1 hr and termination with EVE. **b**) Zoomed in olefin proton signals used for determination of conversion plotted in Figure 2.

C. G3 in $CDCl_3$ ^{1}H-NMRs

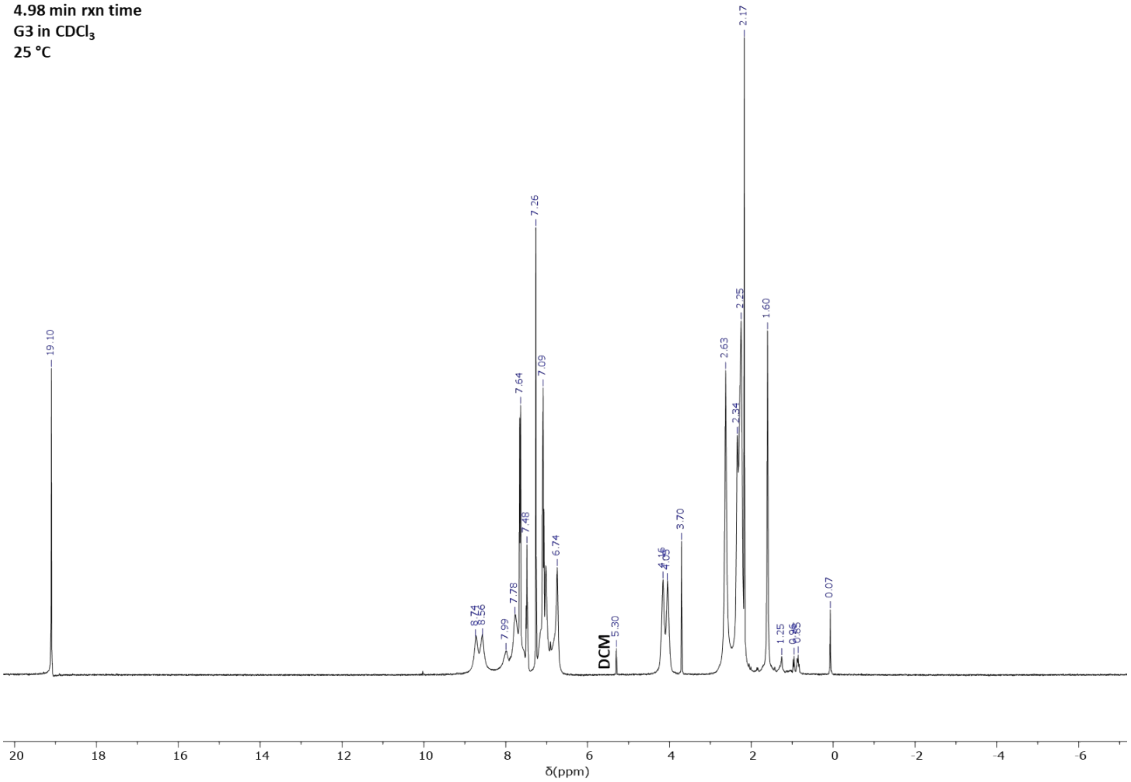


Figure S4. ^{1}H-NMR (600 MHz) of G3 in $CDCl_3$ after 4.98 min.

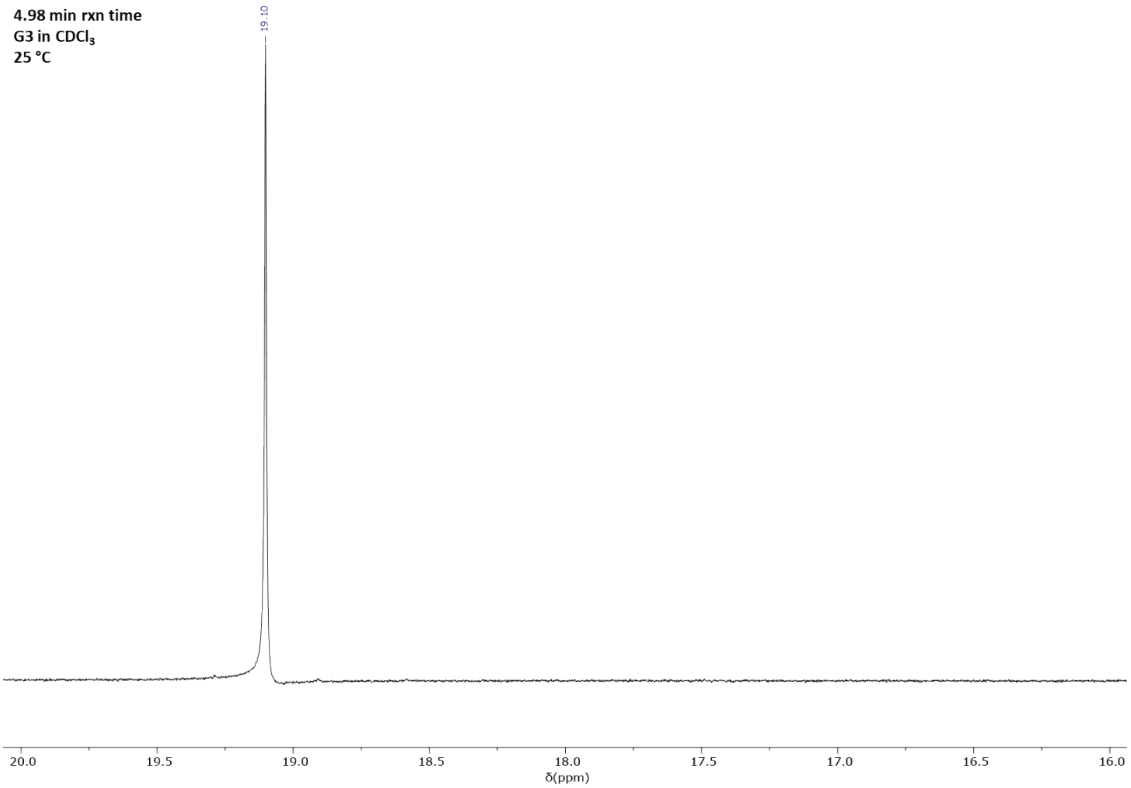


Figure S5. ^{1}H-NMR (600 MHz) of Ru-alkylidene range of G3 in $CDCl_3$ after 4.98 min.

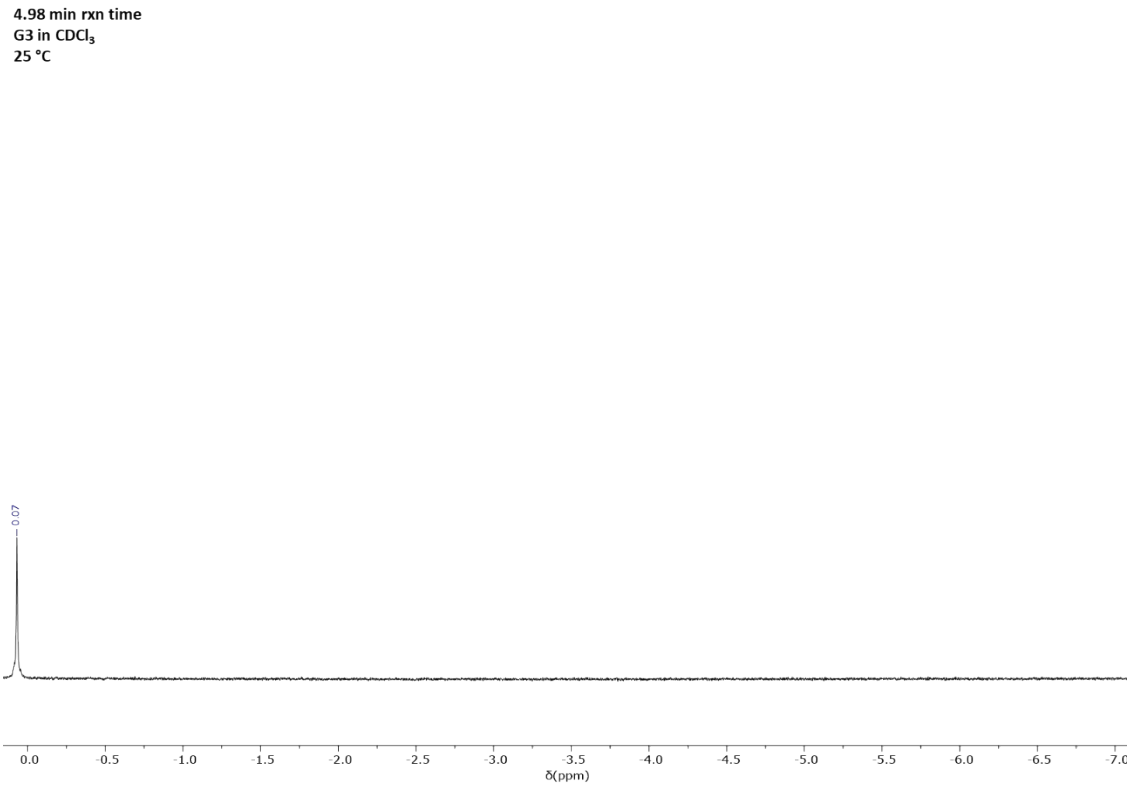


Figure S6. ^{1}H-NMR (600 MHz) of metallacyclobutane range of G3 in $CDCl_3$ after 4.98 min.

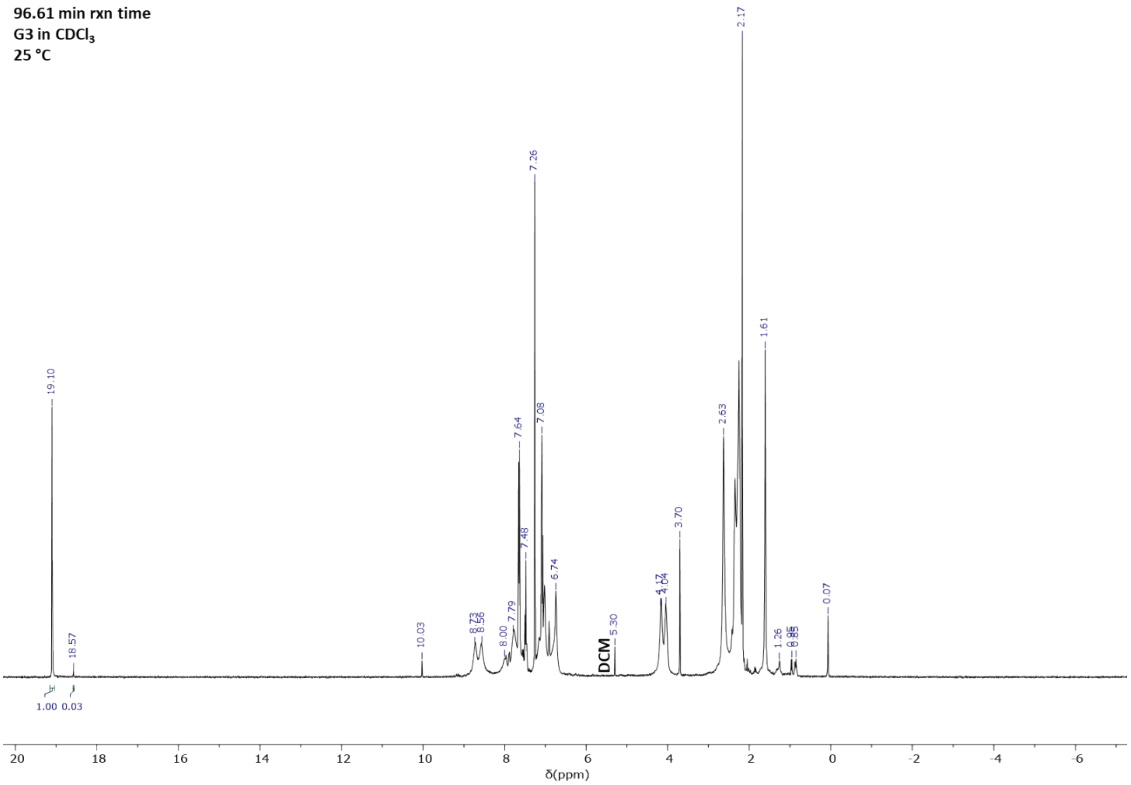


Figure S7. ^{1}H-NMR (600 MHz) of G3 in $CDCl_3$ after 96.61 min.

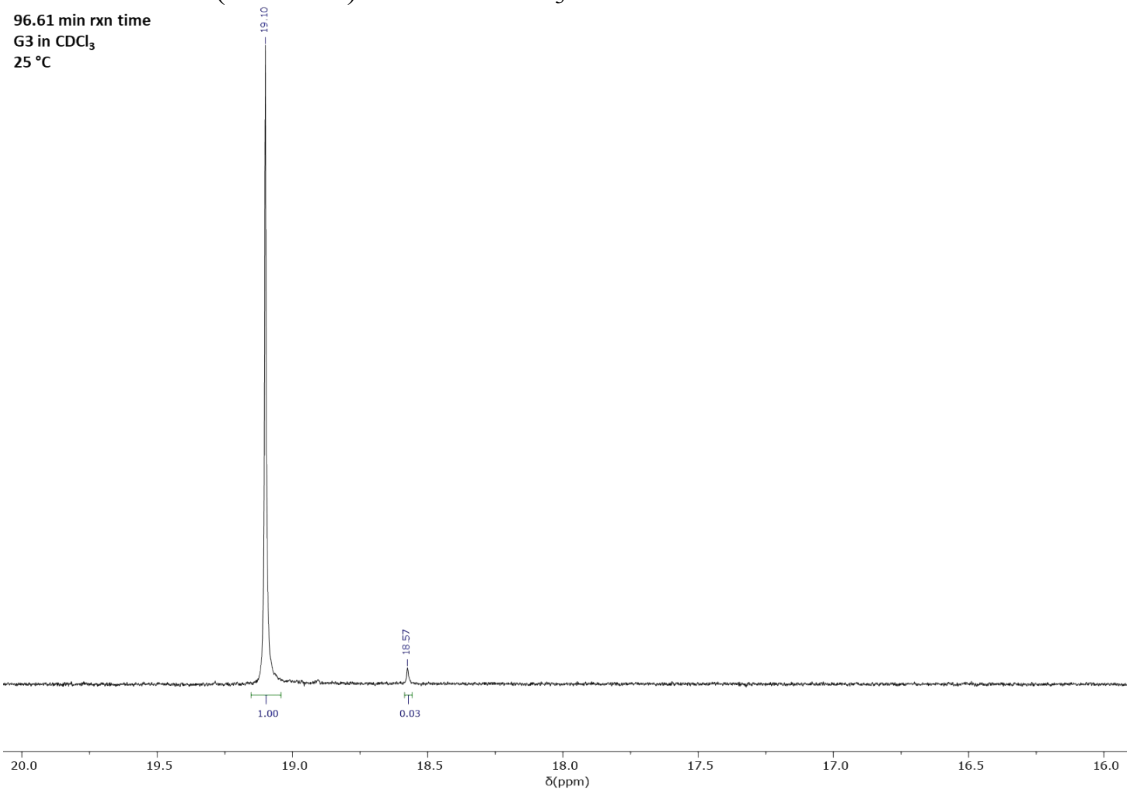


Figure S8. ^{1}H-NMR (600 MHz) of Ru-alkylidene range of G3 in $CDCl_3$ after 96.61 min.

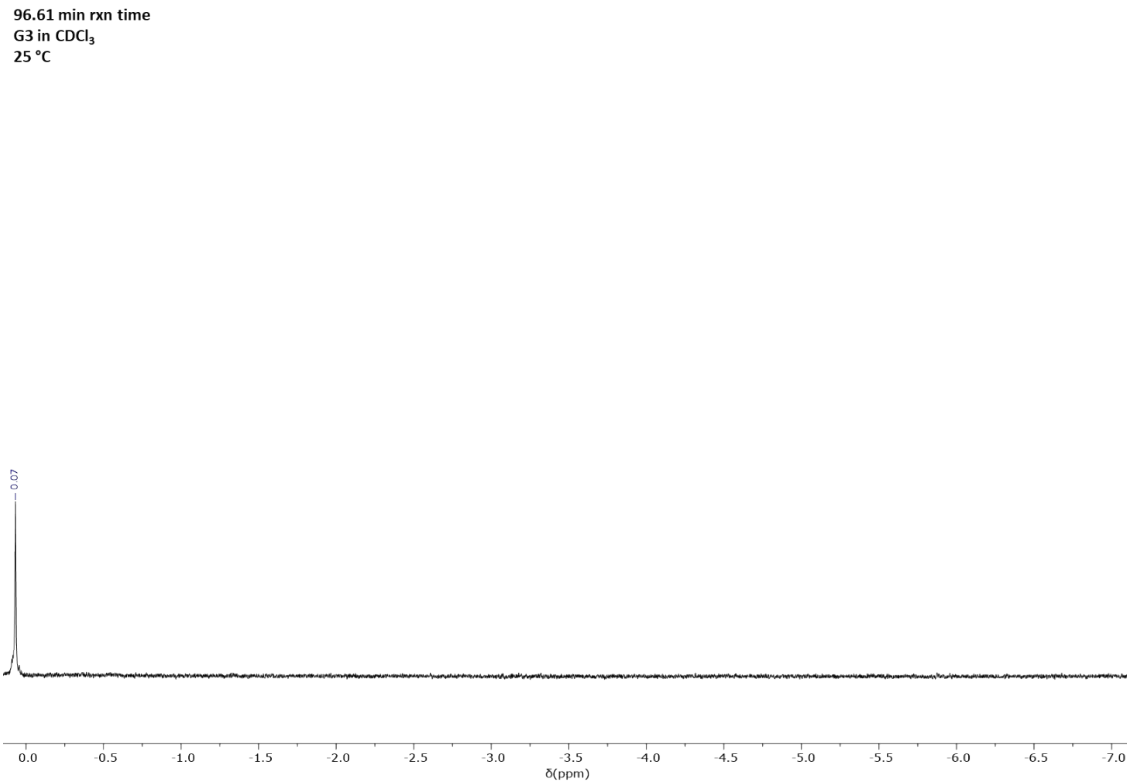


Figure S9. ^{1}H-NMR (600 MHz) of metallacyclobutane range of G3 in $CDCl_3$ after 96.61 min.

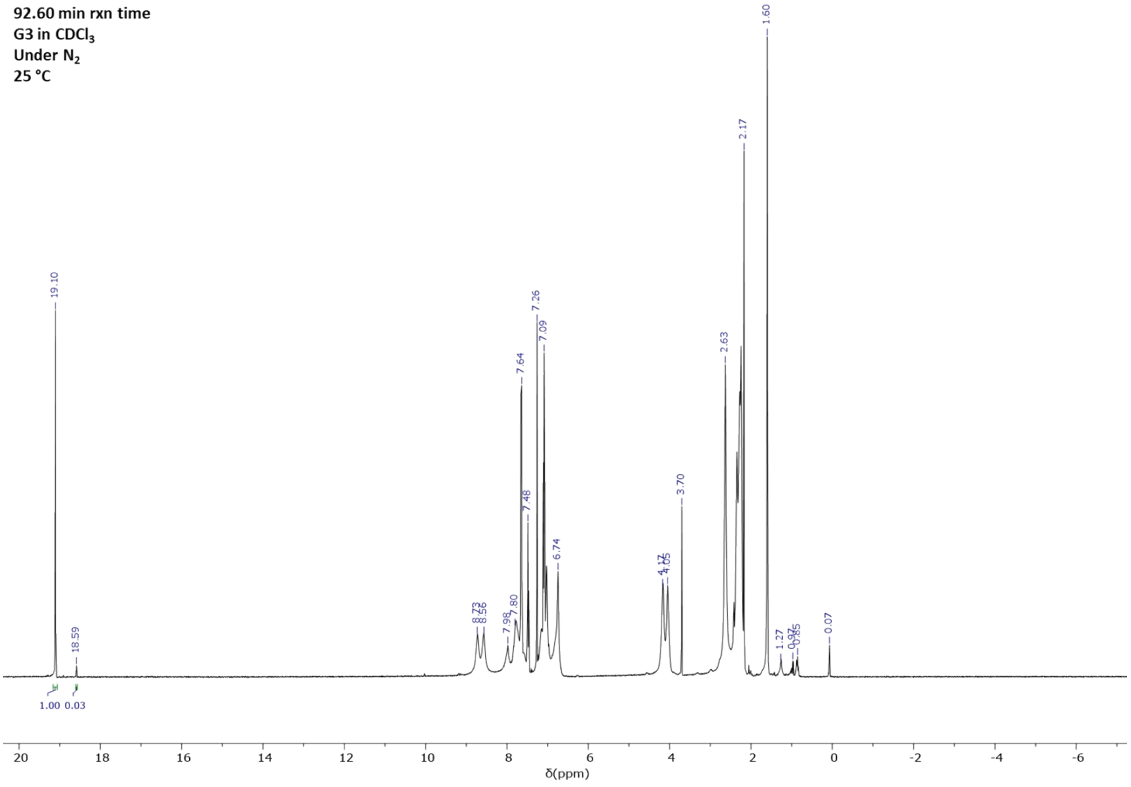


Figure S10. ^{1}H-NMR (600 MHz) of G3 in $CDCl_3$ under Nitrogen after 92.60 min.

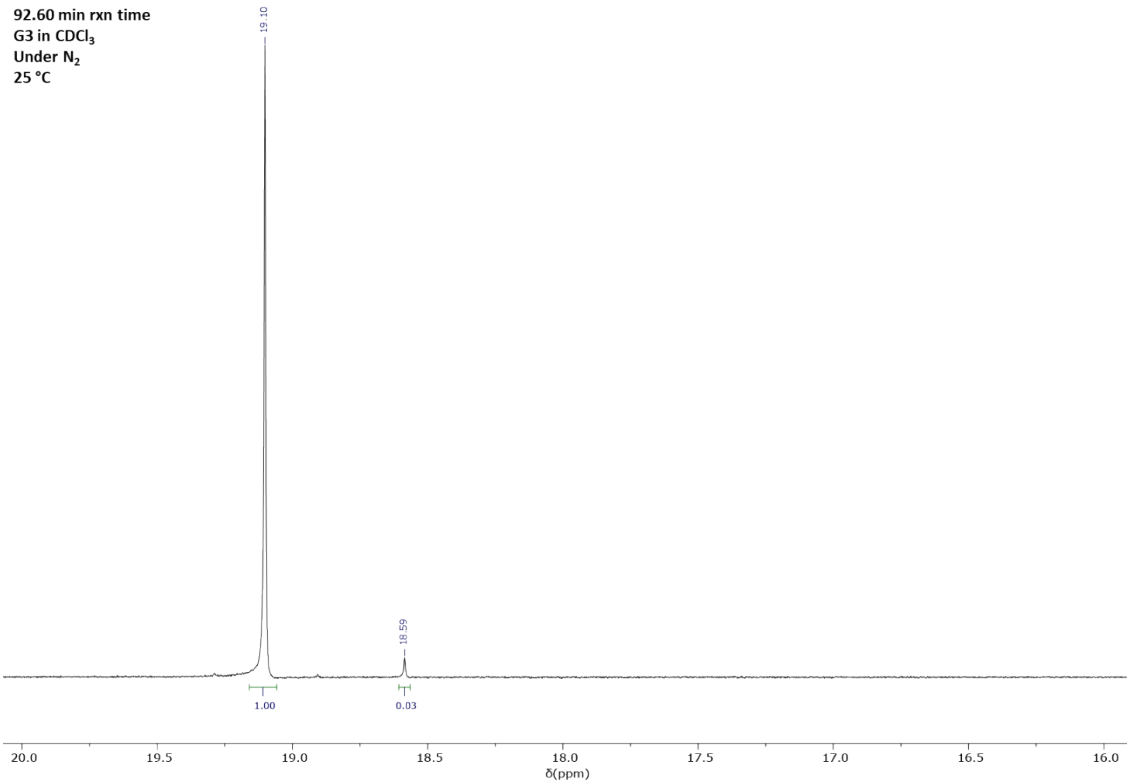


Figure S11. ^{1}H-NMR (600 MHz) of Ru-alkylidene range of G3 in $CDCl_3$ under N_2 after 92.60 min.

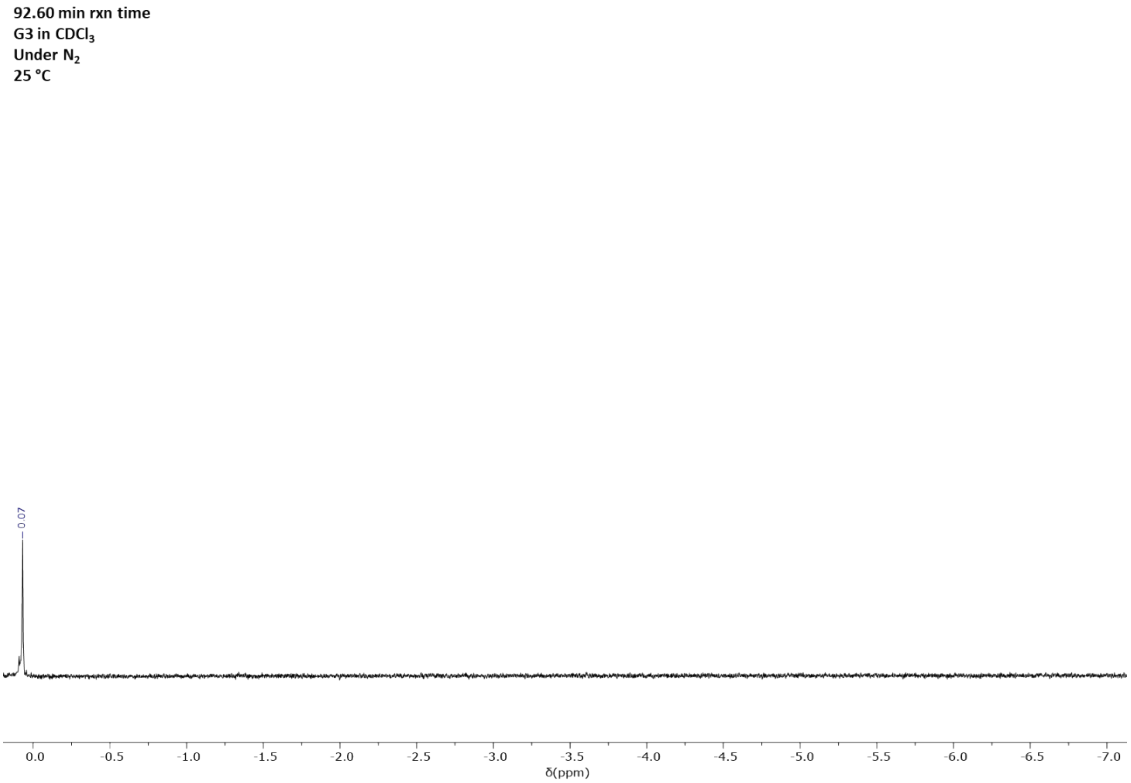


Figure S12. ^{1}H-NMR (600 MHz) of metallacyclobutane range of G3 in $CDCl_3$ after 92.60 min.

D. 10:1 α-pinene:G3 ^{1}H-NMRs

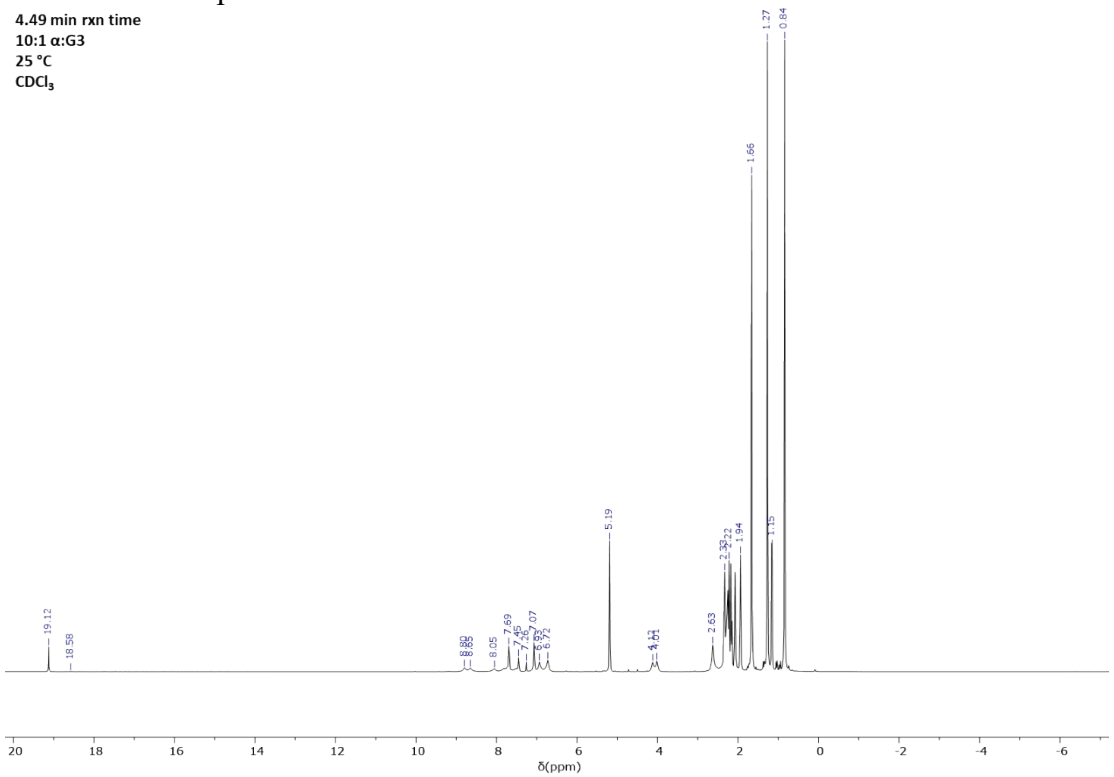


Figure S13. ^{1}H-NMR (600 MHz, $CDCl_3$) of 10:1 α-pinene:G3 polymerization attempt after 4.49 min.

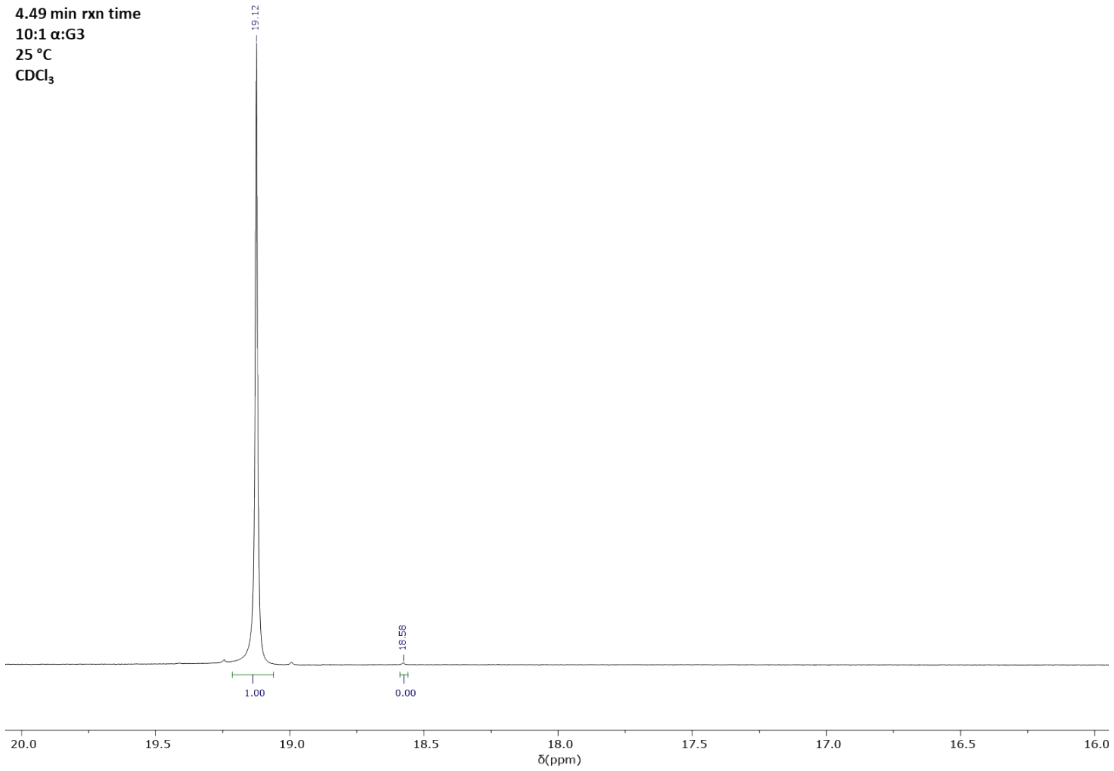


Figure S14. ^{1}H-NMR (600 MHz, $CDCl_3$) of Ru-alkylidene range of 10:1 α-pinene:G3 polymerization attempt after 4.49 min.

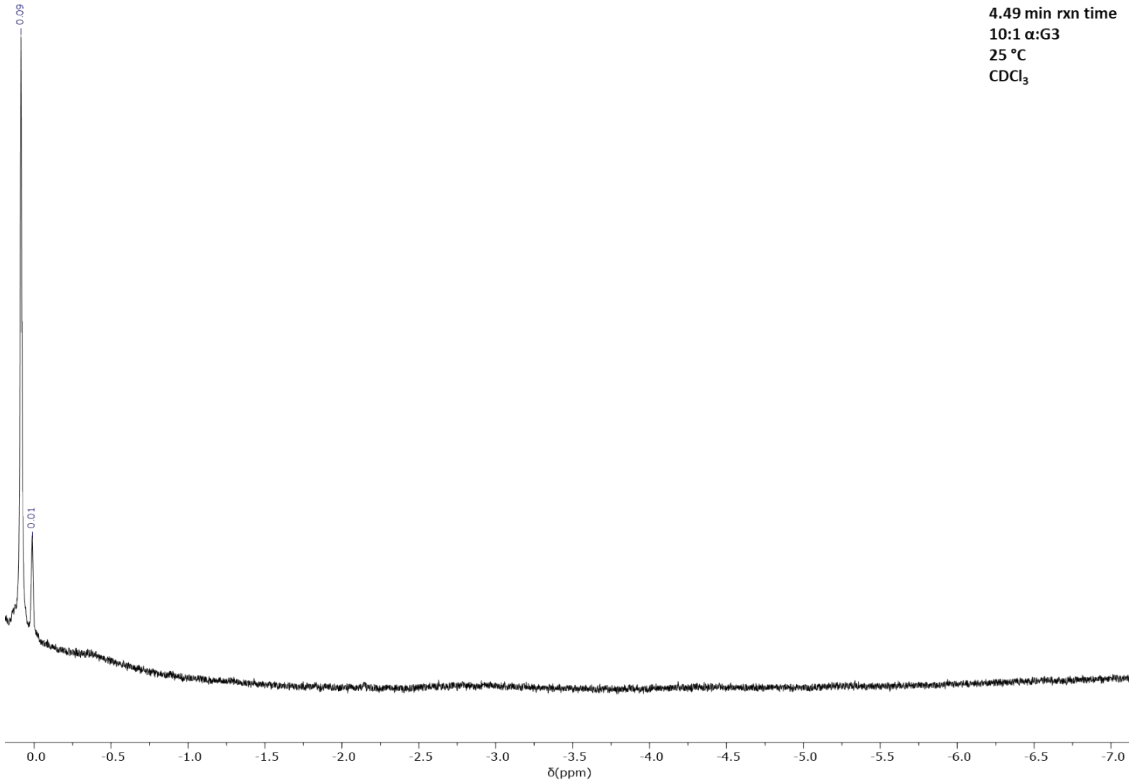


Figure S15. ^{1}H-NMR (600 MHz, $CDCl_3$) of metallacyclobutane range of 10:1 α-pinene:G3 polymerization attempt after 4.49 min.

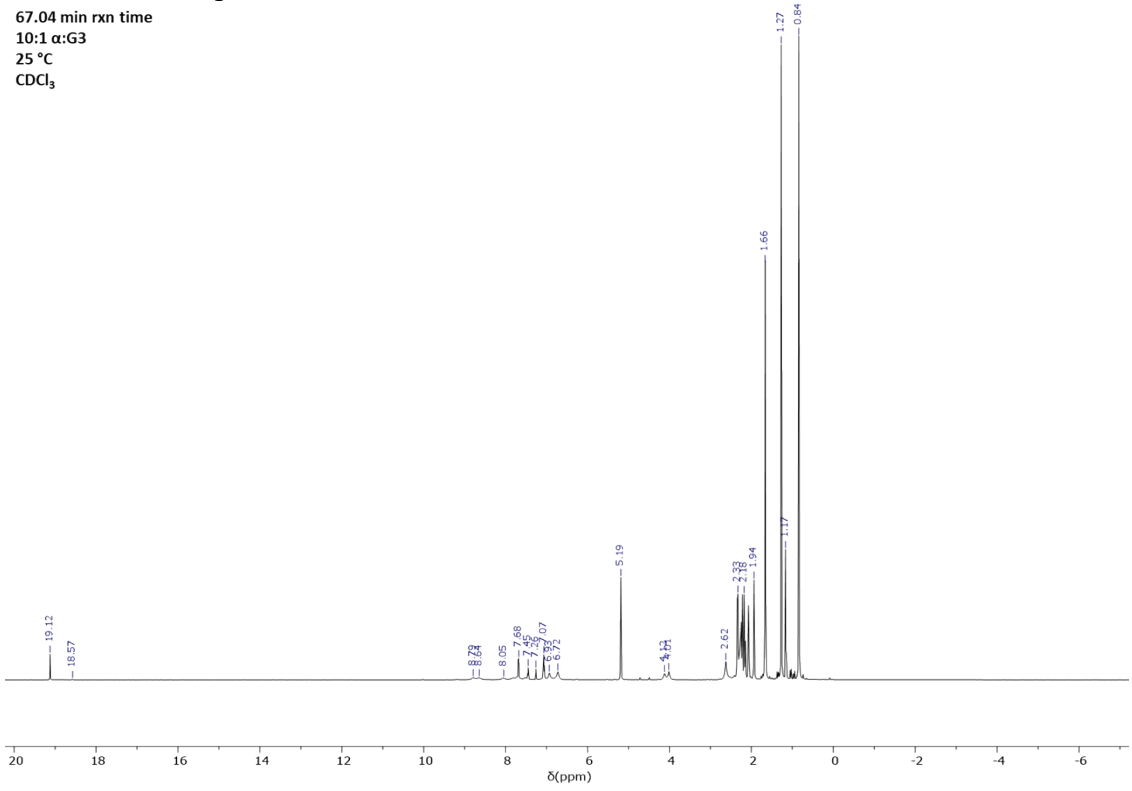


Figure S16. ^{1}H-NMR (600 MHz, $CDCl_3$) of 10:1 α-pinene:G3 polymerization attempt after 67.04 min.

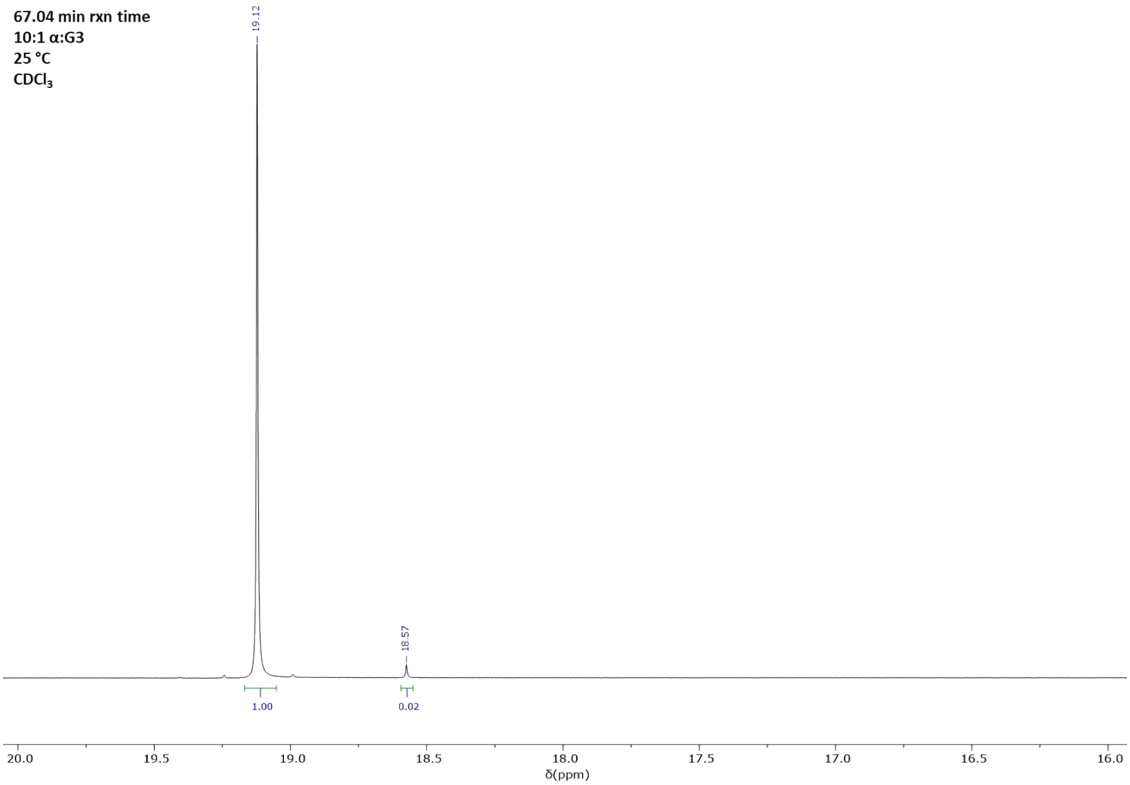


Figure S17. ^{1}H-NMR (600 MHz, $CDCl_3$) of Ru-alkylidene range of 10:1 α-pinene:G3 polymerization attempt after 67.04 min.

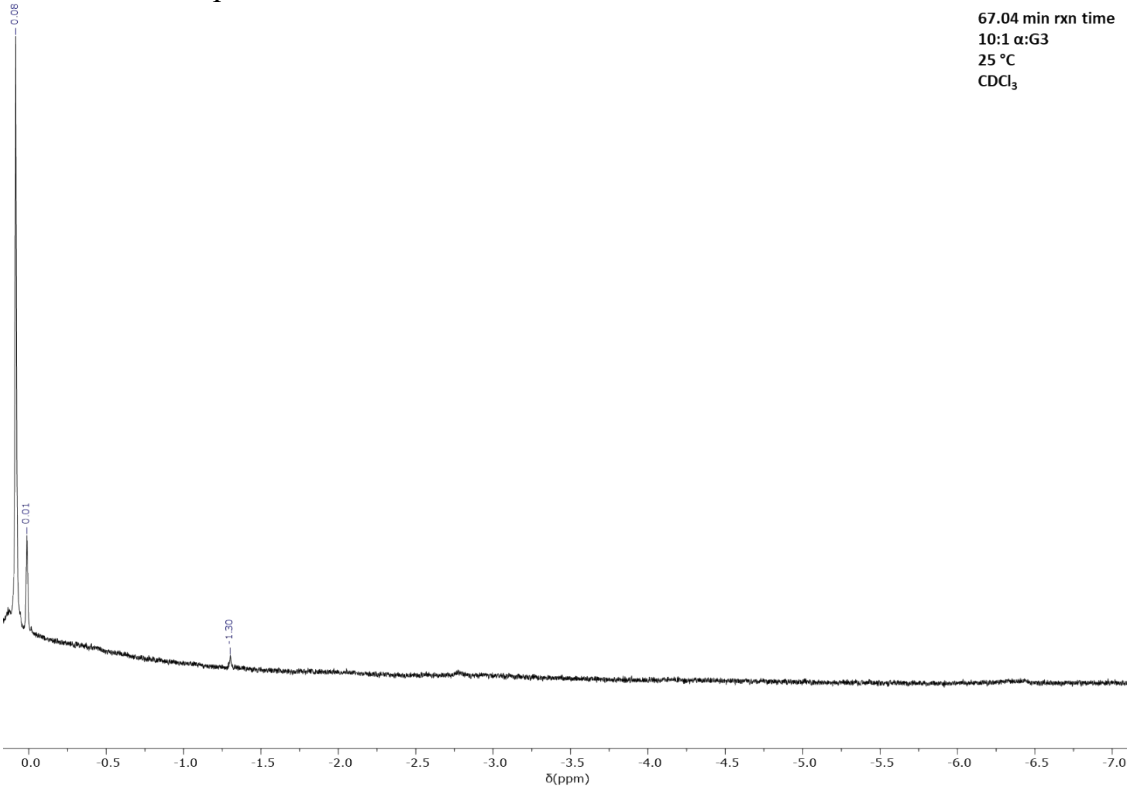


Figure S18. ^{1}H-NMR (600 MHz, $CDCl_3$) of metallacyclobutane range of 10:1 α-pinene:G3 polymerization attempt after 67.04 min.

E. 5:5:1 δ:α:G3 ^{1}H-NMRs

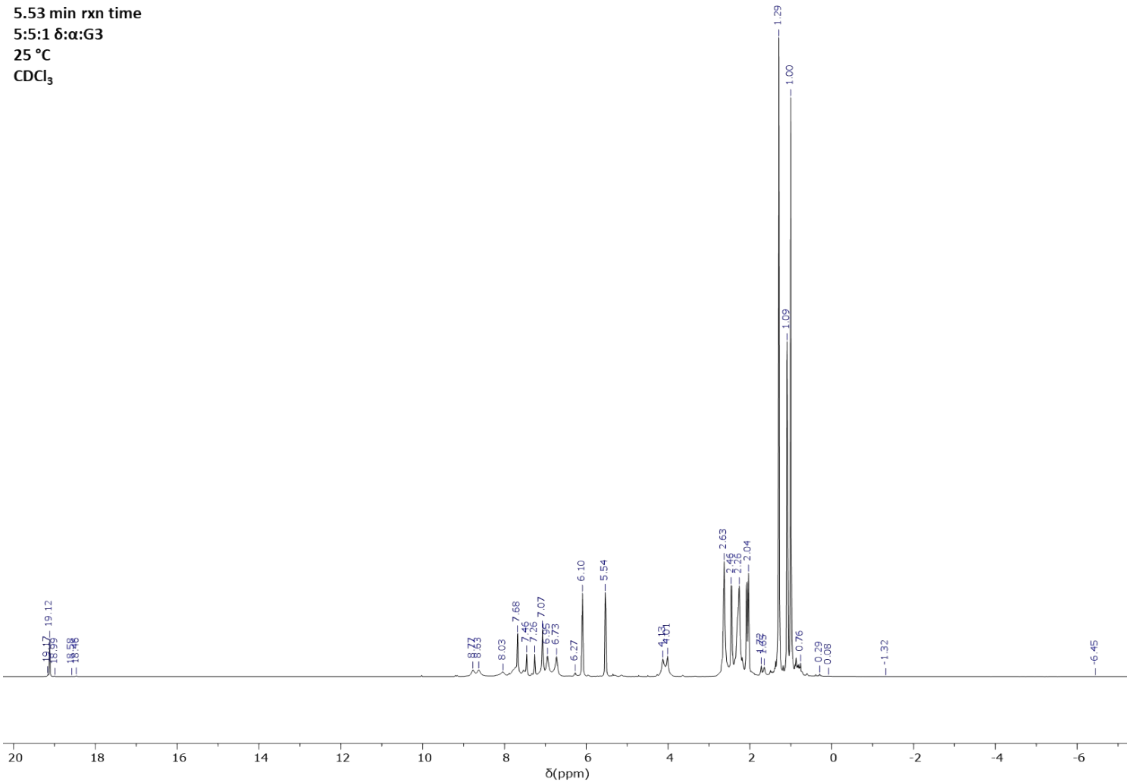


Figure S19. ^{1}H-NMR (600 MHz, $CDCl_3$) of 5:1 δ-pinene:G3 polymerization after 5.53 min.

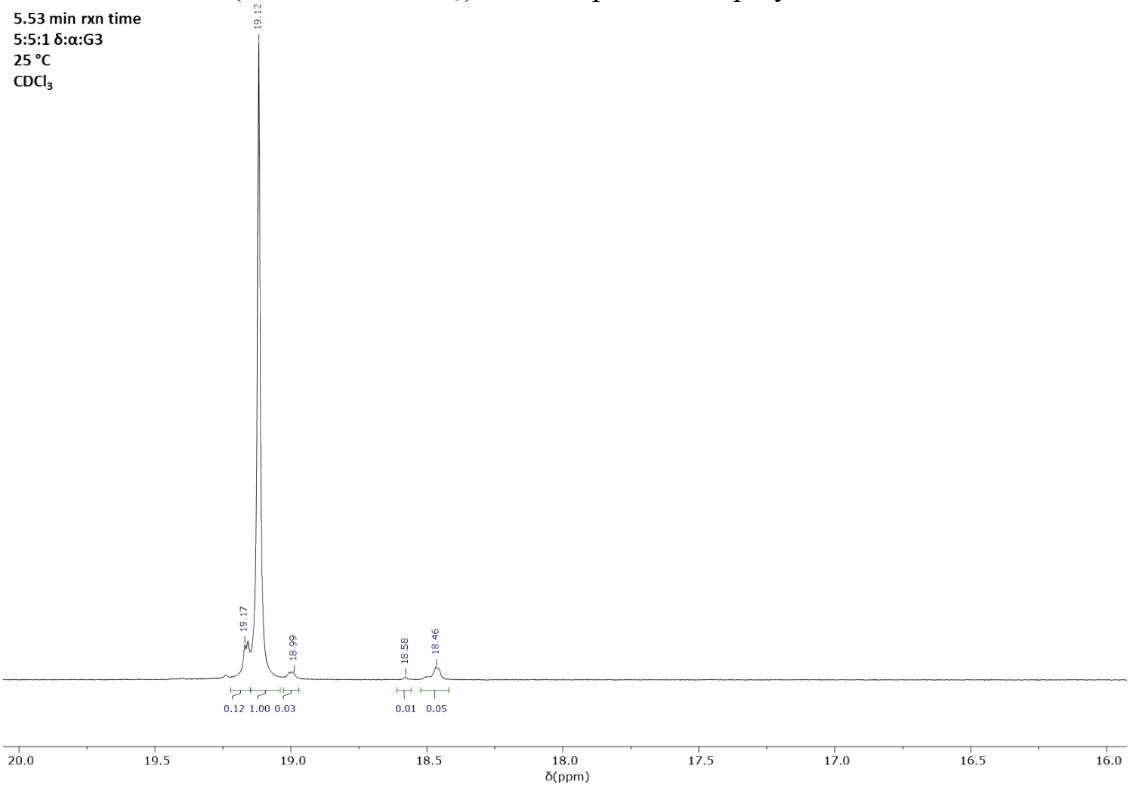


Figure S20. ^{1}H-NMR (600 MHz, $CDCl_3$) of Ru-alkylidene range of 5:1 δ-pinene:G3 polymerization after 5.53 min.

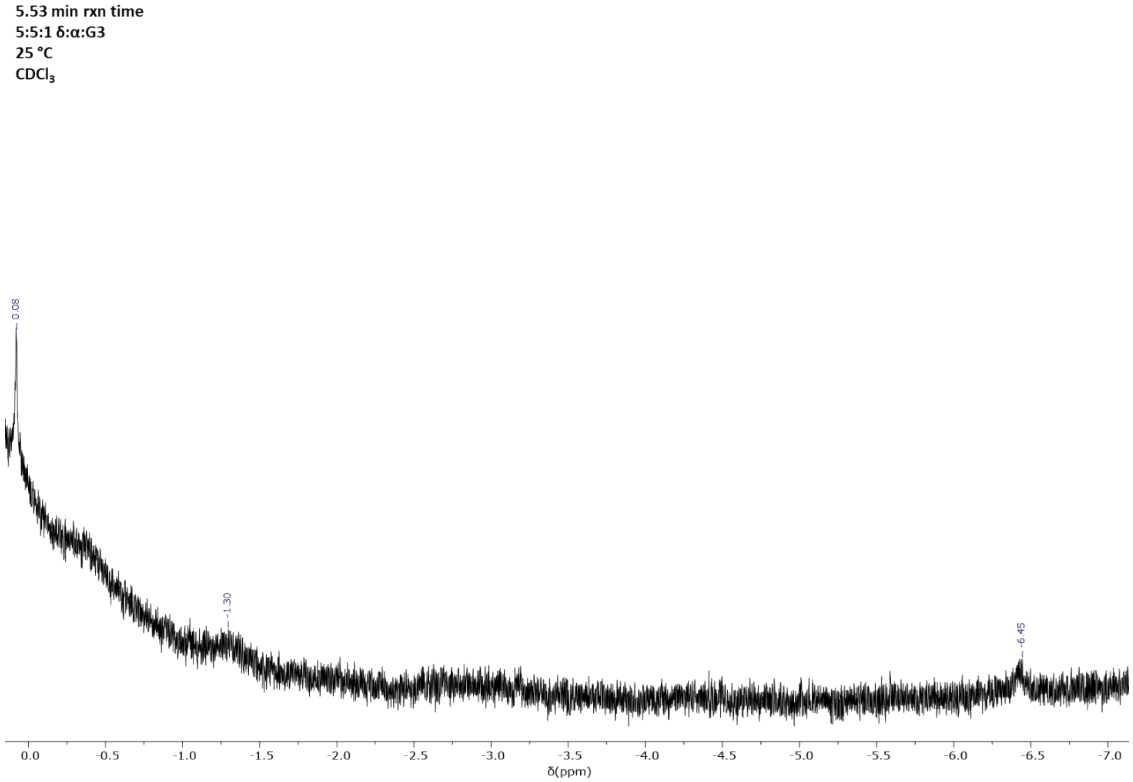


Figure S21. ^{1}H-NMR (600 MHz, $CDCl_3$) of metallacyclobutane range of 5:1 δ-pinene:G3 polymerization after 5.53 min.

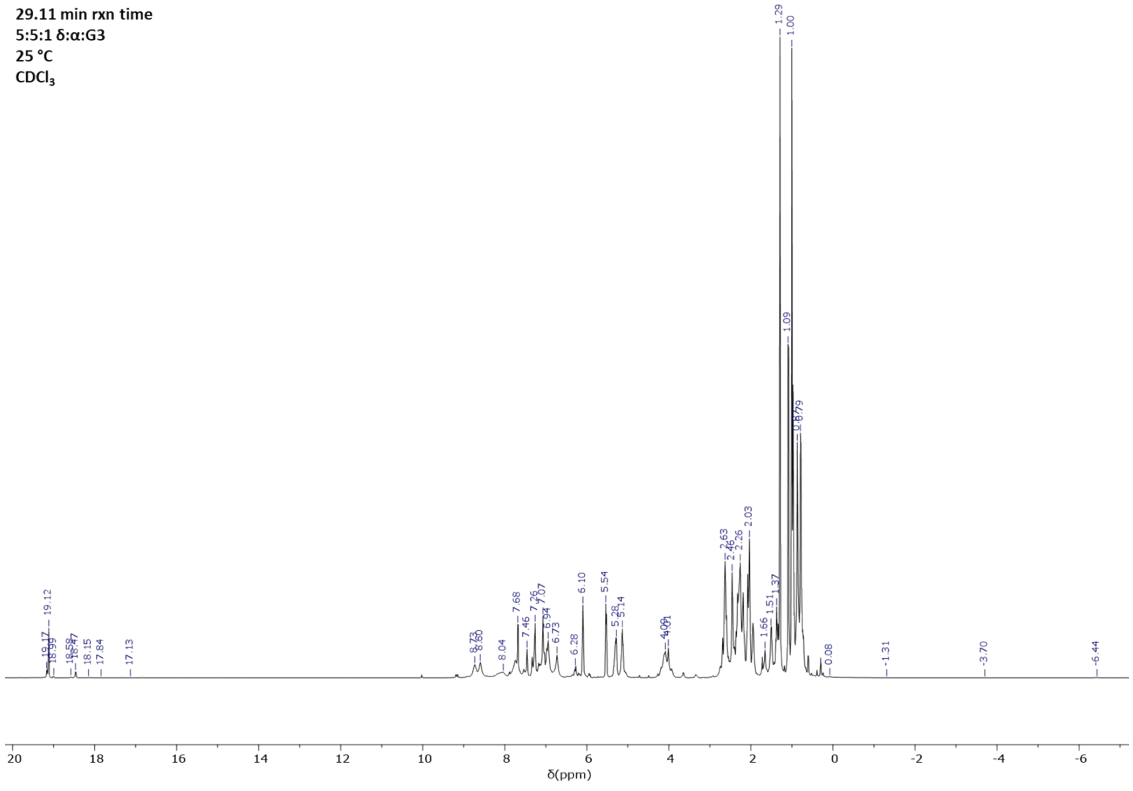


Figure S22. ^{1}H-NMR (600 MHz, $CDCl_3$) of 5:1 δ-pinene:G3 polymerization after 29.11 min.

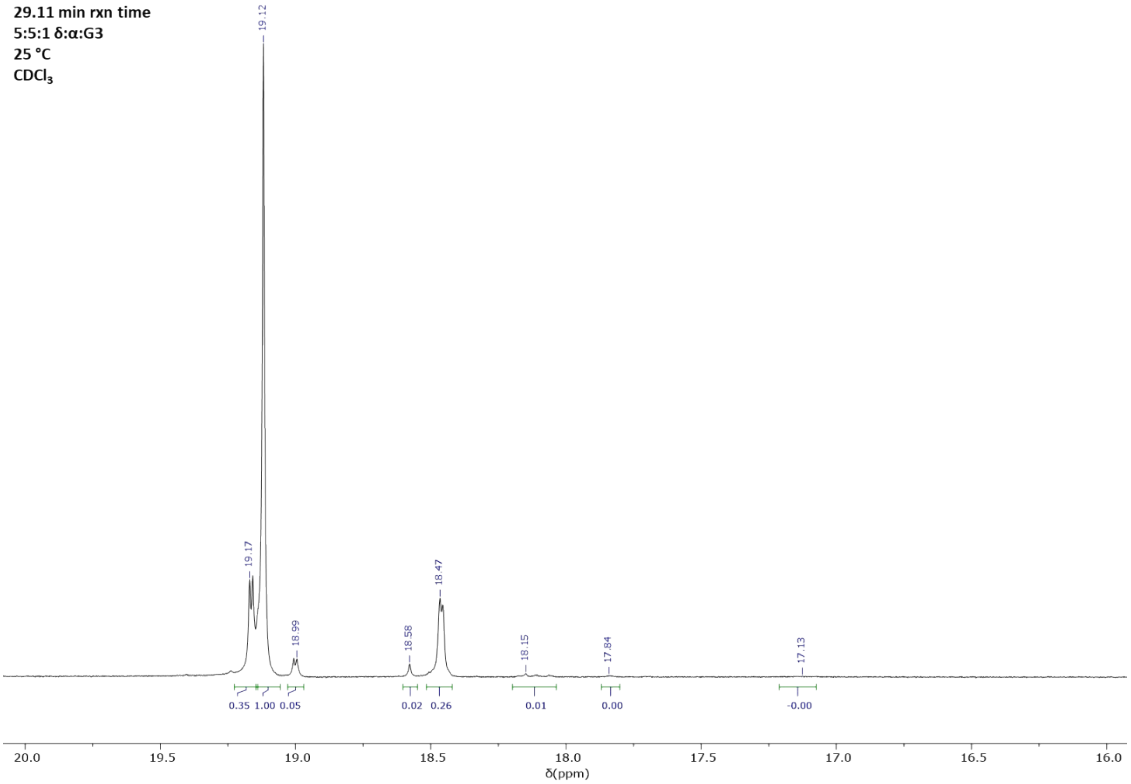


Figure S23. ^{1}H-NMR (600 MHz, $CDCl_3$) of Ru-alkylidene range of 5:1 δ-pinene:G3 polymerization after 29.11 min.

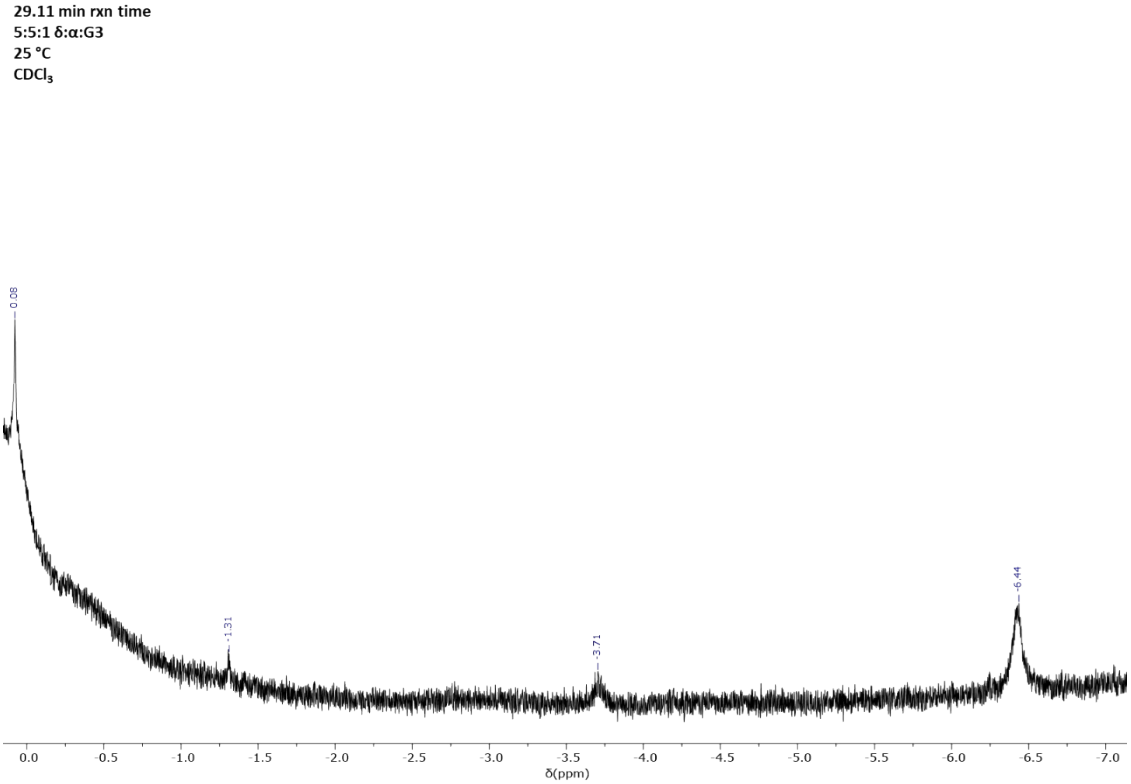


Figure S24. ^{1}H-NMR (600 MHz, $CDCl_3$) of metallacyclobutane range of 5:1 δ-pinene:G3 polymerization after 29.11 min.

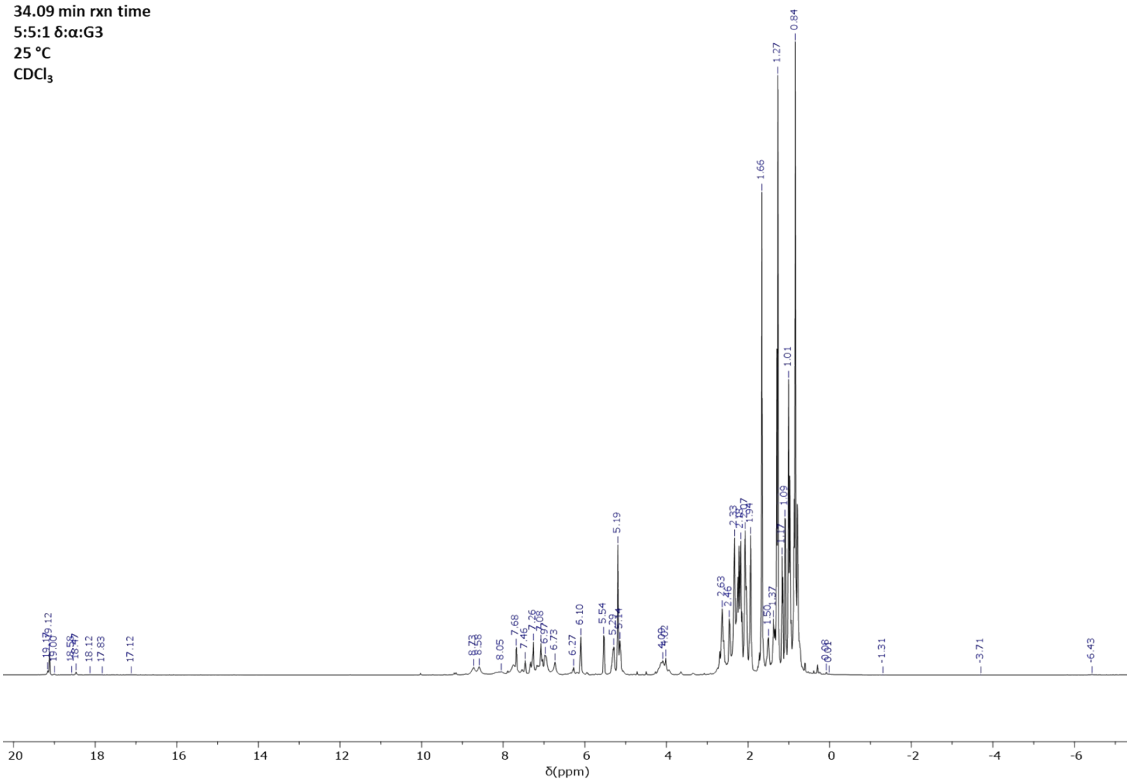


Figure S25. ^{1}H-NMR (600 MHz, $CDCl_3$) of 5:1 δ-pinene:G3 polymerization after 34.09 min, 4.09 min after 5 equivalents of α-pinene was injected.

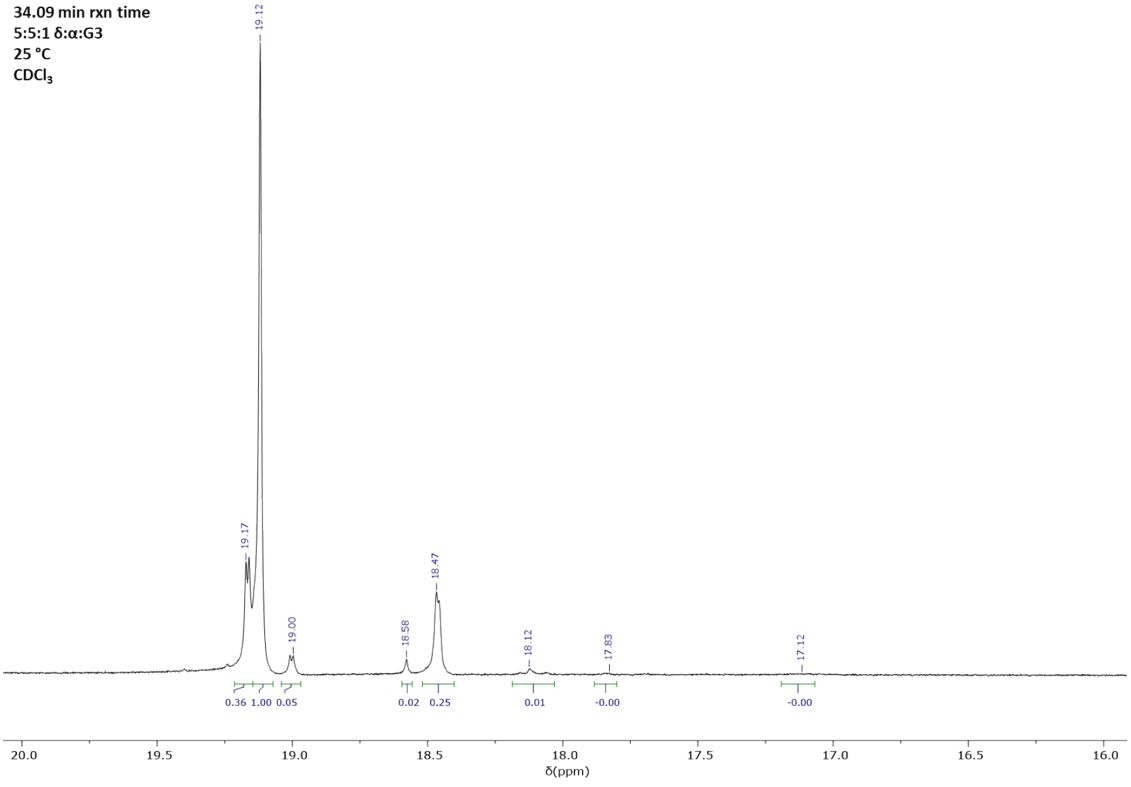


Figure S26. ^{1}H-NMR (600 MHz, $CDCl_3$) of Ru-alkylidene range of 5:1 δ-pinene:G3 polymerization after 34.09 min, 4.09 min after 5 equivalents of α-pinene was injected.

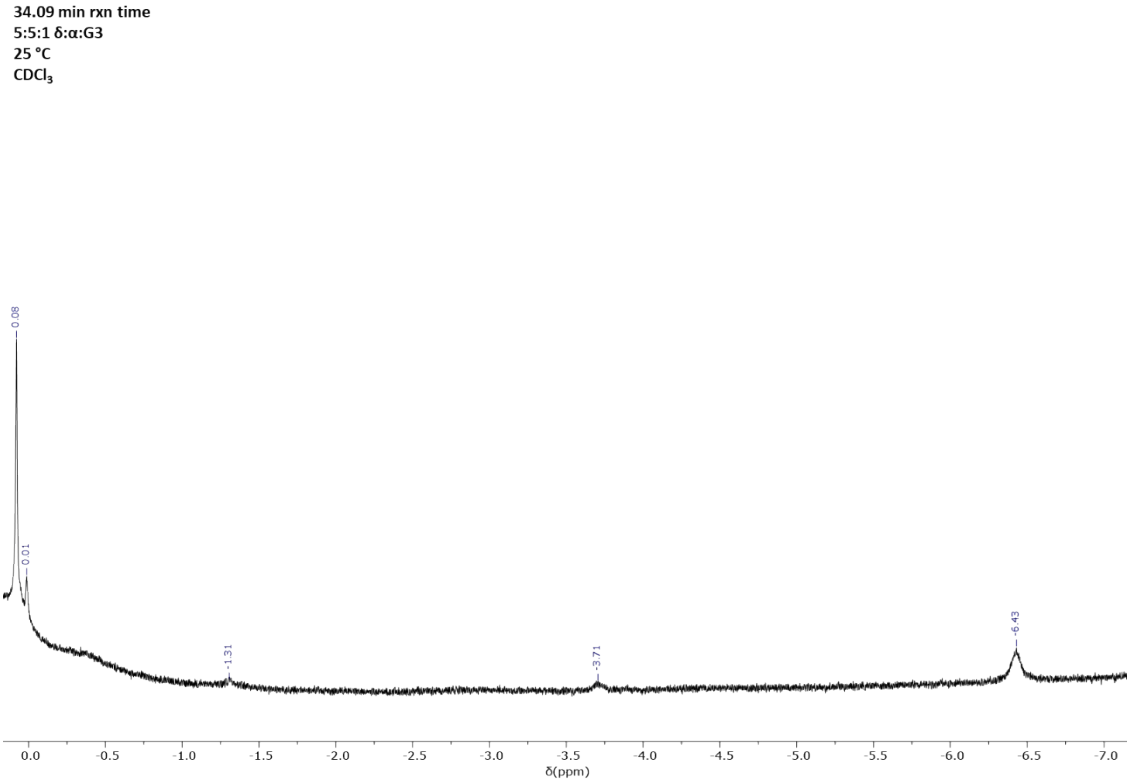


Figure S27. ^{1}H-NMR (600 MHz, $CDCl_3$) of metallacyclobutane range of 5:1 δ-pinene:G3 polymerization after 34.09 min, 4.09 min after 5 equivalents of α-pinene was injected.

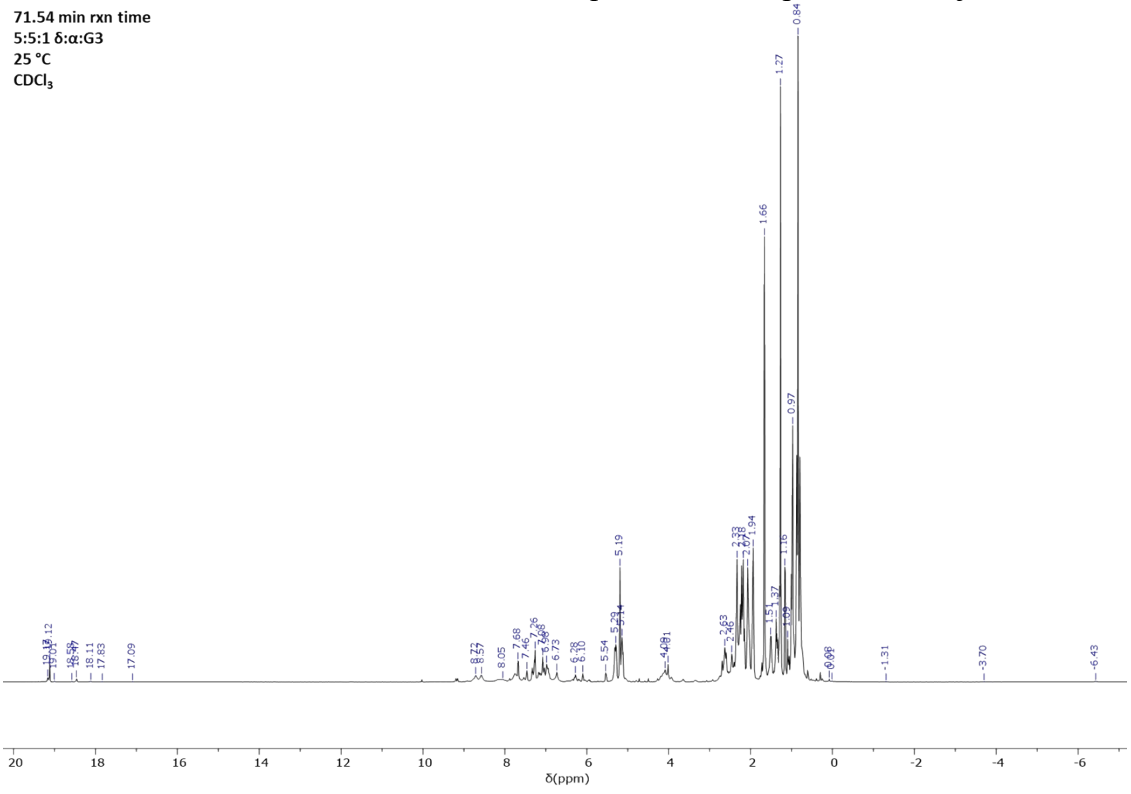


Figure S28. ^{1}H-NMR (600 MHz, $CDCl_3$) of 5:1 δ-pinene:G3 polymerization after 71.54 min, 41.54 min after 5 equivalents of α-pinene was injected.

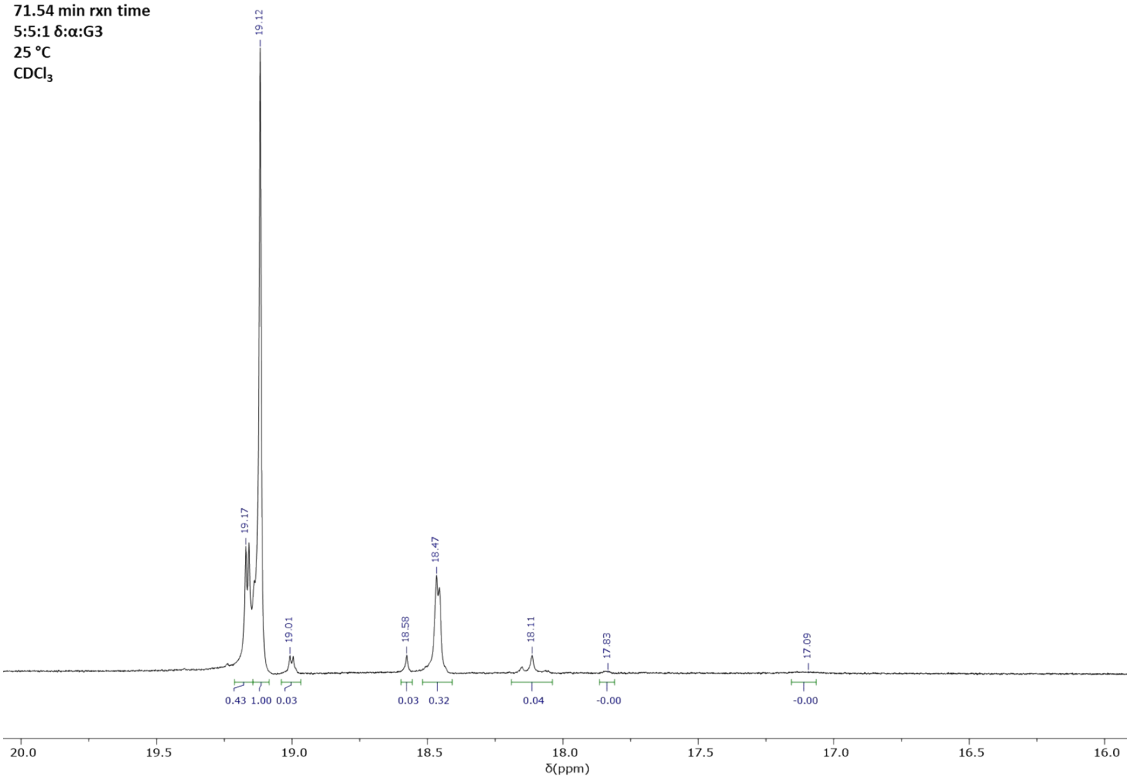


Figure S29. ^{1}H-NMR (600 MHz, $CDCl_3$) of Ru-alkylidene range of 5:1 δ-pinene:G3 polymerization after 71.54 min, 41.54 min after 5 equivalents of α-pinene was injected.

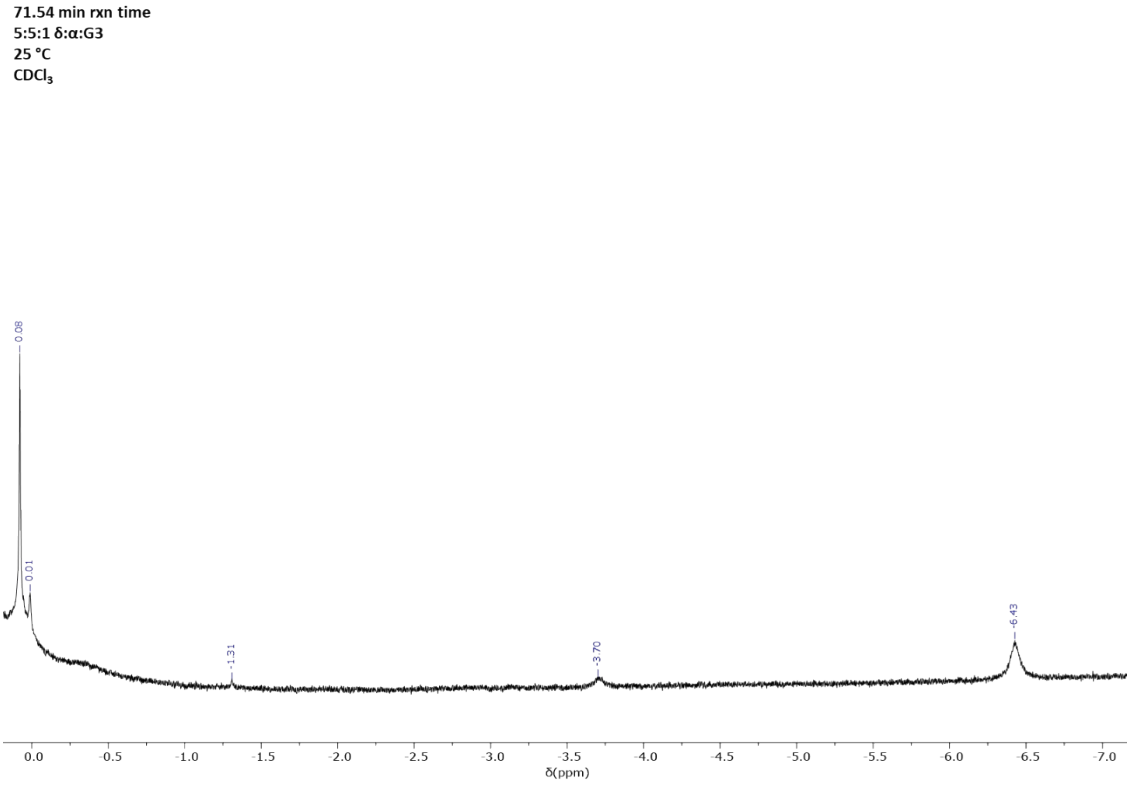
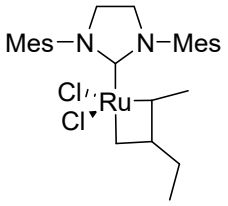


Figure S30. ^{1}H-NMR (600 MHz, $CDCl_3$) of metallacyclobutane range of 5:1 δ-pinene:G3 polymerization after 71.54 min, 41.54 min after 5 equivalents of α-pinene was injected.

IV. Computational Details:

Figure S31. Input files for the geometry, frequency, and GIAO calculations for the ruthenacyclobutane intermediate during a G3 metathesis with a disubstituted monomer.



Optimization Calculation

%chk=GrubbNMR_opt.chk
opt=calcfc PBE1PBE/genECP geom=connectivity int=ultrafine

GrubbNMR_opt.com

0 1

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N	-2.26345315	-0.58514453	-0.04664059
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H	2.61375383	-0.85673443	0.46023003
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H	0.52443390	3.54301994	-1.41228775
H	-0.01817163	3.64072608	0.30060255
H	1.67288724	0.78524946	1.05030491
C	2.57058497	4.08720970	-1.79166064
H	3.45814960	4.59689851	-2.10366440
H	2.01008673	3.78756693	-2.65244861
H	1.97628603	4.74208955	-1.18929768

1 2 1.0 3 1.0 6 1.0 7 1.0 60 1.0
2 54 1.0 58 1.0 66 1.0
3 4 1.5 5 1.5
4 9 1.0 11 1.0
5 8 1.0 12 1.0
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8 9 1.0 13 1.0 43 1.0
9 10 1.0 42 1.0
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11 14 1.5 36 1.5
12 18 1.5 22 1.5
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14 15 1.5 26 1.0
15 16 1.5 53 1.0
16 17 1.5 27 1.0
17 36 1.5 52 1.0
18 19 1.5 23 1.0
19 20 1.5 51 1.0
20 21 1.5 25 1.0
21 22 1.5 50 1.0
22 24 1.0
23 28 1.0 29 1.0 45 1.0
24 30 1.0 31 1.0 44 1.0
25 32 1.0 33 1.0 46 1.0
26 34 1.0 35 1.0 47 1.0
27 40 1.0 41 1.0 48 1.0
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61 62 1.0 63 1.0 67 1.0
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67 68 1.0 69 1.0 70 1.0
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H C N Cl 0
Def2SVP
****
Ru 0
Def2SVP
****

Ru 0
Def2SVP

Frequency Calculation

%chk=GrubbNMR_freq.chk
opt=calcfc freq=noraman PBE1PBE/genECP geom=connectivity int=ultrafine

GrubbNMR_freq.com

0 1
Ru 0.00019600 0.85737800 -0.21510700

C	-1.36901800	2.15371300	-0.71555900
C	0.07986700	-1.13980300	0.07761300
N	-0.99935900	-1.93171800	0.15685300
N	1.18703300	-1.88483800	0.19734100
Cl	0.27713300	0.50654100	-2.56416100
Cl	-0.15507700	1.29018300	2.12949700
C	0.87827000	-3.29588100	0.44344100
C	-0.64035300	-3.34718400	0.26708700
H	-1.15736600	-3.81161800	1.12010300
C	-2.36661400	-1.51191100	0.11344700
C	2.54045800	-1.41843200	0.18253200
H	1.41494200	-3.93826300	-0.27020900
C	-3.03721900	-1.26304800	1.32645800
C	-4.38013100	-0.88199300	1.26925200
C	-5.06520600	-0.75871200	0.05783300
C	-4.37929000	-1.05935100	-1.12120500
C	3.14044100	-1.00328500	1.38579000
C	4.46703700	-0.56519300	1.33989600
C	5.20544900	-0.55534100	0.15495800
C	4.59389300	-1.03314600	-1.00667500
C	3.27072100	-1.48017500	-1.01938900
C	2.40141300	-1.03665600	2.68975700
C	2.66381800	-2.01471100	-2.28135700
C	6.61545100	-0.03991200	0.12718100
C	-2.34299200	-1.39632400	2.64790100
C	-6.49624600	-0.30520500	0.02512300
H	3.07791200	-0.80151800	3.52262800
H	1.96411100	-2.02850700	2.88603600
H	2.26523000	-3.03287700	-2.14472800
H	1.83209000	-1.37226700	-2.61384800
H	6.63422600	1.03139500	-0.13471400
H	7.22462000	-0.56760900	-0.62125000
H	-3.06260200	-1.31735500	3.47401700
H	-1.82320800	-2.36231000	2.74511100
C	-3.03740600	-1.45175100	-1.12269200
C	-2.35614800	-1.80956600	-2.40907800
H	-1.53122500	-1.11293000	-2.63558800
H	-1.92502400	-2.82279100	-2.37206700
H	-7.02146300	-0.68522300	-0.86296700
H	-7.04565000	-0.63550500	0.91878500
H	-0.94367300	-3.88852100	-0.64418900
H	1.19862900	-3.58225500	1.45878400
H	3.41286800	-2.05645800	-3.08368000
H	1.57485700	-0.30637800	2.70061700
H	7.10463300	-0.14503900	1.10635500
H	-1.58753500	-0.60120200	2.76648000

H	-6.55641400	0.79576600	-0.00514800
H	-3.06955200	-1.78381400	-3.24389900
H	5.16552300	-1.06815100	-1.93874300
H	4.93877900	-0.23220800	2.26904800
H	-4.90665200	-1.00209100	-2.07791000
H	-4.90661700	-0.68077100	2.20678400
C	-2.53789400	2.47826700	0.17181500
H	-3.25380900	1.64257800	0.12629500
H	-2.25732900	2.62939800	1.22008900
H	-3.06652600	3.37303300	-0.20380100
C	-0.04986600	3.06571900	-0.66639000
H	0.05297700	3.37025500	-1.71988300
C	1.29192100	2.28999300	-0.37872700
C	-0.19685400	4.26344100	0.27423100
H	-1.18203700	4.72732000	0.10894300
H	-0.19009700	3.89610800	1.31248900
H	1.76705200	2.58770800	0.56578400
H	1.96440400	2.23918300	-1.24328000
H	-1.66582000	2.01780900	-1.76557500
C	0.88378000	5.31428100	0.06755300
H	0.71972000	6.17785500	0.72986200
H	1.88850600	4.91927500	0.28259500
H	0.89056300	5.68795400	-0.96943600

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2 54 1.0 58 1.0 66 1.0
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67 68 1.0 69 1.0 70 1.0
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 69
 70

H C N Cl 0
Def2SVP
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Ru     0
Def2SVP
****

RU     0
Def2SVP

--------------------------------------------------------------------------
GIAO Calculation
--------------------------------------------------------------------------
%mem=80MW
%chk=GrubbNMR_NMR.chk
# nmr=giao scrf=(solvent=chloroform) guess=tcheck geom=connectivity
M06/genecp

GrubbNMR_NMR.com

0 1
 Ru             0.00035300    0.85725800   -0.21516000
 C             -1.36842400    2.15421700   -0.71537600
 C              0.07949200   -1.13993400    0.07762600
 N             -0.99981300   -1.93174300    0.15671900
 N              1.18658400   -1.88507300    0.19749500
 Cl             0.27674300    0.50640200   -2.56427100
 Cl            -0.15459700    1.29008400    2.12947200
 C              0.87765800   -3.29609300    0.44347500
 C             -0.64097200   -3.34723400    0.26703000
 H             -1.15809000   -3.81158800    1.12002600
 C             -2.36699100   -1.51166100    0.11336600
 C              2.54004100   -1.41876500    0.18265700
 H              1.41429400   -3.93848800   -0.27019200
 C             -3.03748100   -1.26253700    1.32637500
 C             -4.38030200   -0.88112700    1.26918300
 C             -5.06538700   -0.75777800    0.05778600
 C             -4.37959700   -1.05872400   -1.12126000
 C              3.14011100   -1.00378800    1.38593200
 C              4.46671100   -0.56571600    1.34001200
 C              5.20505100   -0.55573500    0.15502900
 C              4.59342300   -1.03341300   -1.00661800
 C              3.27023800   -1.48041300   -1.01930700
```

C	2.40113700	-1.03722600	2.68993000
C	2.66329300	-2.01491000	-2.28127200
C	6.61507600	-0.04036600	0.12725000
C	-2.34325600	-1.39590300	2.64781300
C	-6.49630300	-0.30389100	0.02504500
H	3.07780000	-0.80271500	3.52284400
H	1.96329500	-2.02889200	2.88589600
H	2.26485600	-3.03314100	-2.14468100
H	1.83147700	-1.37253800	-2.61368100
H	6.63388900	1.03102500	-0.13429000
H	7.22412900	-0.56786400	-0.62141500
H	-3.06284600	-1.31681900	3.47393600
H	-1.82361300	-2.36196200	2.74502300
C	-3.03782200	-1.45145700	-1.12275800
C	-2.35667300	-1.80954900	-2.40912500
H	-1.53173400	-1.11298000	-2.63578000
H	-1.92560600	-2.82278900	-2.37197000
H	-7.02169700	-0.68402200	-0.86289200
H	-7.04573600	-0.63375700	0.91885000
H	-0.94428400	-3.88857600	-0.64424700
H	1.19792300	-3.58259400	1.45881400
H	3.41229000	-2.05650200	-3.08365200
H	1.57496000	-0.30651800	2.70101200
H	7.10436700	-0.14585200	1.10633300
H	-1.58768700	-0.60088600	2.76638500
H	-6.55616100	0.79708800	-0.00556400
H	-3.07012400	-1.78388100	-3.24390900
H	5.16500400	-1.06834300	-1.93871800
H	4.93851300	-0.23285200	2.26917700
H	-4.90699000	-1.00143300	-2.07794600
H	-4.90669900	-0.67969500	2.20671900
C	-2.53707900	2.47918100	0.17214300
H	-3.25326800	1.64371900	0.12677300
H	-2.25634200	2.63027400	1.22037500
H	-3.06546900	3.37409200	-0.20345800
C	-0.04897900	3.06562300	-0.66638600
H	0.05399700	3.37011500	-1.71987700
C	1.29259900	2.28932200	-0.37880000
C	-0.19527900	4.26341100	0.27426100
H	-1.18029100	4.72771700	0.10914800
H	-0.18850900	3.89608000	1.31252000
H	1.76790900	2.58692800	0.56565800
H	1.96498200	2.23833300	-1.24342300
H	-1.66543600	2.01836500	-1.76533500
C	0.88577500	5.31377600	0.06737800
H	0.72221900	6.17742700	0.72970800

H	1.89036900	4.91833300	0.28222900
H	0.89252400	5.68743500	-0.96961500

1 2 1.0 3 1.0 60 1.0
2 54 1.0 58 1.0 66 1.0
3 4 1.5 5 1.5
4 9 1.0 11 1.0
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9 10 1.0 42 1.0
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11 14 1.5 36 1.5
12 18 1.5 22 1.5
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15 16 1.5 53 1.0
16 17 1.5 27 1.0
17 36 1.5 52 1.0
18 19 1.5 23 1.0
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21 22 1.5 50 1.0
22 24 1.0
23 28 1.0 29 1.0 45 1.0
24 30 1.0 31 1.0 44 1.0
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26 34 1.0 35 1.0 47 1.0
27 40 1.0 41 1.0 48 1.0
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37 38 1.0 39 1.0 49 1.0
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61 62 1.0 63 1.0 67 1.0
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H C N Cl 0
Def2TZVPP
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Ru 0
Def2TZVPP
****

RU 0
Def2TZVPP

Figure S32. Exemplary abbreviated output files for the geometry and frequency calculations for the ruthenacyclobutane intermediate during a G3 metathesis with a disubstituted monomer.

Optimization Output

Standard Orientation:
Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	44	0	0.000196	0.857378	-0.215107
2	6	0	-1.369018	2.153713	-0.715559
3	6	0	0.079867	-1.139803	0.077613
4	7	0	-0.999359	-1.931718	0.156853
5	7	0	1.187033	-1.884838	0.197341
6	17	0	0.277133	0.506541	-2.564161
7	17	0	-0.155077	1.290183	2.129497
8	6	0	0.878270	-3.295881	0.443441
9	6	0	-0.640353	-3.347184	0.267087
10	1	0	-1.157366	-3.811618	1.120103
11	6	0	-2.366614	-1.511911	0.113447
12	6	0	2.540458	-1.418432	0.182532
13	1	0	1.414942	-3.938263	-0.270209
14	6	0	-3.037219	-1.263048	1.326458
15	6	0	-4.380131	-0.881993	1.269252
16	6	0	-5.065206	-0.758712	0.057833
17	6	0	-4.379290	-1.059351	-1.121205
18	6	0	3.140441	-1.003285	1.385790
19	6	0	4.467037	-0.565193	1.339896
20	6	0	5.205449	-0.555341	0.154958
21	6	0	4.593893	-1.033146	-1.006675
22	6	0	3.270721	-1.480175	-1.019389
23	6	0	2.401413	-1.036656	2.689757
24	6	0	2.663818	-2.014711	-2.281357
25	6	0	6.615451	-0.039912	0.127181
26	6	0	-2.342992	-1.396324	2.647901
27	6	0	-6.496246	-0.305205	0.025123
28	1	0	3.077912	-0.801518	3.522628
29	1	0	1.964111	-2.028507	2.886036
30	1	0	2.265230	-3.032877	-2.144728
31	1	0	1.832090	-1.372267	-2.613848
32	1	0	6.634226	1.031395	-0.134714
33	1	0	7.224620	-0.567609	-0.621250
34	1	0	-3.062602	-1.317355	3.474017
35	1	0	-1.823208	-2.362310	2.745111
36	6	0	-3.037406	-1.451751	-1.122692
37	6	0	-2.356148	-1.809566	-2.409078
38	1	0	-1.531225	-1.112930	-2.635588
39	1	0	-1.925024	-2.822791	-2.372067
40	1	0	-7.021463	-0.685223	-0.862967
41	1	0	-7.045650	-0.635505	0.918785
42	1	0	-0.943673	-3.888521	-0.644189

43	1	0	1.198629	-3.582255	1.458784
44	1	0	3.412868	-2.056458	-3.083680
45	1	0	1.574857	-0.306378	2.700617
46	1	0	7.104633	-0.145039	1.106355
47	1	0	-1.587535	-0.601202	2.766480
48	1	0	-6.556414	0.795766	-0.005148
49	1	0	-3.069552	-1.783814	-3.243899
50	1	0	5.165523	-1.068151	-1.938743
51	1	0	4.938779	-0.232208	2.269048
52	1	0	-4.906652	-1.002091	-2.077910
53	1	0	-4.906617	-0.680771	2.206784
54	6	0	-2.537894	2.478267	0.171815
55	1	0	-3.253809	1.642578	0.126295
56	1	0	-2.257329	2.629398	1.220089
57	1	0	-3.066526	3.373033	-0.203801
58	6	0	-0.049866	3.065719	-0.666390
59	1	0	0.052977	3.370255	-1.719883
60	6	0	1.291921	2.289993	-0.378727
61	6	0	-0.196854	4.263441	0.274231
62	1	0	-1.182037	4.727320	0.108943
63	1	0	-0.190097	3.896108	1.312489
64	1	0	1.767052	2.587708	0.565784
65	1	0	1.964404	2.239183	-1.243280
66	1	0	-1.665820	2.017809	-1.765575
67	6	0	0.883780	5.314281	0.067553
68	1	0	0.719720	6.177855	0.729862
69	1	0	1.888506	4.919275	0.282595
70	1	0	0.890563	5.687954	-0.969436

Item	Value	Threshold	Converged?
Maximum Force	0.000022	0.000450	YES
RMS Force	0.000002	0.000300	YES
Maximum Displacement	0.001197	0.001800	YES
RMS Displacement	0.000254	0.001200	YES

Predicted change in Energy=-6.380383D-09
Optimization completed.
-- Stationary point found.

Job cpu time: 2 days 20 hours 34 minutes 46.3 seconds.
File lengths (MBytes): RWF= 1104 Int= 0 D2E= 0 Chk= 40 Scr= 16
Normal termination of Gaussian 09 at Fri Apr 23 09:01:53 2021.

Frequency Output

Standard Orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.000353	0.857258	-0.215160
2	6	0	-1.368424	2.154217	-0.715376
3	6	0	0.079492	-1.139934	0.077626
4	7	0	-0.999813	-1.931743	0.156719
5	7	0	1.186584	-1.885073	0.197495
6	17	0	0.276743	0.506402	-2.564271
7	17	0	-0.154597	1.290084	2.129472
8	6	0	0.877658	-3.296093	0.443475
9	6	0	-0.640972	-3.347234	0.267030
10	1	0	-1.158090	-3.811588	1.120026
11	6	0	-2.366991	-1.511661	0.113366
12	6	0	2.540041	-1.418765	0.182657
13	1	0	1.414294	-3.938488	-0.270192
14	6	0	-3.037481	-1.262537	1.326375
15	6	0	-4.380302	-0.881127	1.269183
16	6	0	-5.065387	-0.757778	0.057786
17	6	0	-4.379597	-1.058724	-1.121260
18	6	0	3.140111	-1.003788	1.385932
19	6	0	4.466711	-0.565716	1.340012
20	6	0	5.205051	-0.555735	0.155029
21	6	0	4.593423	-1.033413	-1.006618
22	6	0	3.270238	-1.480413	-1.019307
23	6	0	2.401137	-1.037226	2.689930
24	6	0	2.663293	-2.014910	-2.281272
25	6	0	6.615076	-0.040366	0.127250
26	6	0	-2.343256	-1.395903	2.647813
27	6	0	-6.496303	-0.303891	0.025045
28	1	0	3.077800	-0.802715	3.522844
29	1	0	1.963295	-2.028892	2.885896
30	1	0	2.264856	-3.033141	-2.144681
31	1	0	1.831477	-1.372538	-2.613681
32	1	0	6.633889	1.031025	-0.134290
33	1	0	7.224129	-0.567864	-0.621415
34	1	0	-3.062846	-1.316819	3.473936
35	1	0	-1.823613	-2.361962	2.745023
36	6	0	-3.037822	-1.451457	-1.122758
37	6	0	-2.356673	-1.809549	-2.409125
38	1	0	-1.531734	-1.112980	-2.635780
39	1	0	-1.925606	-2.822789	-2.371970
40	1	0	-7.021697	-0.684022	-0.862892
41	1	0	-7.045736	-0.633757	0.918850
42	1	0	-0.944284	-3.888576	-0.644247

43	1	0	1.197923	-3.582594	1.458814
44	1	0	3.412290	-2.056502	-3.083652
45	1	0	1.574960	-0.306518	2.701012
46	1	0	7.104367	-0.145852	1.106333
47	1	0	-1.587687	-0.600886	2.766385
48	1	0	-6.556161	0.797088	-0.005564
49	1	0	-3.070124	-1.783881	-3.243909
50	1	0	5.165004	-1.068343	-1.938718
51	1	0	4.938513	-0.232852	2.269177
52	1	0	-4.906990	-1.001433	-2.077946
53	1	0	-4.906699	-0.679695	2.206719
54	6	0	-2.537079	2.479181	0.172143
55	1	0	-3.253268	1.643719	0.126773
56	1	0	-2.256342	2.630274	1.220375
57	1	0	-3.065469	3.374092	-0.203458
58	6	0	-0.048979	3.065623	-0.666386
59	1	0	0.053997	3.370115	-1.719877
60	6	0	1.292599	2.289322	-0.378800
61	6	0	-0.195279	4.263411	0.274261
62	1	0	-1.180291	4.727717	0.109148
63	1	0	-0.188509	3.896080	1.312520
64	1	0	1.767909	2.586928	0.565658
65	1	0	1.964982	2.238333	-1.243423
66	1	0	-1.665436	2.018365	-1.765335
67	6	0	0.885775	5.313776	0.067378
68	1	0	0.722219	6.177427	0.729708
69	1	0	1.890369	4.918333	0.282229
70	1	0	0.892524	5.687435	-0.969615

Item	Value	Threshold	Converged?
Maximum Force	0.000000	0.000450	YES
RMS Force	0.000000	0.000300	YES
Maximum Displacement	0.000084	0.001800	YES
RMS Displacement	0.000020	0.001200	YES

Predicted change in Energy=-1.710658D-11
Optimization completed.
-- Stationary point found.

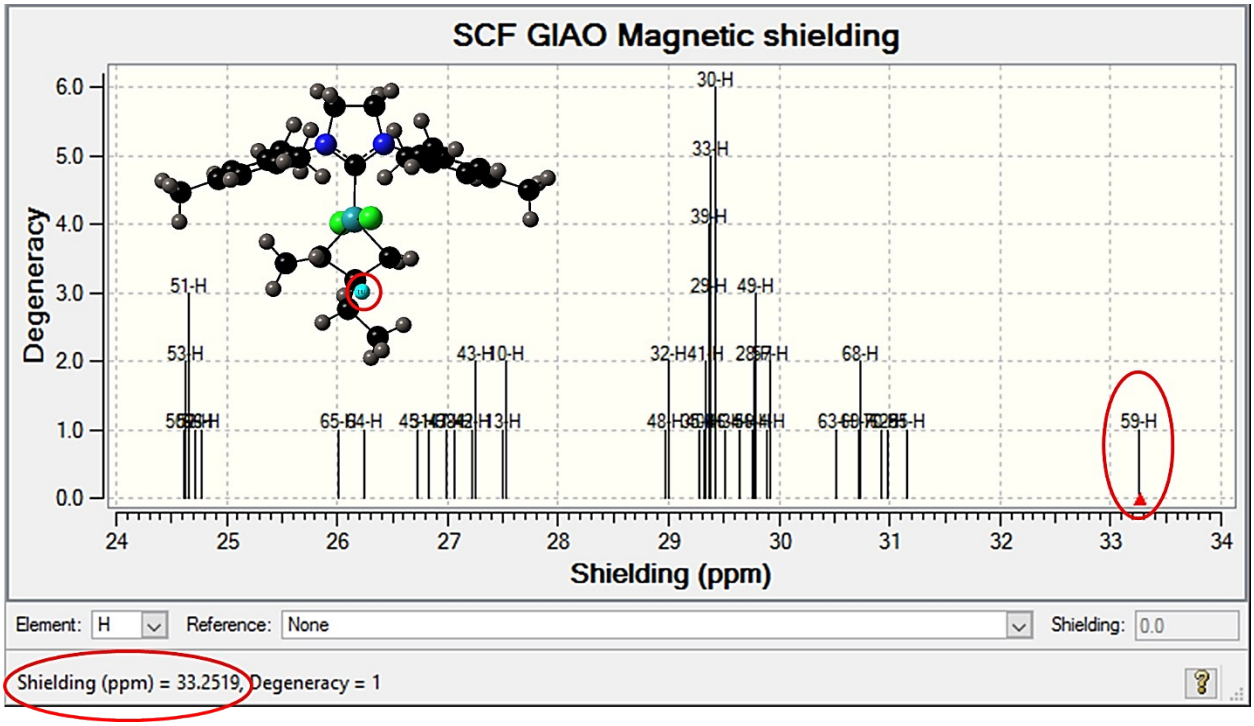
- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Zero-point correction= 0.594836 (Hartree/Particle)
Thermal correction to Energy= 0.631754
Thermal correction to Enthalpy= 0.632698
Thermal correction to Gibbs Free Energy= 0.524548
Sum of electronic and zero-point Energies= -2173.259549

```
 Sum of electronic and thermal Energies=          -2173.222631
 Sum of electronic and thermal Enthalpies=        -2173.221687
 Sum of electronic and thermal Free Energies=     -2173.329837
          Item                   Value          Threshold  Converged?
 Maximum Force                   0.000000       0.000450     YES
 RMS     Force                   0.000000       0.000300     YES
 Maximum Displacement            0.000105       0.001800     YES
 RMS     Displacement            0.000026       0.001200     YES
 Predicted change in Energy=-2.072470D-11
 Optimization completed.
   -- Stationary point found.
[NImag=0]

Job cpu time:       1 days  8 hours 54 minutes 20.1 seconds.
File lengths (MBytes):  RWF=   4160 Int=      0 D2E=      0 Chk=     48 Scr=     16
Normal termination of Gaussian 09 at Sat May  1 10:11:22 2021.
```

Figure S33. Example ^{1}H NMR δ (ppm) determination for proton H_a.



δ = (TMS Absolute Shielding – Ru-H# Absolute Shielding)

H#59
δ = (31.565- 33.2519)
δ = -1.69 ppm

V. References

1. V. Forcina, A. García-Domínguez and G. C. Lloyd-Jones, *Faraday Discussions*, 2019, **220**, 179-195.
2. M. S. Sanford, J. A. Love and R. H. Grubbs, *Organometallics*, 2001, **20**, 5314-5318.
3. M. R. Yarolimek, H. R. Bookbinder, B. M. Coia and J. G. Kennemur, *ACS Macro Letters*, 2021, **10**, 760-766.