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Supplementary Information

Electrochemically-Controlled, Ruthenium-Catalyzed Olefin Metathesis

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General Information

All reactions were carried out in anhydrous solvents and performed under ambient conditions unless otherwise noted. Commercial reagents and anhydrous solvents were purchased from Sigma-Aldrich, TCI, Matrix, Alfa-Aesar, and Oakwood Scientific. Thin layer chromatography was performed on SiliCycle® 250 µm, 60 Å plates. Chromatographic purification was accomplished by flash chromatography on SiliCycle® Silica Flash® 40-63 µm, 60 Å. Visualization was accomplished with 254 nm UV light, I_2, or $KMnO_4$. $RuCl_2(CHPh)(SIMes)_2$ was supplied by Umicore.

All electrochemical reactions were carried out under N_2 in 1.5 dr vials fitted with Teflon caps using a PS-305DM Dr. Meter DC Power Supply. Copper wire was purchased from Sigma-Aldrich (1.0 mm in diameter, 99.99% Cu). Copper electrodes were prepared by cutting the wire into 60 mm long pieces. Graphite electrodes (HB mechanical pencil refills, 1.3 mm in diameter, 60 mm in length) were purchased from Amazon.com.

Unless otherwise noted, ^1H NMR (500 MHz), ^{13}C (126 MHz), and ^{19}F (471 MHZ) spectra were taken on a Bruker 500 MHz spectrometer at ambient temperature and recorded in $CDCl_3$ Chemical shifts (δ) are in parts per million relative to $CDCl_3$ (^1H: 7.26 ppm, ^{13}C: 77.16 ppm). Data for ^1H and ^{13}C NMR is reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constant (Hz), integration.

Polymer characterization data was obtained on an Agilent 1260 Infinity GPC in chloroform calibrated against polystyrene standards. Polymer samples were dissolved in chloroform (~2 mg/mL) and stirred at room temperature overnight.

All cyclic voltammetry studies were performed on a CH Instruments Model 1232B potentiostat using an EDAQ 1-mm disk glassy carbon working electrode in conjunction with an EDAQ Ag/AgCl reference electrode and a platinum wire from VWR as a counter electrode. All experiments were performed in anhydrous acetone and anhydrous dichloromethane.

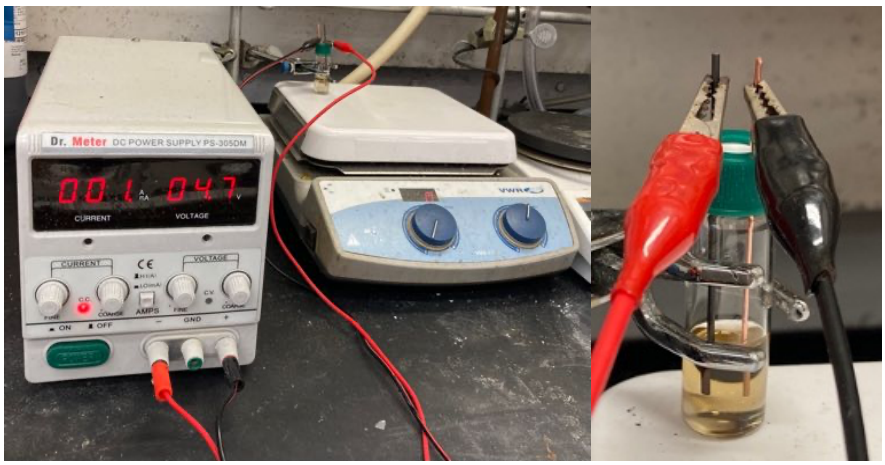
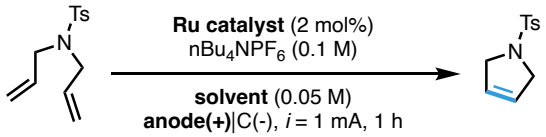


Figure S1: Electrochemical setup

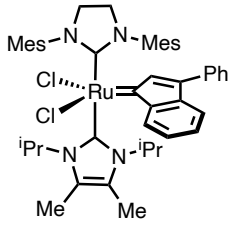
Ru Catalyst, Solvent, and Anode Screens

To a vial equipped with a magnetic stir bar was added 77.5 mg nBu_4NPF_6. In a N_2 glovebox, 0.002 mmol of the Ru catalyst and 25.0 μL of diallyl tosylamide were added to the vial, which was then diluted to 2 mL with anhydrous solvent. The two electrodes were inserted through a Teflon cap so that the inter-electrode distance and height from the bottom of the vial were 5 mm and 7 mm, respectively. The vial was capped, removed from the glovebox, and the electrodes were connected to the power supply. Stirring was initiated, and a constant current of 1 mA was applied for 1 h. After 1 hour, the vial was concentrated. NMR yields were taken in $CDCl_3$ with 0.1 mmol mesitylene as internal standard.



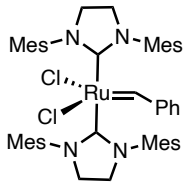
Entry	Ru catalyst	Solvent	Anode	Yield[b]
1	Ru_1	Acetone	C	0
2	Ru_1	Acetone	Pt	0
3	Ru_1	Acetone	Cu	12
4	Ru_1	Acetone	Zn	0
5	Ru_1	1:1 DCM:Acetone	Cu	46
6	Ru_1	3:1 DCM:Acetone	Cu	70
7	Ru_1	DCM	Cu	63
8	**Ru_2**	**3:1 DCM:Acetone**	**Cu**	**97**
9[c]	Ru_2	3:1 DCM:Acetone	Cu	92
10[d]	Ru_2	3:1 DCM:Acetone	Cu	0
11[e]	Ru_2	3:1 DCM:Acetone	Cu	trace

Ru Catalysts



$RuCl_2(SIMes)(I^iPrMe)(Ind)$

(Ru_1)



$RuCl_2(CHPh)(SIMes)_2$

(Ru_2)

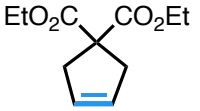
[a]All optimization reactions were conducted on a 0.1 mmol scale
[b]Yield by ^1H NMR using mesitylene as internal standard
[c]Ran for 5 minutes
[d]Ran without an applied current and without electrodes
[e]Ran without an applied current

Product Synthesis and Characterization Data

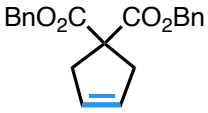
Representative Procedure for Ring Closing Metathesis

To a 1.5 dr vial equipped with a magnetic stir bar, 77.5 mg of nBu_4NPF_6 is added (0.2 mmol). The vial is taken to a N_2 glovebox, where 3.5 mg of $RuCl_2(CHPh)(SIMes)_2$ (0.004 mmol, 2 mol%) is added. 0.2 mmol of the substrate is pipetted into the vial, along with 1.5 mL of anhydrous dichloromethane and 0.5 mL of anhydrous acetone. The vial is sealed with a Teflon cap equipped with a copper anode and graphite cathode. Once removed from the glovebox, the vial is connected to the power supply, and a constant current of 1 mA is applied for 2 h. After 2 h, the reaction mixture is concentrated under vacuum, then 27.8 µL of mesitylene (0.2 mmol) was added as an internal standard. The reaction mixture was stirred before an aliquot was removed and analyzed by ^{1}H NMR. The desired product was purified by flash column chromatography on silica gel (80:20 Hexanes:EtOAc, visualized by I_2 or $KMnO_4$).

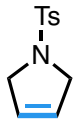
Compounds with only NMR yields reported were not isolated due to low yields or poor starting material/product separation by TLC.



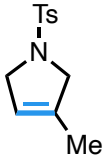
diethyl cyclopent-3-ene-1,1-dicarboxylate. 98% yield (NMR). Characterization data consistent with previously reported data.[1]



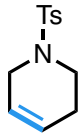
dibenzyl cyclopent-3-ene-1,1-dicarboxylate. 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3933 – 7.2362 (m, 10H), 5.6372 (s, 2H), 5.1559 (s, 4H), 3.0816 (s, 4H). Characterization data consistent with previously reported data.[2]



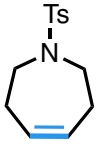
1-tosyl-2,5-dihydro-1H-pyrrole. 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7839 – 7.6812 (m, 2H), 7.3801 – 7.3060 (m, 2H), 5.6768 (s, 2H), 4.1448 (s, 4H), 2.4490 (s, 3H). Characterization data consistent with previously reported data.[3]



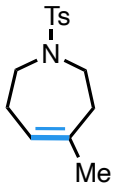
3-methyl-1-tosyl-2,5-dihydro-1H-pyrrole. 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7783 – 7.7019 (m, 2H), 7.3776 – 7.3048 (m, 2H), 5.2698 (h, J = 1.8 Hz, 1H), 4.0942 (dh, J = 6.4, 2.0 Hz, 2H), 3.9885 (dddq, J = 5.3, 3.1, 2.2, 1.1 Hz, 2H), 2.4484 (s, 3H), 1.6824 (tt, J = 2.1, 1.0 Hz, 3H). Characterization data consistent with previously reported data.[4]



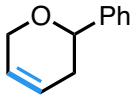
1-tosyl-1,2,3,6-tetrahydropyridine. 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7343 – 7.6582 (m, 2H), 7.3761 – 7.3031 (m, 2H), 5.7700 (dtd, J = 9.9, 3.9, 1.9 Hz, 1H), 5.6316 (dtt, J = 10.2, 3.3, 2.0 Hz, 1H), 3.6374 – 3.5646 (m, 2H), 3.1994 (t, J = 5.7 Hz, 2H), 2.4493 (s, 3H), 2.2300 (dddd, J = 7.7, 3.8, 2.9, 2.0 Hz, 2H). Characterization data consistent with previously reported data.[5]



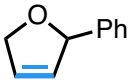
1-tosyl-2,3,6,7-tetrahydro-1H-azepine. 85% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.7128 – 7.6471 (m, 2H), 7.3612 (d, J = 8.0 Hz, 2H), 5.7865 (t, J = 3.4 Hz, 2H), 3.3201 – 3.2488 (m, 4H), 2.4558 (s, 3H), 2.3289 (q, J = 4.4 Hz, 4H). Characterization data consistent with previously reported data.[6]



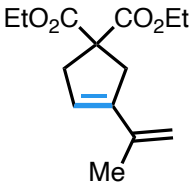
4-methyl-1-tosyl-2,3,6,7-tetrahydro-1H-azepine. 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6813 (d, *J* = 7.9 Hz, 2H), 7.3151 (d, *J* = 7.9 Hz, 2H), 5.4990 (s, 1H), 3.2954 (td, *J* = 8.3, 5.0 Hz, 4H), 2.4426 (s, 3H), 2.2578 (dq, *J* = 11.1, 5.4 Hz, 4H), 1.7013 (s, 3H). Characterization data consistent with previously reported data.[7]



2-phenyl-3,6-dihydro-2H-pyran. 69% yield (NMR). Characterization data consistent with previously reported data.[8]



2-phenyl-2,5-dihydrofuran. 63% yield. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.4269 – 7.2679 (m, 5H), 6.0840 (ddt, *J* = 6.2, 2.4, 1.6 Hz, 1H), 5.9299 (dtd, *J* = 6.2, 2.5, 1.6 Hz, 1H), 5.8003 (ddt, *J* = 6.1, 4.0, 2.0 Hz, 1H), 4.8842 (dddd, *J* = 12.8, 6.1, 2.4, 1.6 Hz, 1H), 4.7756 (dddd, *J* = 12.8, 4.1, 2.5, 1.6 Hz, 1H). Characterization data consistent with previously reported data.[9]

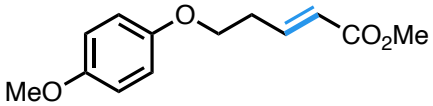


diethyl 3-(prop-1-en-2-yl)cyclopent-3-ene-1,1-dicarboxylate. 39% yield (NMR). Characterization data consistent with previously reported data.[10]

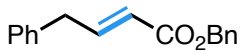
Representative Procedure for Cross Metathesis

To a 1.5 dr vial equipped with a stir bar, 77.5 mg of nBu_4NPF_6 is added (0.2 mmol). The vial is taken to a N_2 glovebox, where 3.5 mg of $RuCl_2(CHPh)(SIMes)_2$ (0.004 mmol, 2 mol%) is added. 0.2 mmol of the substrate and 0.4 mmol of the other are pipetted into the vial, along with 1.5 mL of anhydrous dichloromethane and 0.5 mL of anhydrous acetone. The vial is sealed with a septum cap equipped with a copper anode and graphite cathode. Once removed from the glovebox, the vial is connected to the power supply and allowed to stir at a constant current of 1 mA for 2 h. After 2 h, the reaction mixture is concentrated under vacuum, then 27.8 µL of mesitylene (0.2 mmol) was added as an internal standard. The reaction mixture was stirred before an aliquot was removed and analyzed by ^{1}H NMR. The desired product was purified by flash column chromatography on silica gel (80:20 Hexanes:EtOAc, visualized by I_2 or $KMnO_4$).

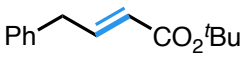
Compounds with only NMR yields reported were not isolated due to low yields or poor starting material/product separation by TLC.



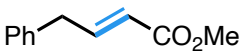
methyl (E)-5-(4-methoxyphenoxy)pent-2-enoate. 54% yield (NMR), 26% (isolated). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.0670 (dt, *J* = 15.7, 6.9 Hz, 1H), 6.8530 (s, 4H), 5.9833 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.0529 (t, *J* = 6.3 Hz, 2H), 3.7927 (s, 3H), 3.7626 (s, 3H), 2.6865 (qd, *J* = 6.5, 1.6 Hz, 2H). Characterization data consistent with previously reported data.[11]



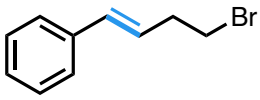
benzyl (E)-4-phenylbut-2-enoate. 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3930 – 7.3011 (m, 7H), 7.2746 (d, *J* = 7.3 Hz, 1H), 7.2499 – 7.1331 (m, 3H), 5.9292 – 5.8828 (m, 1H), 5.1991 (s, 2H), 3.5559 (dd, *J* = 6.7, 1.7 Hz, 2H). Characterization data consistent with previously reported data.[12]



tert-butyl (E)-4-phenylbut-2-enoate. 40% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.3409 (d, *J* = 14.9 Hz, 1H), 7.3030 – 7.1793 (m, 4H), 7.0169 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.7562 (dt, *J* = 15.5, 1.7 Hz, 1H), 3.5189 (dd, *J* = 6.8, 1.6 Hz, 2H), 1.4936 (s, 9H). Characterization data consistent with previously reported data.[13]



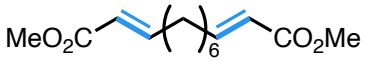
methyl (E)-4-phenylbut-2-enoate. 37% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.3608 – 7.1848 (m, 5H), 7.1329 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.8450 (dt, *J* = 15.6, 1.7 Hz, 1H), 3.7414 (s, 3H), 3.5476 (dd, *J* = 6.8, 1.7 Hz, 2H). Characterization data consistent with previously reported data.[14]



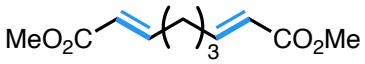
(E)-(4-bromobut-1-en-1-yl)benzene. 17% yield (NMR). Characterization data consistent with previously reported data.[15]

Representative Procedure for Ring Opening Cross Metathesis

To a 1.5 dr vial equipped with a stir bar, 77.5 mg of nBu_4NPF_6 is added (0.2 mmol). The vial is taken to a N_2 glovebox, where 3.5 mg of $RuCl_2(CHPh)(SIMes)_2$ (0.004 mmol, 2 mol%) is added. 0.2 mmol of the substrate and 0.4 mmol of the other are pipetted into the vial, along with 1.5 mL of anhydrous dichloromethane and 0.5 mL of anhydrous acetone. The vial is sealed with a septum cap equipped with a copper anode and graphite cathode. Once removed from the glovebox, the vial is connected to the power supply and allowed to stir at a constant current of 1 mA for 2 h. After 2 h, the reaction mixture is concentrated under vacuum, then 27.8 µL of mesitylene (0.2 mmol) was added as an internal standard. The reaction mixture was stirred before an aliquot was removed and analyzed by ^{1}H NMR. The desired product was purified by flash column chromatography on silica gel (80:20 Hexanes:EtOAc, visualized by I_2 or $KMnO_4$).



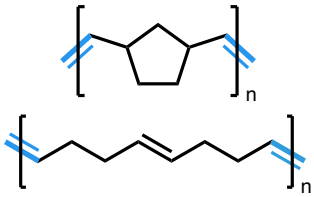
Dimethyl (2E,10E)-dodeca-2,10-dienedioate. 29% yield (NMR). Characterization data consistent with previously reported data.[2]



dimethyl (2E,7E)-nona-2,7-dienedioate. 25% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.9385 (dt, *J* = 15.8, 7.0 Hz, 2H), 5.8998 – 5.7808 (m, 2H), 3.7317 (s, 6H), 2.2380 (q, *J* = 7.3 Hz, 4H), 1.6725 – 1.6125 (m, 2H). Characterization data consistent with previously reported data.[16]

Representative Procedure for Ring Opening Metathesis Polymerization

To a 1.5 dr vial equipped with a stir bar, 77.5 mg of nBu_4NPF_6 is added (0.2 mmol). The vial is taken to a N_2 glovebox, where 3.5 mg of $RuCl_2(CHPh)(SIMes)_2$ (0.00004 mmol, 0.02 mol%) is added. 0.2 mmol of the substrate is pipetted into the vial, along with 1.5 mL of anhydrous dichloromethane and 0.5 mL of anhydrous acetone. The vial is sealed with a septum cap equipped with a copper anode and graphite cathode. Once removed from the glovebox, the vial is connected to the power supply and allowed to stir at a constant current of 1 mA for 30 min. After 30 min, the reaction mixture is concentrated under vacuum, then 27.8 µL of mesitylene (0.2 mmol) was added as an internal standard. The reaction mixture was stirred before an aliquot was removed and analyzed by ^1H NMR. The resulting polymer was washed thoroughly with methanol and DCM, then dried under vacuum.



Poly(bicyclo[2.2.1]hept-2-ene). Conversion: 59%. Polymer too insoluble for analysis.

Poly(1,5-cyclooctadiene). Conversion: 15%. MW 2630. PDI = 1.34

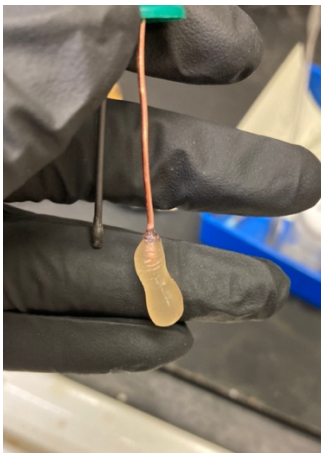


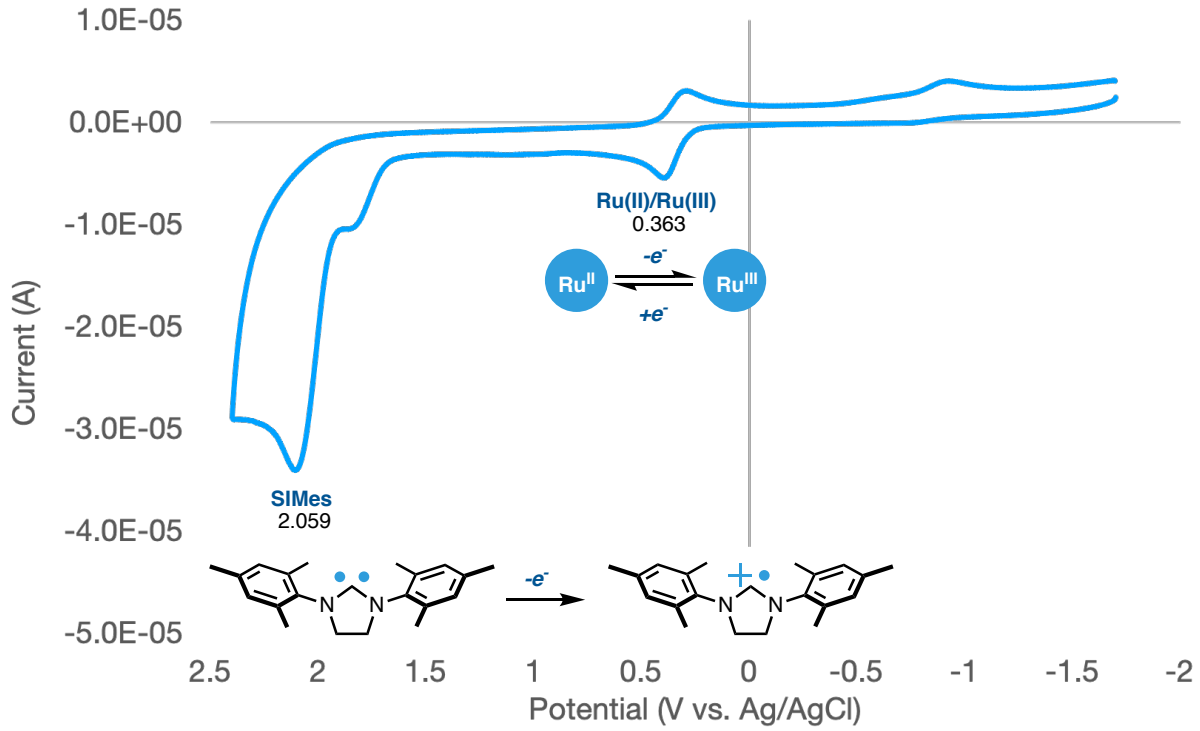
Figure S2: Polymer obtained from the ROMP of bicyclo[2.2.1]hept-2-ene.

Electrochemical Data

Cyclic voltammetry studies were run using a glassy carbon electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. For all studies, tetrabutylammonium hexafluorophosphate was used as the electrolyte in a solution of anhydrous dichloromethane while argon was bubbled through the solution prior to data collection. Sweeps of negative (reductive) and positive (oxidative) on first pass were run.

To an electrochemical cell with a stir bar, 77.5 mg (0.2 mmol) of nBu_4NPF_6 is added. The cell is transferred to a glovebox, where 5.00 mg (0.006 mmol) of $(RuCl_2)(CHPh)(SIMes)_2$ is added, along with 2 mL dry dichloromethane. The electrodes are added, and the cell is bubbled with Ar for 10 minutes with stirring through a bubbler containing dry dichloromethane.

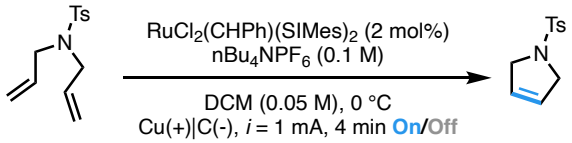
$(RuCl_2)(CHPh)(SIMes)_2$ in DCM

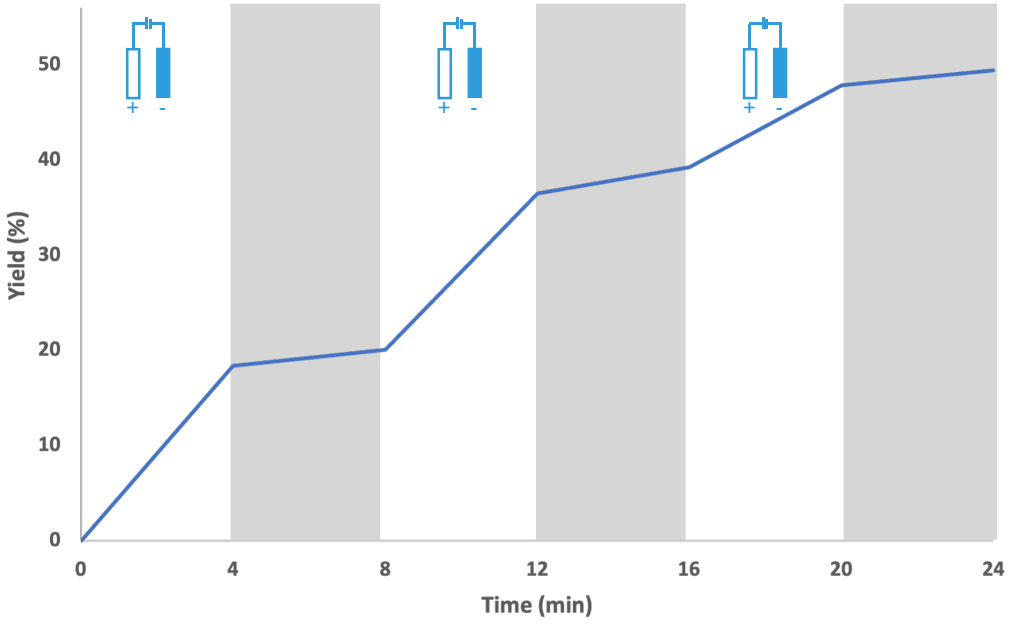


Temporal Control Experiment

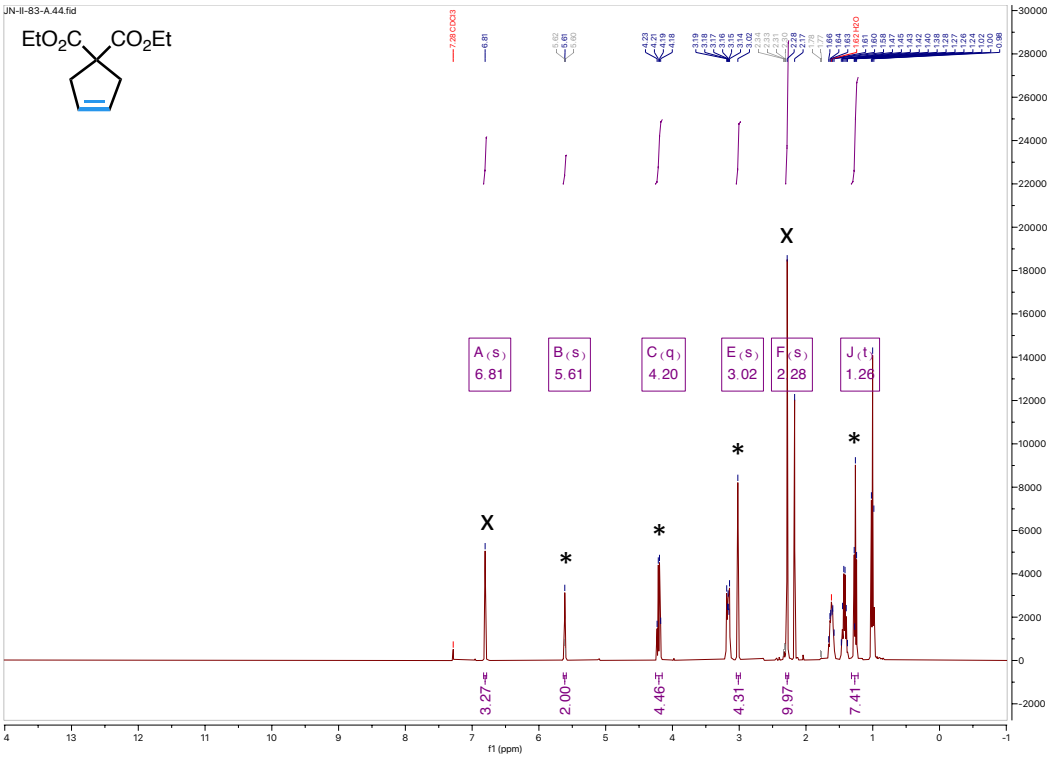
To a scintillation vial, 387.4 mg nBu_4NPF_6 (1 mmol) is added. The vial is brought into an N_2 glovebox, where 8.8 mg $RuCl_2(CHPh)(SIMes)_2$ (0.01 mmol, 2 mol%), 125.0 μL diallyl tosylamide (0.5 mmol, 1 equiv.), 69.6 μL mesitylene (0.5 mmol, 1 equiv.), and 10 mL d^2-DCM are added, in that order. The vial is sealed with a septum into which a graphite cathode and a copper anode are inserted. The vial is then placed into a 0°C ice/water bath, and an N_2-filled balloon is inserted through the septum. After connecting the electrodes to the power supply, the vial is stirred while undergoing alternating 4-min periods of applied current (1 mA) and no current. Aliquots are taken at the end of each period, where 100 μL is placed into an NMR tube and is immediately quenched with 100 μL of a 0.04 M solution of ethyl vinyl ether in d^2-DCM. The tube is filled with an additional 300 μL d^2-DCM and placed into a -78 °C dry ice/acetone bath. NMR analysis is conducted immediately after all the aliquots are taken.

Time (min)	Int	[Yield]	% Yield	% Yield/min
0	0	0	0	--
4	0.081749	18.393525	18	4.598
8	0.089249	20.081025	20	0.422
12	0.162281	36.513225	35	4.108
16	0.174489	39.260025	37	0.687
20	0.212897	47.901825	48	2.160
24	0.219724	49.437900	49	0.384

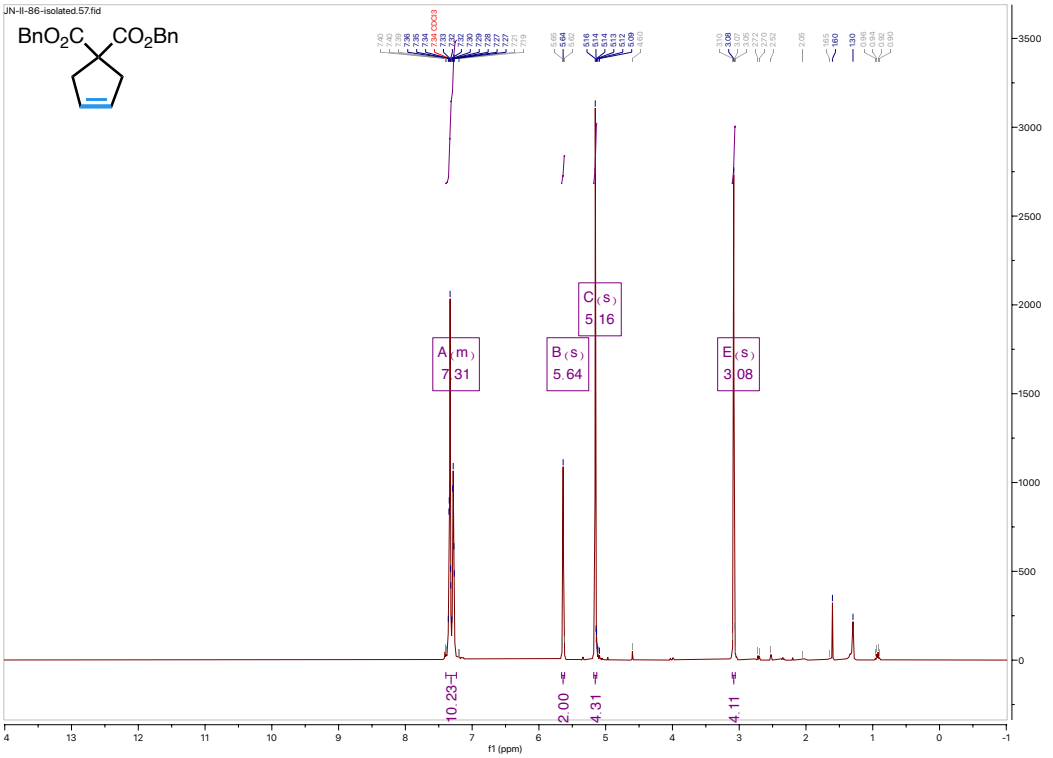


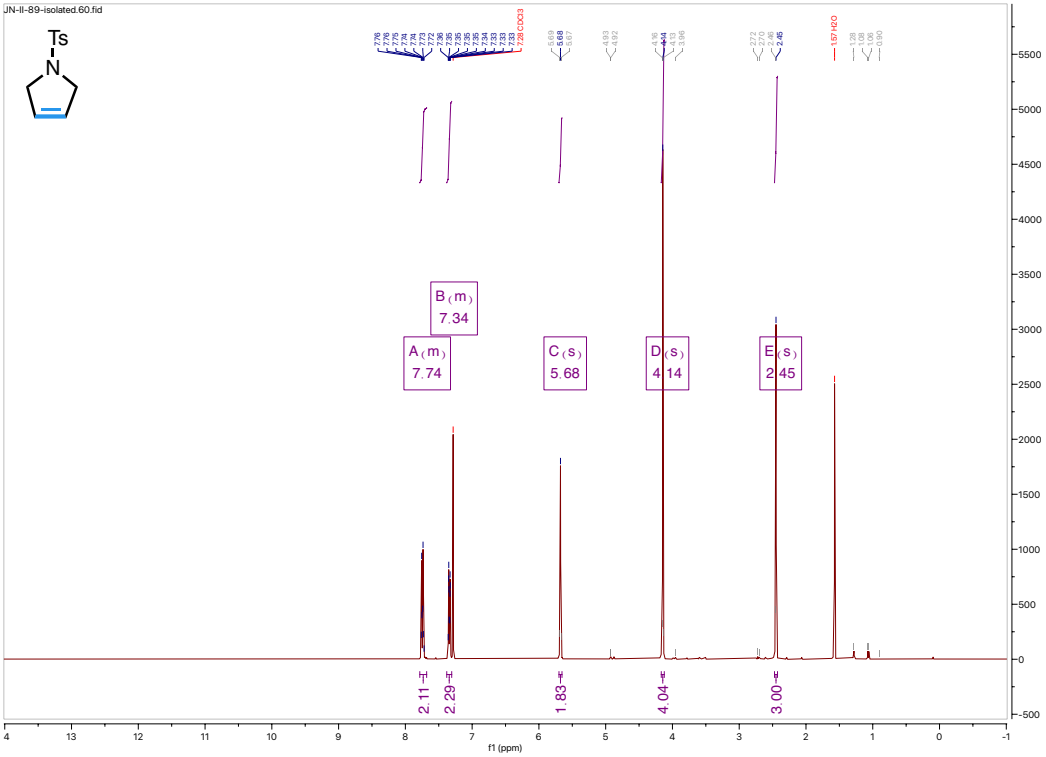


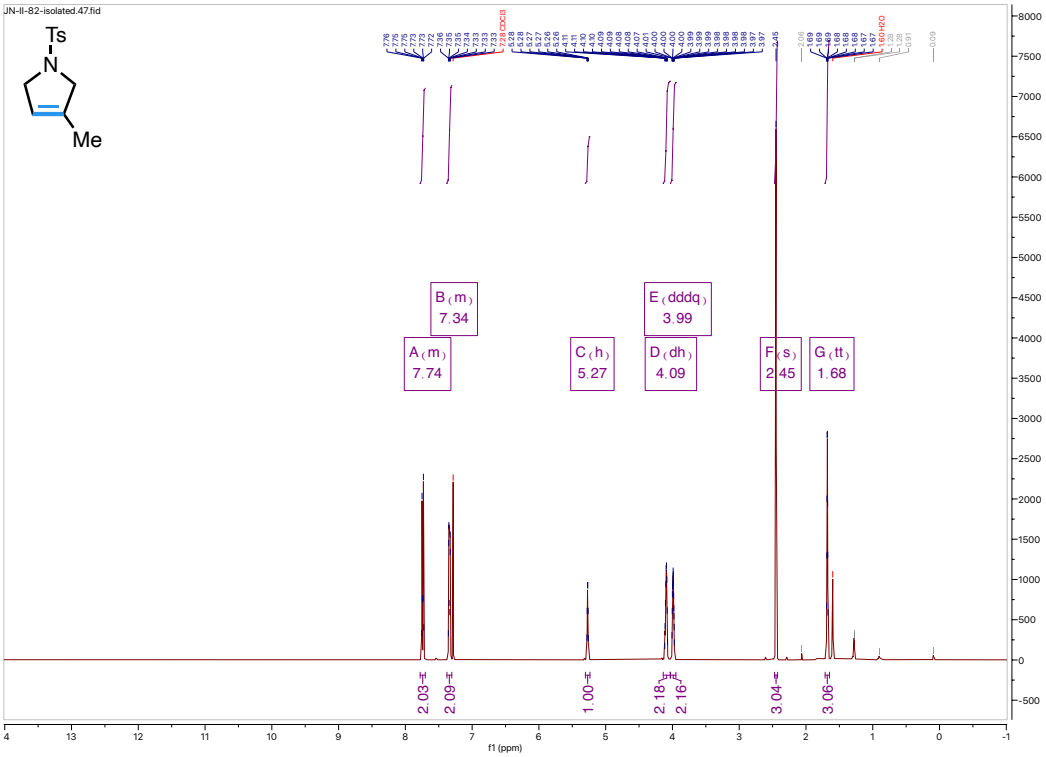
^{1}H NMR Spectra

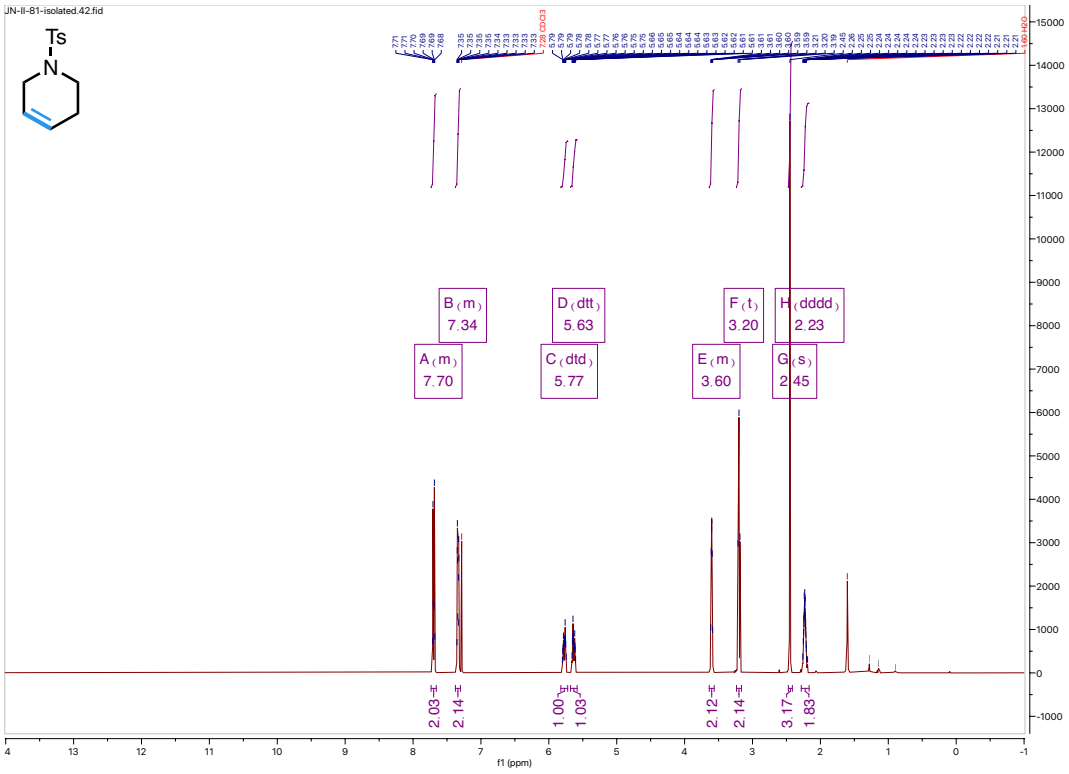


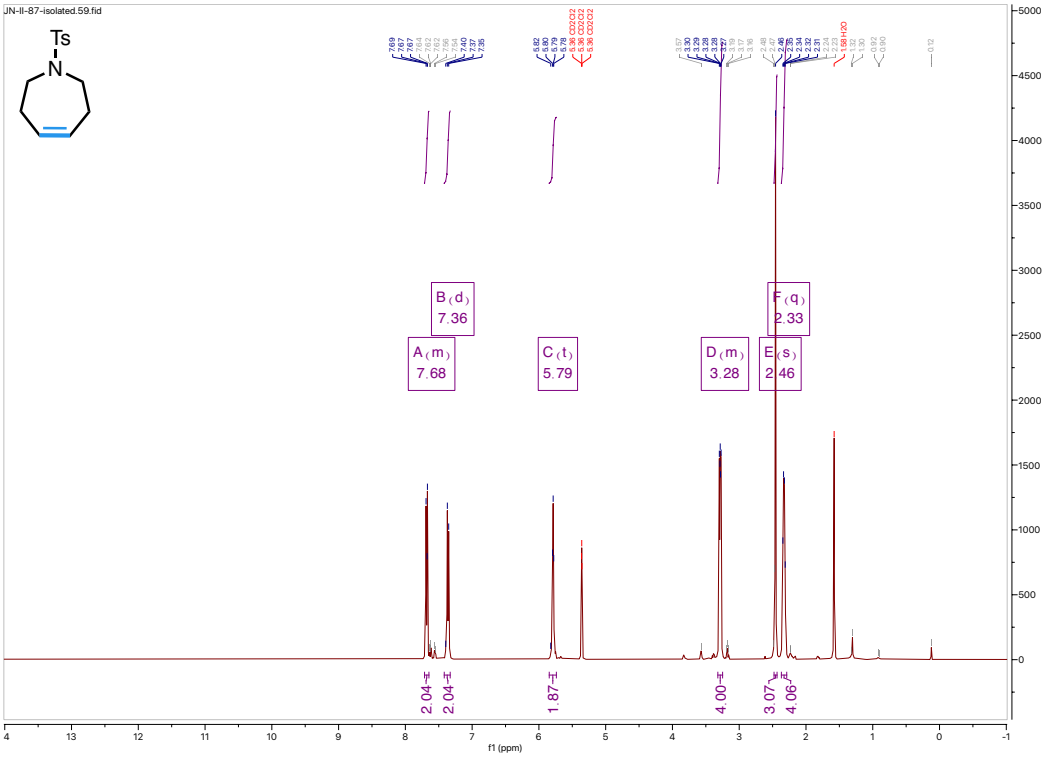
* = product x = mesitylene (internal standard)

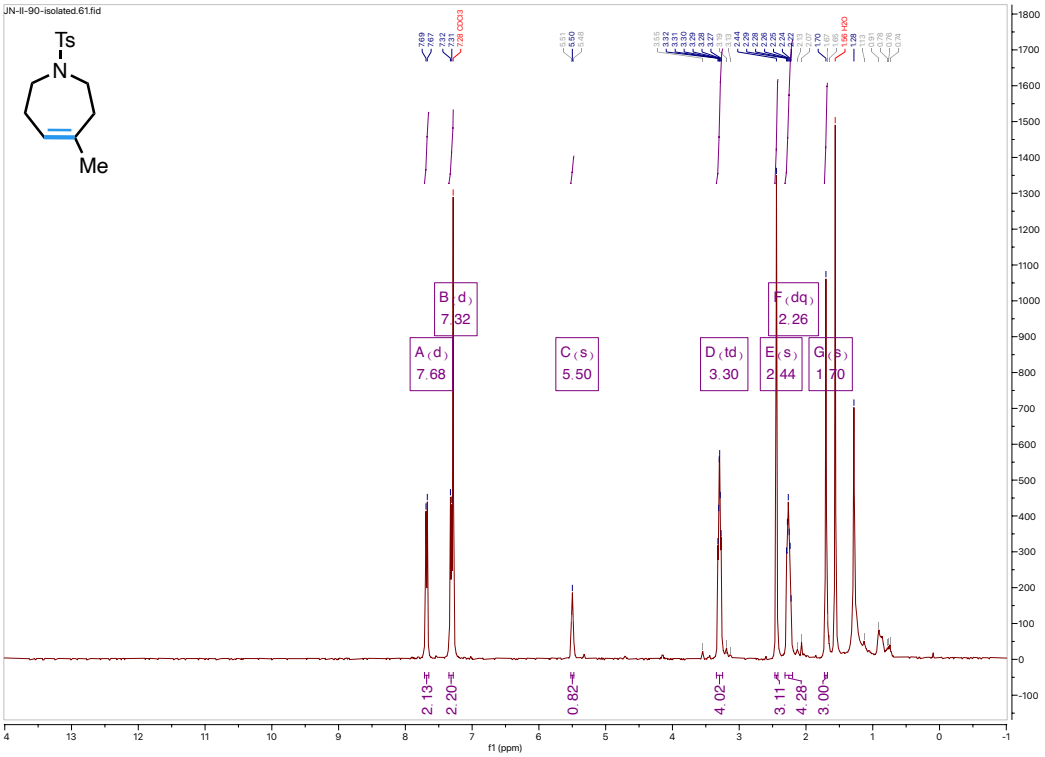


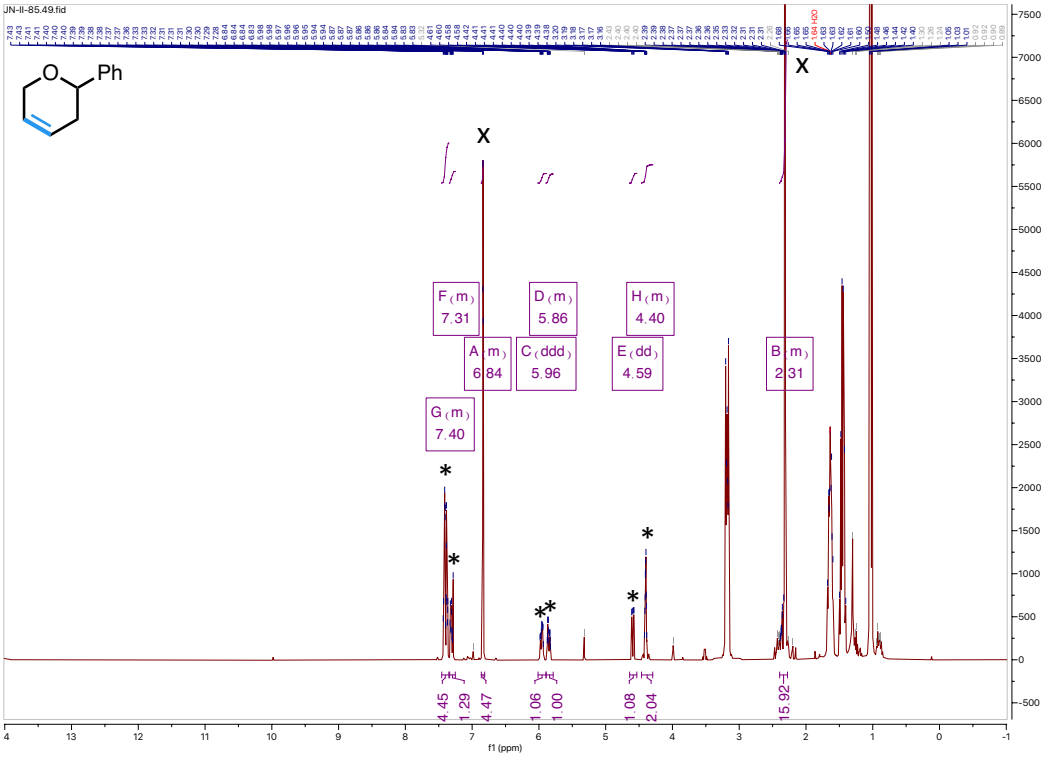

JN-II-89-isolated.60.fid
Ts
N
B (m) 7.34
A (m) 7.74
C (s) 5.68
D (s) 4.14
E (s) 2.45
2.11
2.29
1.83
4.04
3.00
f1 (ppm)


JN-II-82-isolated.47.fid
Ts
N
Me
B (m) 7.34
A (m) 7.74
C (h) 5.27
E (dddq) 3.99
D (dh) 4.09
F (s) 2.45
G (tt) 1.68
2.03
2.09
1.00
2.18
2.16
3.04
3.06
f1 (ppm)

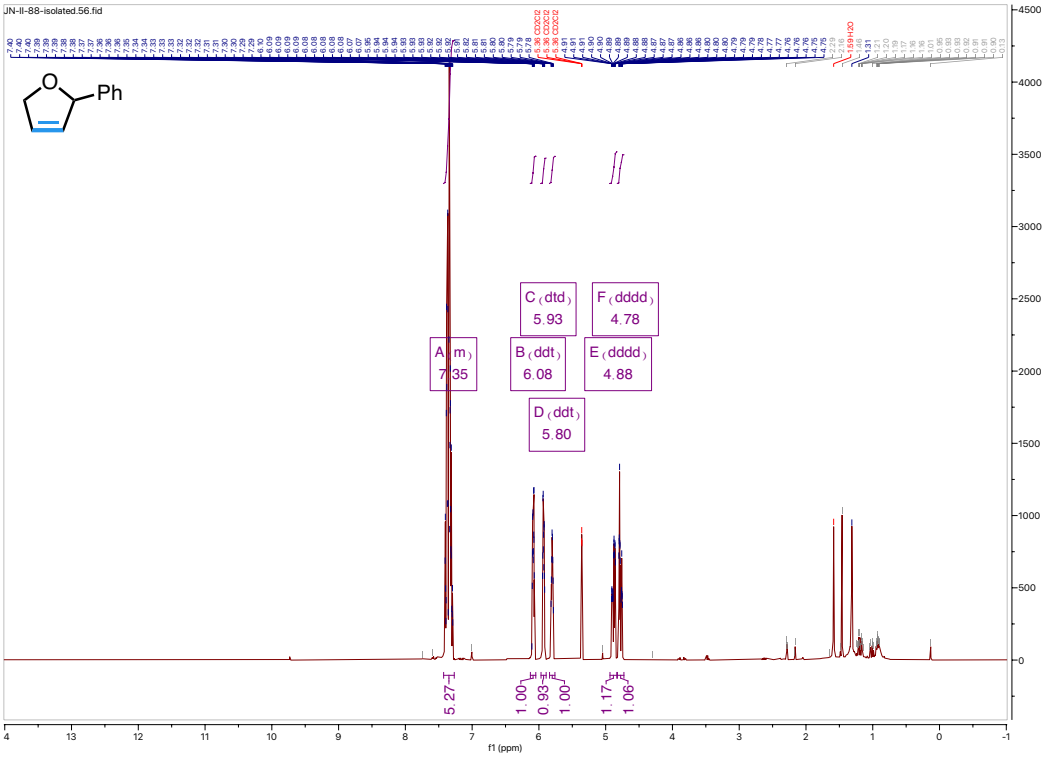

JN-II-81-isolated.42.fid
Ts
N
B (m) 7.34
D (dtt) 5.63
F (t) 3.20
H (dddd) 2.23
A (m) 7.70
C (dtd) 5.77
E (m) 3.60
G (s) 2.45
2.03
2.14
1.00
1.03
2.12
2.14
3.17
1.83
f1 (ppm)

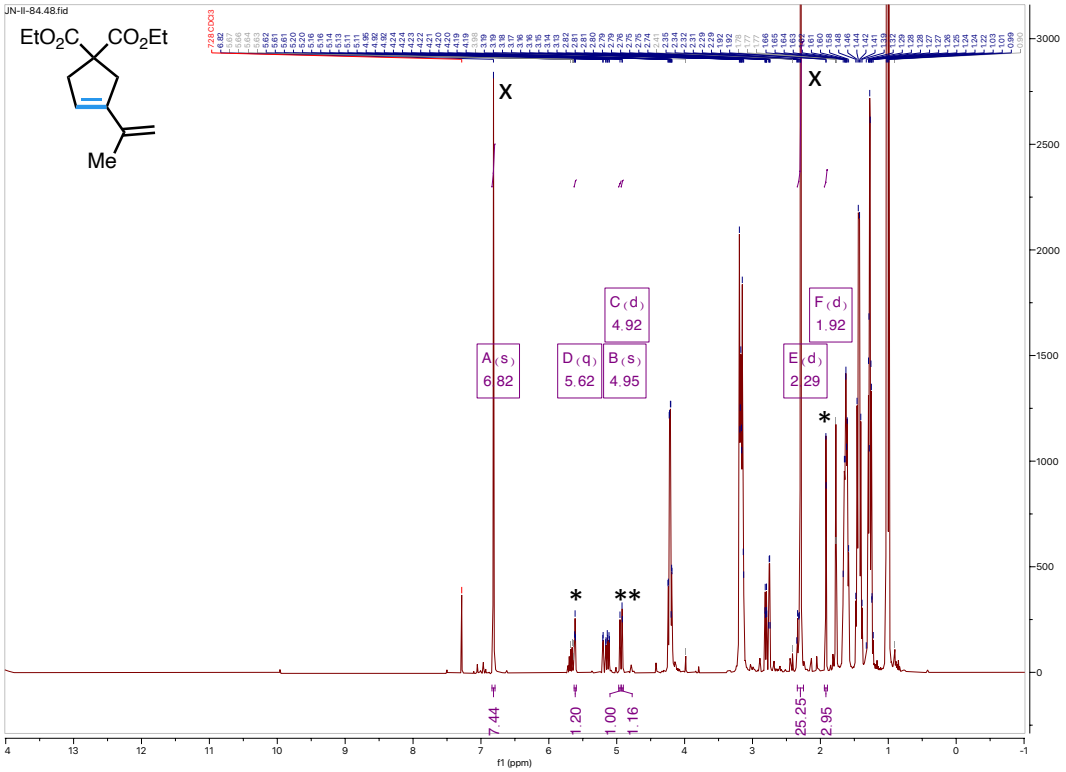

JN-II-87-isolated.59.fid
Ts
N
B (d) 7.36
F (q) 2.33
A (m) 7.68
C (t) 5.79
D (m) 3.28
E (s) 2.46
2.04
2.04
1.87
4.00
3.07
4.06
f1 (ppm)



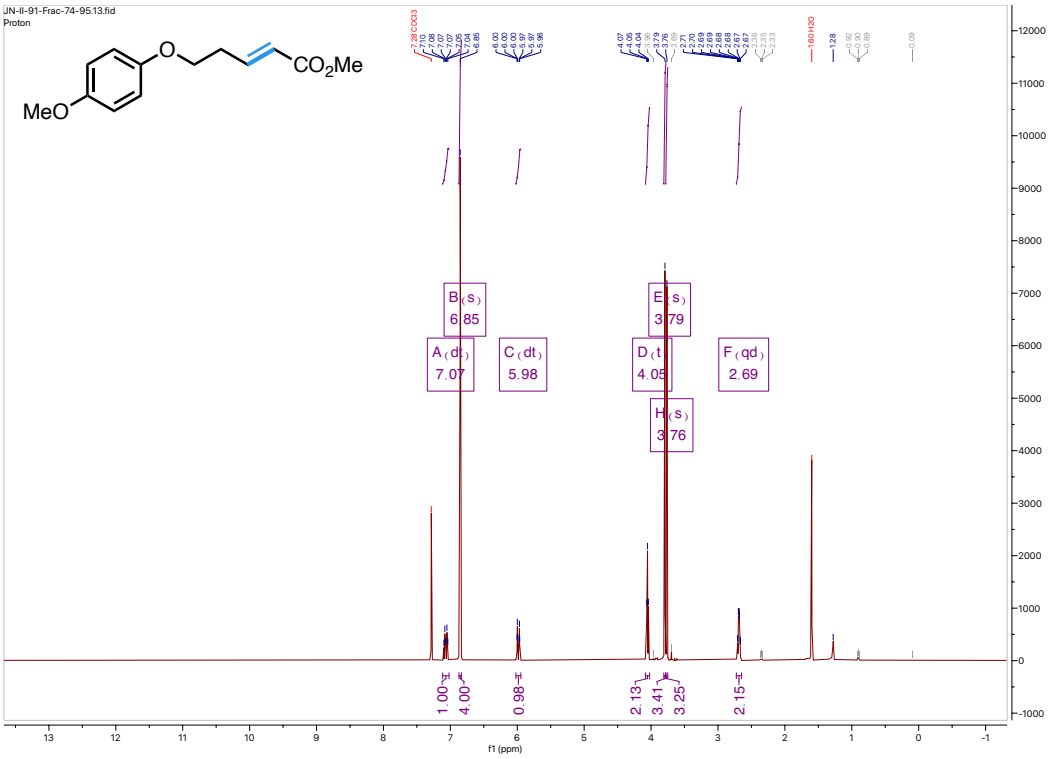


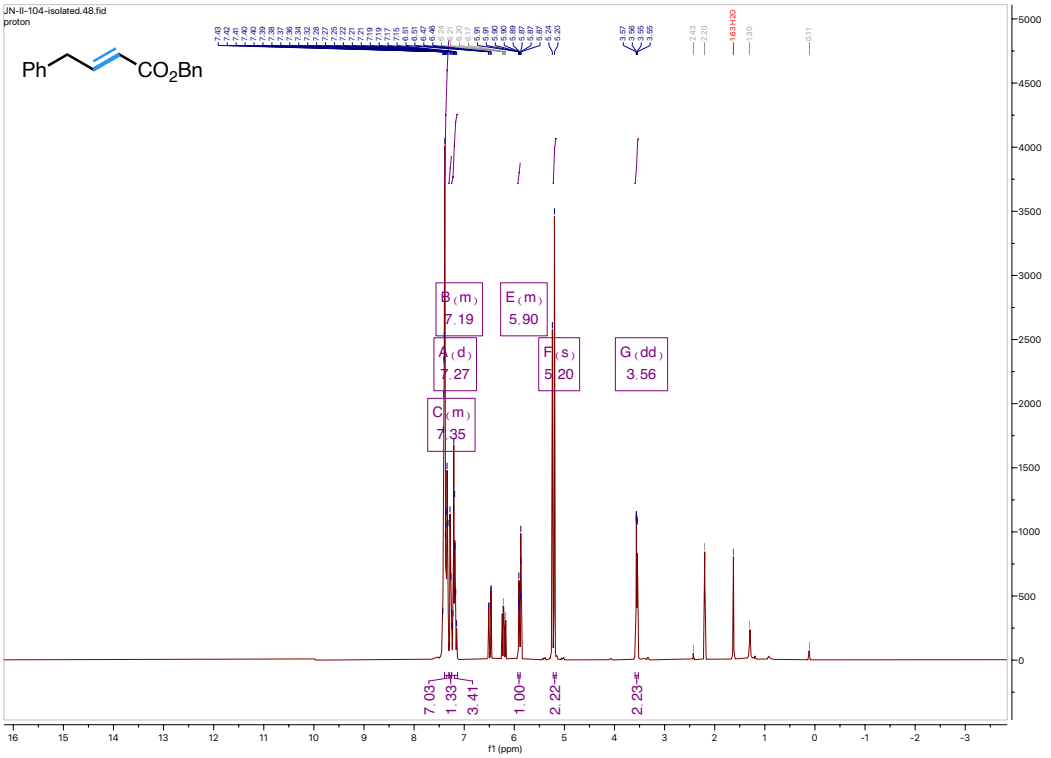
* = product x = mesitylene (internal standard)

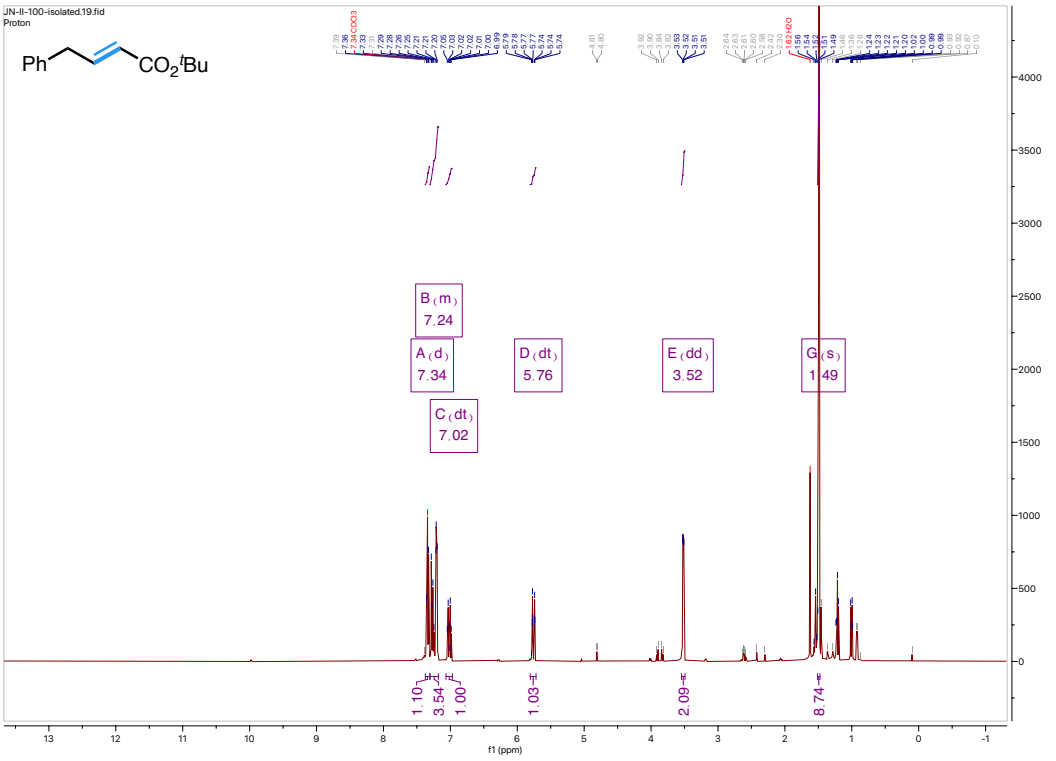


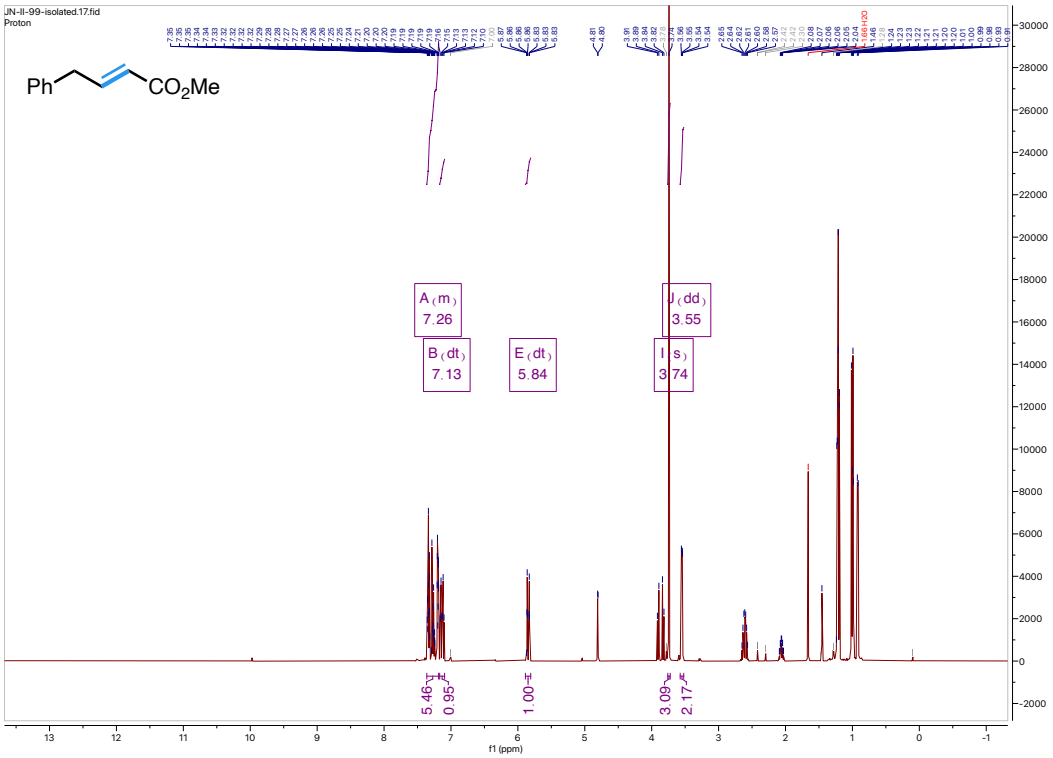


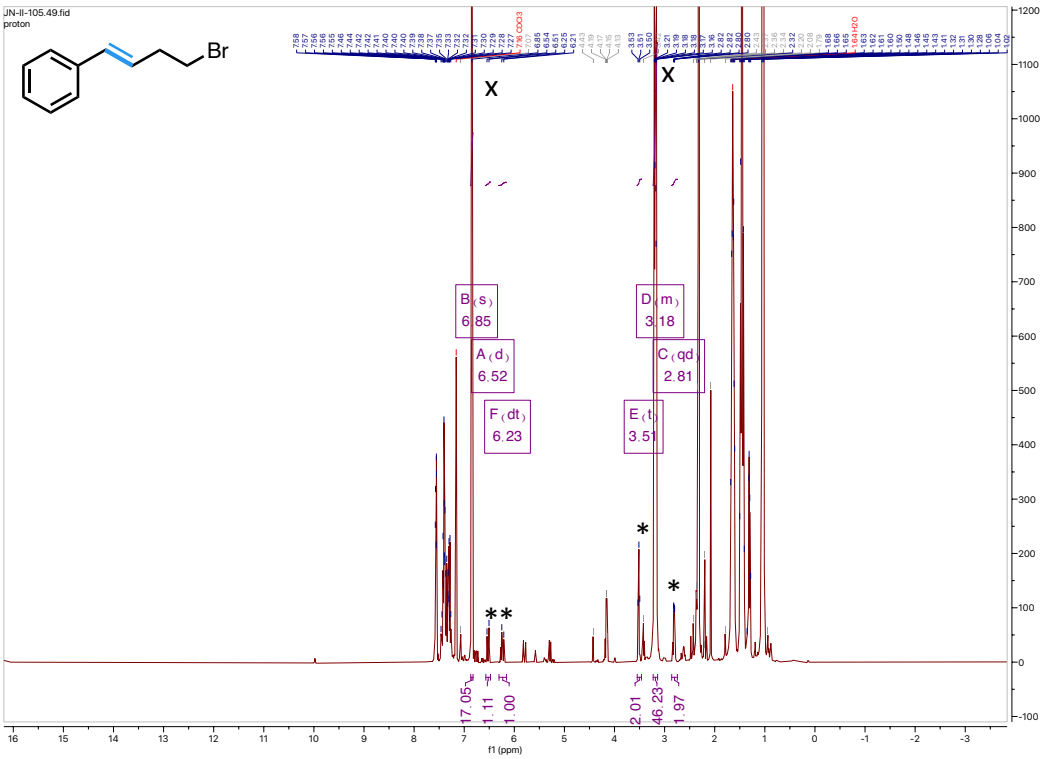
* = product x = mesitylene (internal standard)


JN-II-91-Frac-74-95.13.fid
Proton
MeO
O
CO2Me
B (s) 6.85
A (dt) 7.07
C (dt) 5.98
E (s) 3.79
D (t) 4.05
F (qd) 2.69
H (s) 3.76
1.00
4.00
0.98
2.13
3.41
3.25
2.15
f1 (ppm)

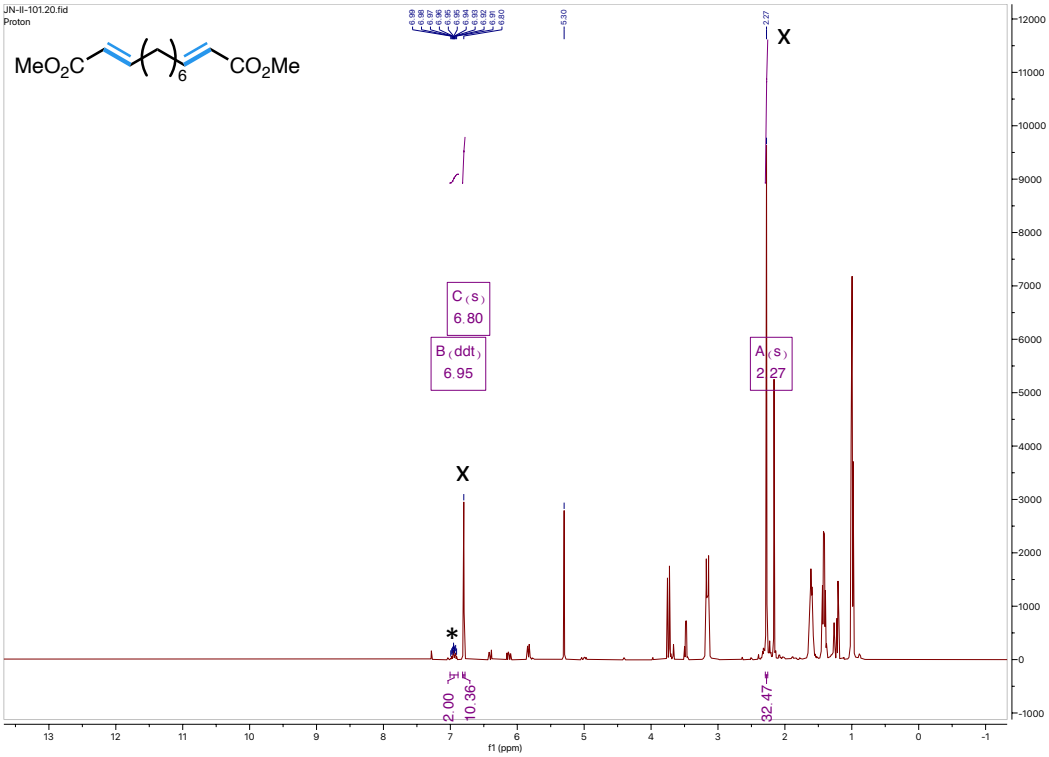

JN-II-104-isolated.48.fid
proton
Ph
CO2Bn
B (m) 7.19
E (m) 5.90
A (d) 7.27
F (s) 5.20
G (dd) 3.56
C (m) 7.35
7.03
1.33
3.41
1.00
2.22
2.23
f1 (ppm)


JN-II-100-isolated.19.fid
Proton
Ph
CO2tBu
B (m) 7.24
A (d) 7.34
D (dt) 5.76
E (dd) 3.52
G (s) 1.49
C (dt) 7.02
1.10
3.54
1.00
1.03
2.09
8.74
f1 (ppm)

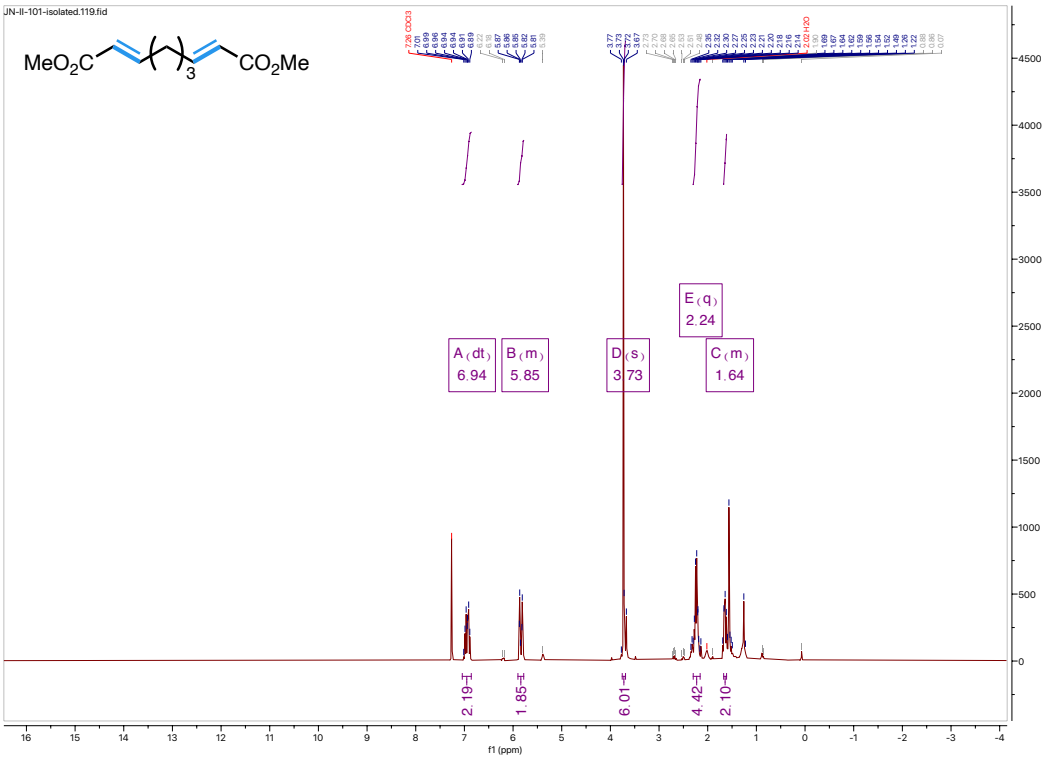

JN-II-99-isolated.17.fid
Proton
Ph
CO2Me
A (m) 7.26
J (dd) 3.55
B (dt) 7.13
E (dt) 5.84
I (s) 3.74
5.46
0.95
1.00
3.09
2.17
f1 (ppm)

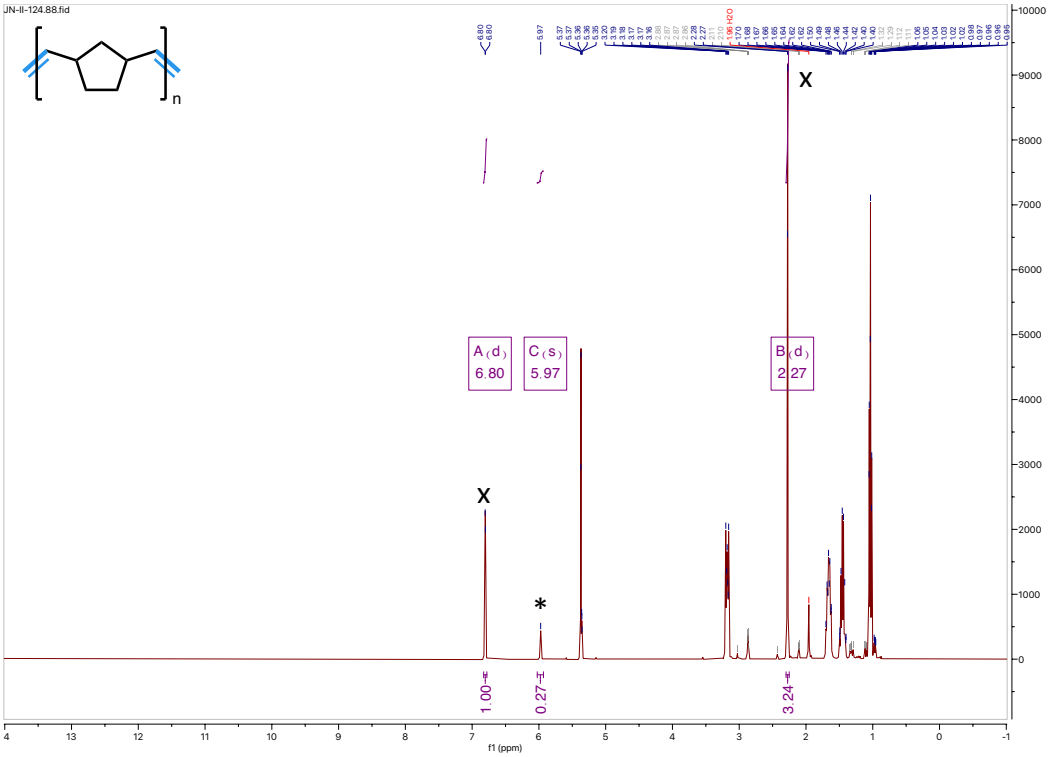


* = product x = mesitylene (internal standard)

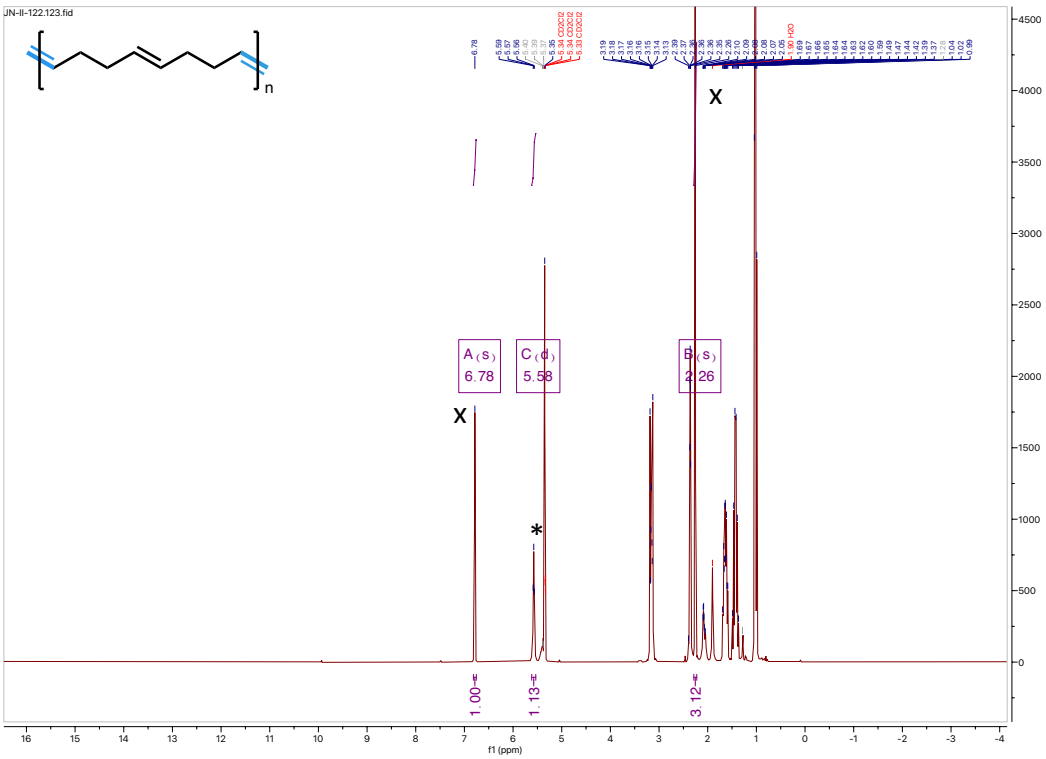


* = product x = mesitylene (internal standard)





* = substrate x = mesitylene (internal standard)



* = substrate x = mesitylene (internal standard)

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