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## Supporting Information

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## 1. General information

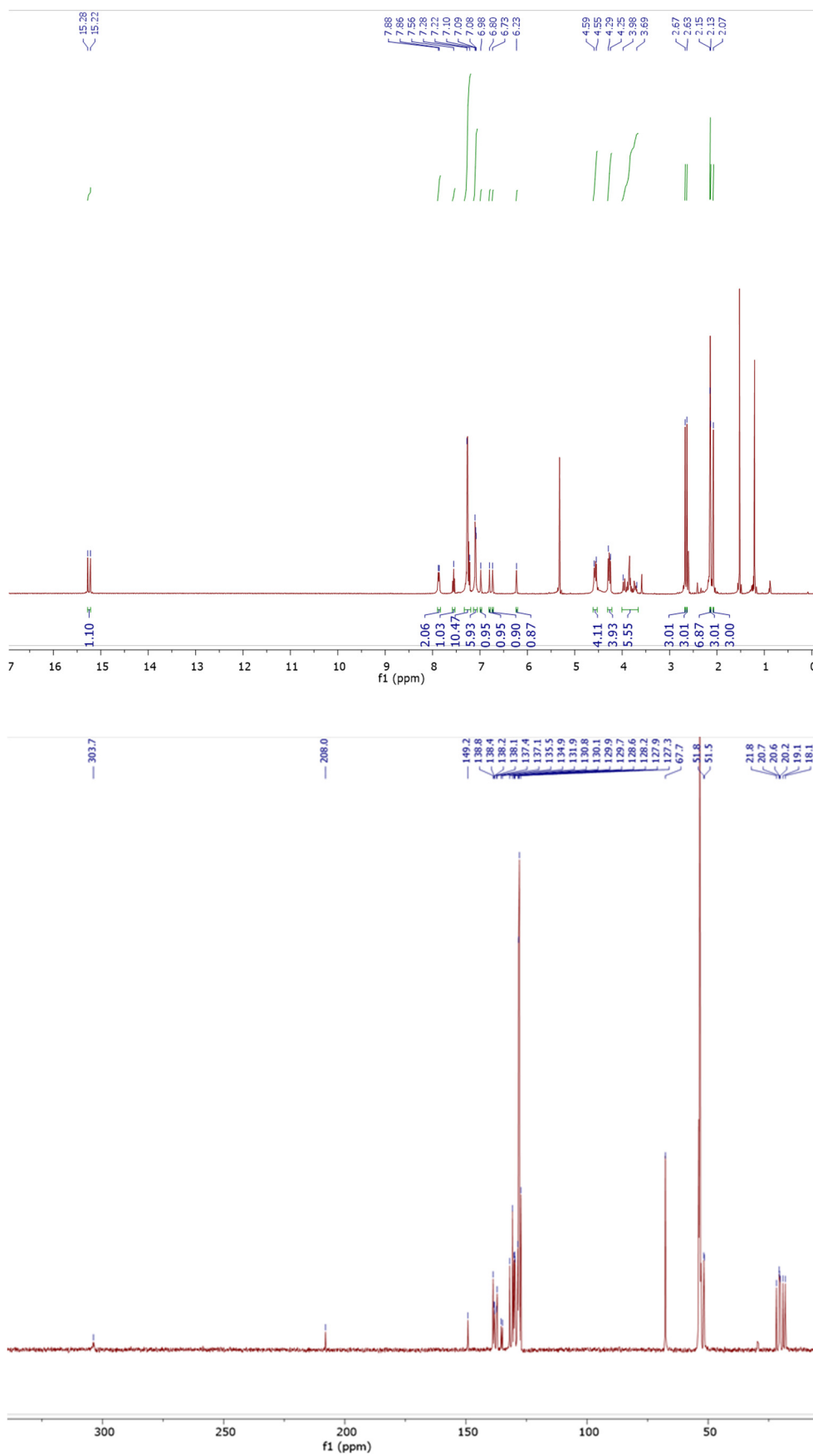
All commercially available solvents and reagents were of reagent grade and used without further purification unless otherwise stated. Purification by column chromatography was performed on Fluka silica gel 60 (40–60  $\mu\text{m}$ ). TLC analyses were performed using Merck pre-coated silica gel (0.2 mm) aluminum sheets.

All nuclear magnetic resonance (NMR) spectra were acquired on Bruker DPX 400 or DPX 500 instruments; chemical shifts, given in ppm, are relative to  $\text{Me}_4\text{Si}$  as the internal standard or the residual solvent peak. HRMS analyses were done on a Q Exactive<sup>TM</sup> Focus by Thermo Fisher with an ESI probe.

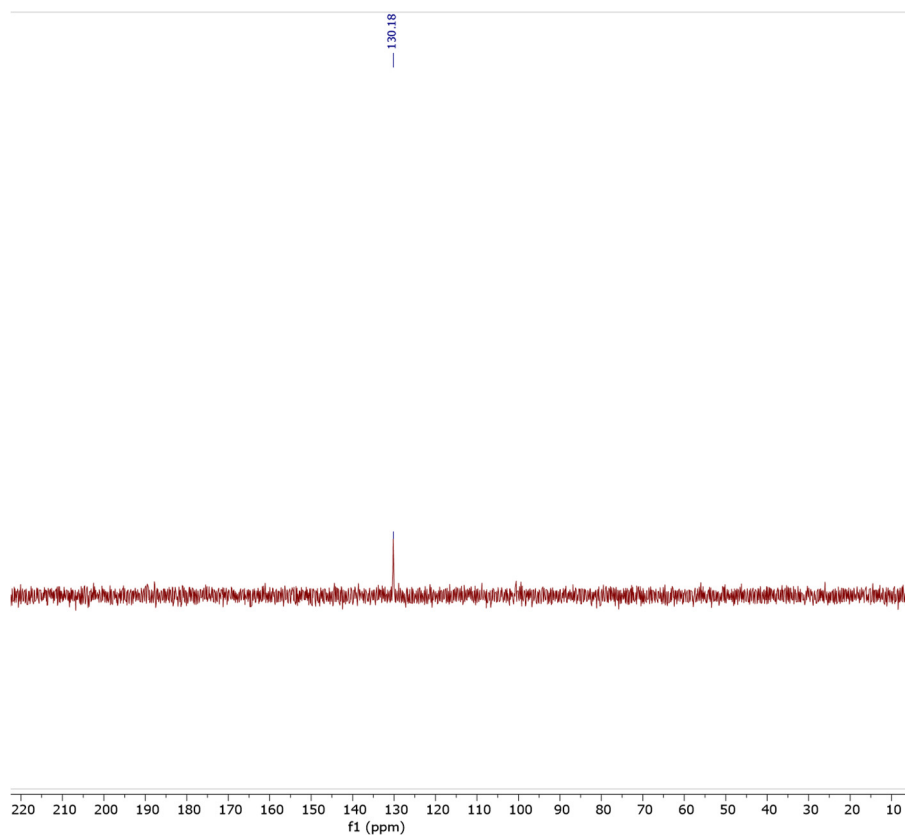
Irradiation experiments were carried out using a Luzchem LZC-ORG photoreactor and were carried out in 5 mm NMR tubes at room temperature.

X-ray experimental data: Single crystals of *cis*-**Ru-Phos-Br<sub>2</sub>** and *cis*-**Ru-Phos-I<sub>2</sub>** were obtained by slow diffusion of pentane into dichloromethane solution of the complexes, respectively, at 5 °C.

## 2. Copies of NMR and HRMS spectra for catalysts

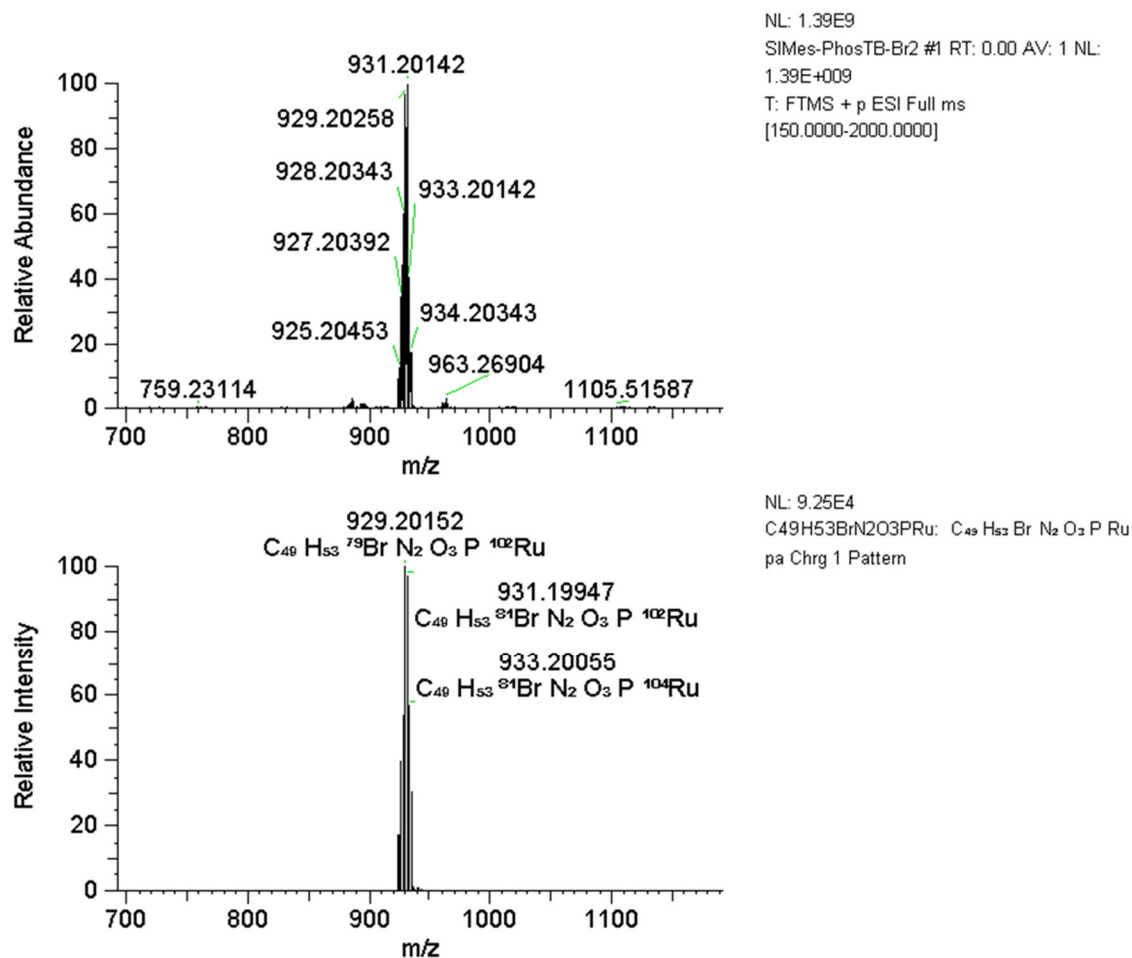


**Figure S1.** NMR spectra of *cis*-Ru-Phos-Br<sub>2</sub> top: <sup>1</sup>H NMR (400 MHz, DCM-*d*<sub>2</sub>), bottom: <sup>13</sup>C NMR (125 MHz, DCM-*d*<sub>2</sub>).

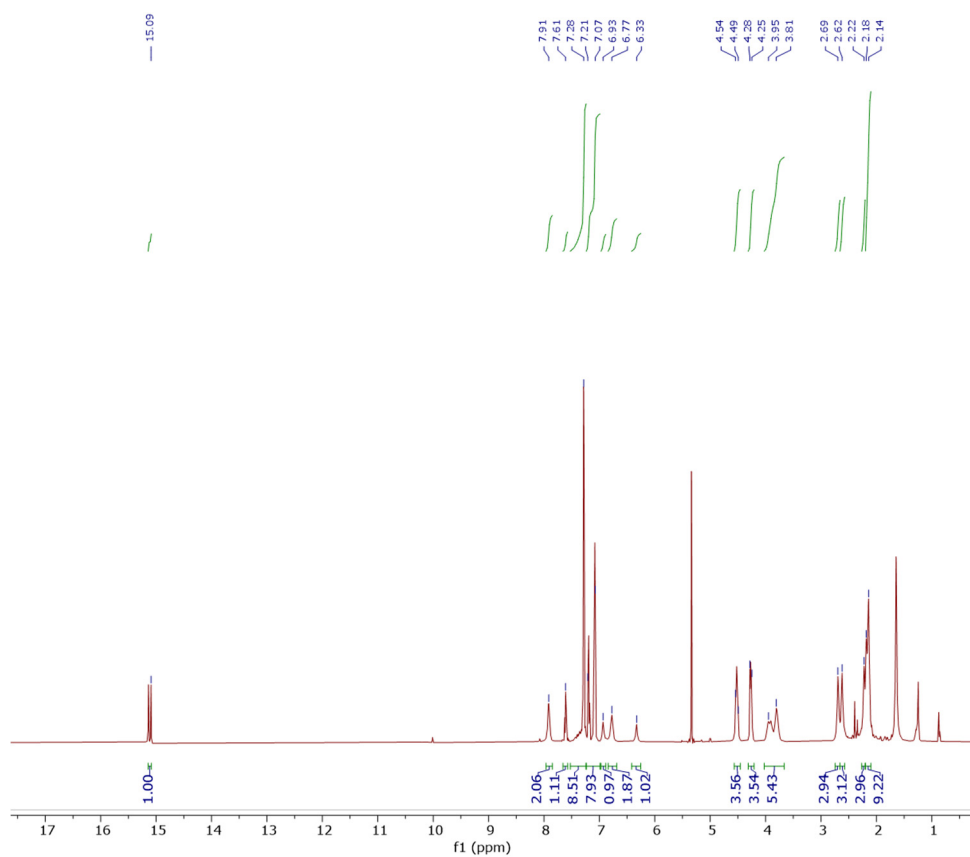
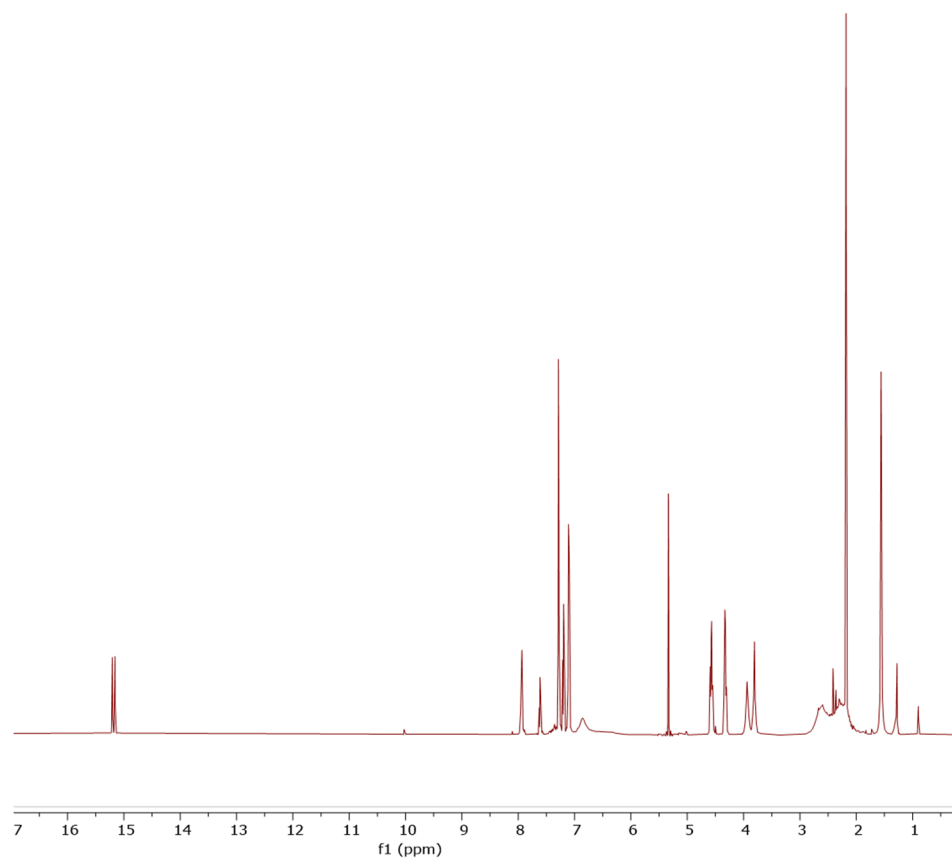


**Figure S2.** <sup>31</sup>P-NMR spectra of *cis*-Ru-Phos-Br<sub>2</sub> (202 MHz, DCM-*d*<sub>2</sub>)

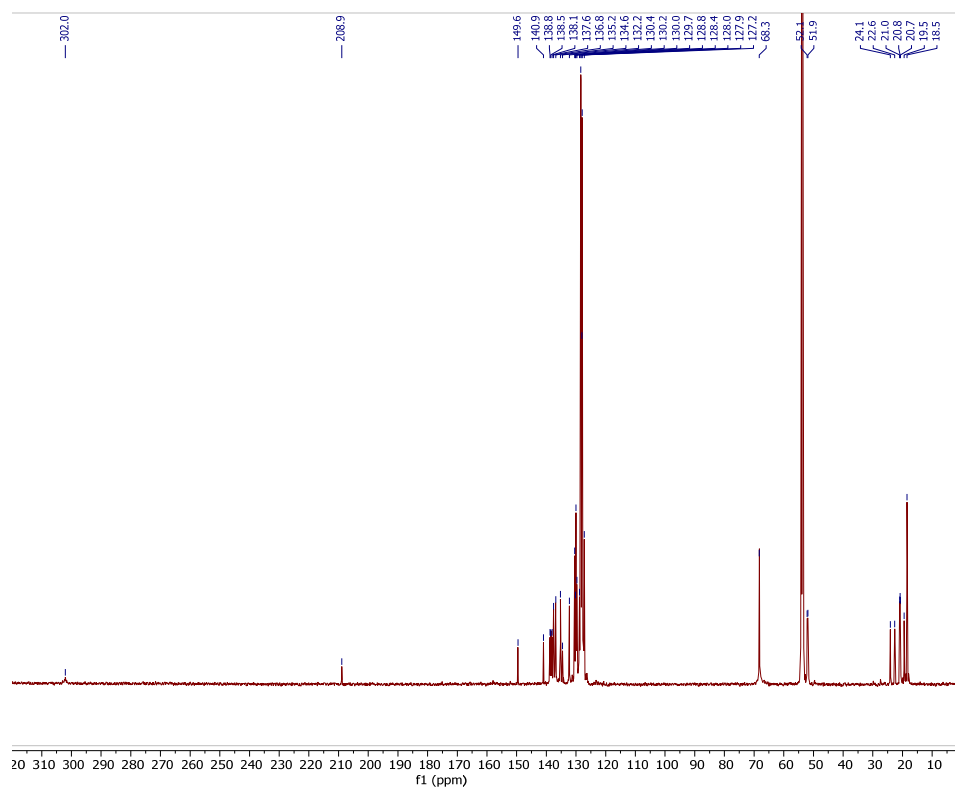




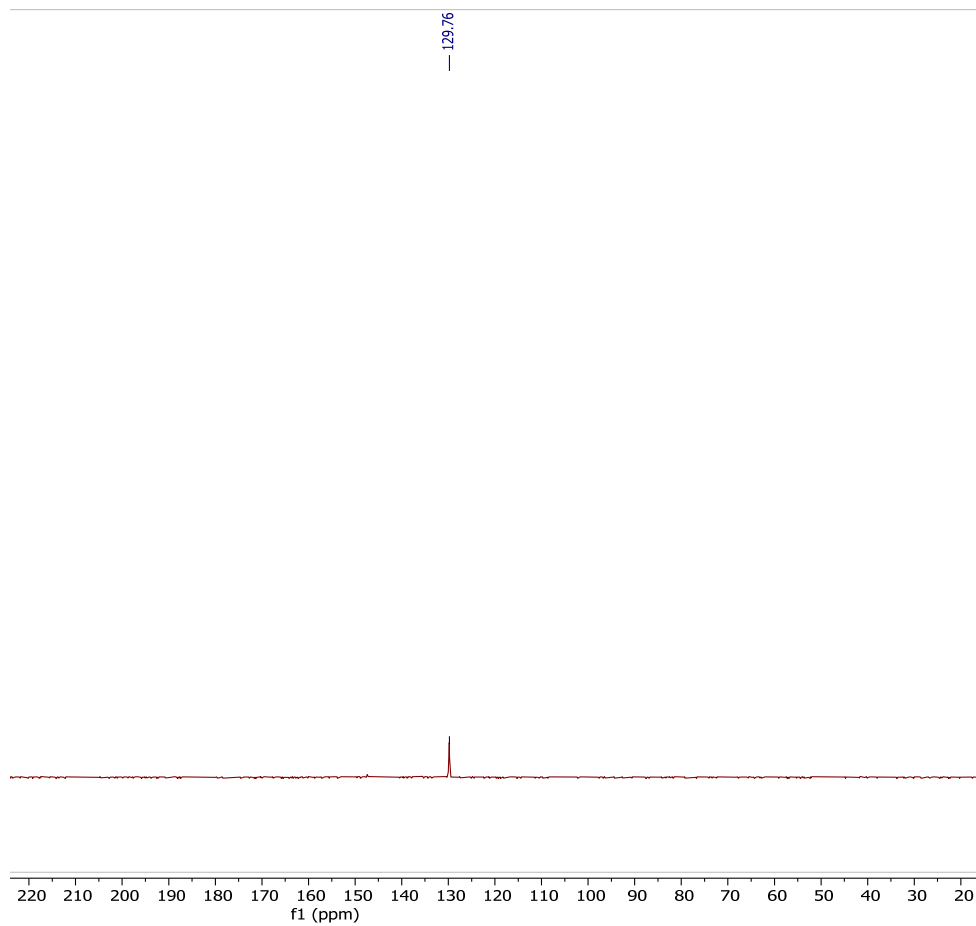
**Figure S3.** Experimental (above) and simulated (down) HRMS chromatogram of *cis*-Ru-Phos-Br<sub>2</sub>



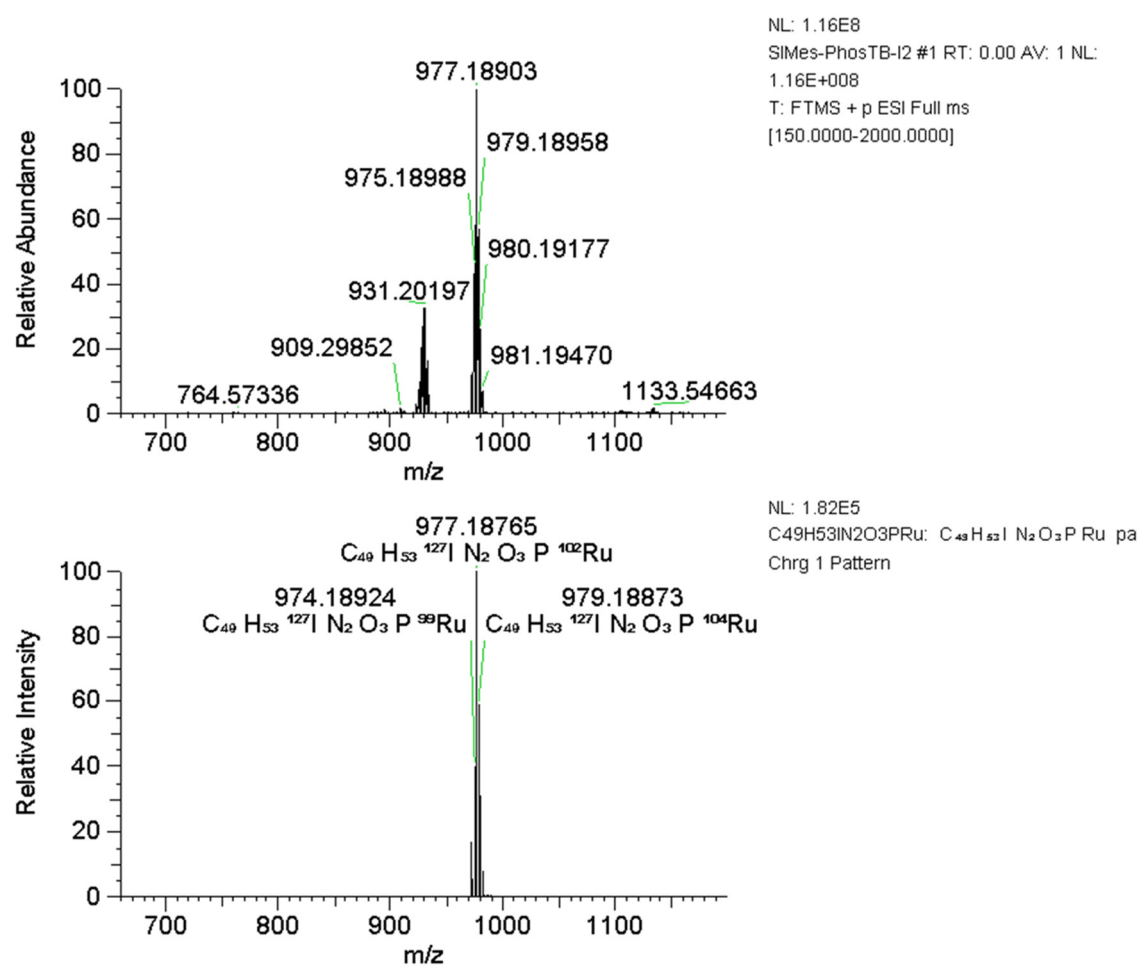
**Figure S4.** NMR spectra of *cis*-**Ru-Phos-I<sub>2</sub>** top: <sup>1</sup>H NMR (500 MHz, DCM-*d*<sub>2</sub>, RT), bottom: <sup>1</sup>H NMR (500 MHz, DCM-*d*<sub>2</sub>, -8 °C).



**Figure S5.** <sup>13</sup>C NMR spectra (125 MHz, DCM-*d*<sub>2</sub>, -8°C.) of *cis*-Ru-Phos-I<sub>2</sub>



**Figure S6.**  $^{31}\text{P}$ -NMR spectra of *cis*-Ru-Phos-I<sub>2</sub> (202 MHz, DCM-d<sub>2</sub>)



**Figure S7.** Experimental (above) and simulated (down) HRMS chromatogram of *cis*-Ru-Phos-I<sub>2</sub>

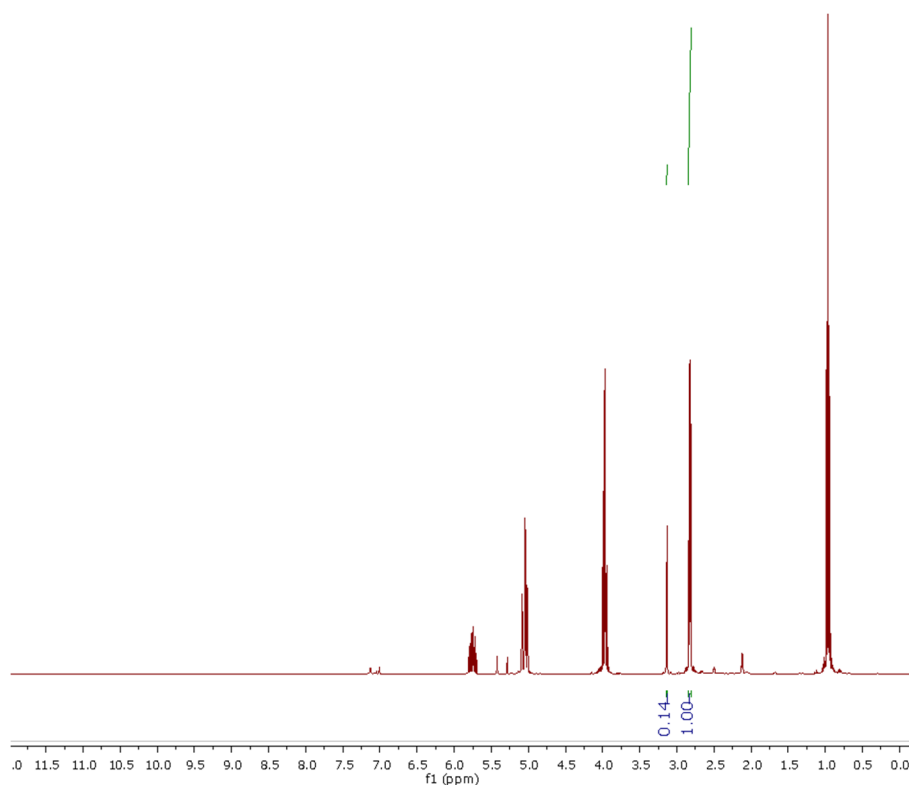
### 3. X-ray crystallographic data and structure refinement

CCDC 2297786 and 2297788 of *cis*-Ru-Phos-Br<sub>2</sub> and *cis*-Ru-Phos-I<sub>2</sub> contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

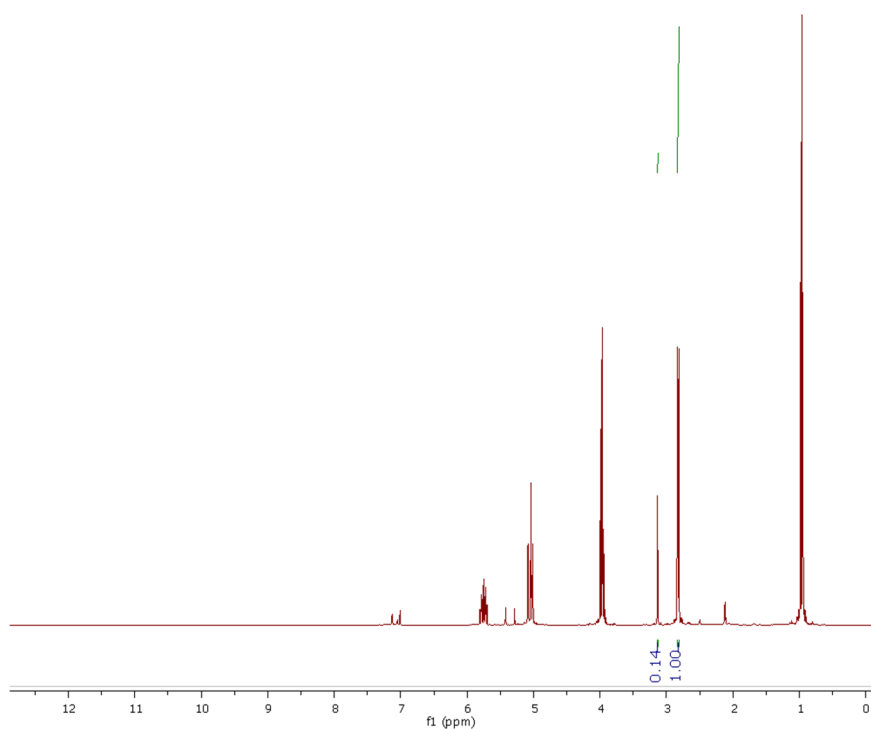
**Table S1.** Crystallographic data for *cis*-Ru-Phos-Br<sub>2</sub> and *cis*-Ru-Phos-I<sub>2</sub>

	<i>cis</i> -Ru-Phos-Br <sub>2</sub>	<i>cis</i> -Ru-Phos-I <sub>2</sub>
Chemical formula	C <sub>50</sub> H <sub>55</sub> Br <sub>2</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub> PRu	C <sub>50</sub> H <sub>55</sub> Cl <sub>2</sub> I <sub>2</sub> N <sub>2</sub> O <sub>3</sub> Pru
Formula Weight	1094.72	1188.70
Temperature (K)	200(1)	100.15
Crystal size (mm <sup>3</sup> )	0.41×0.12×0.11	0.27 × 0.18 × 0.15
Crystal system	monoclinic	triclinic
Space group	P21/n	P-1
<i>a</i> (Å)	9.3148(2)	11.2704(2)
<i>b</i> (Å)	32.3906(9)	19.1081(3)
<i>c</i> (Å)	16.3494(5)	24.2629(4)
$\alpha$ (°)	90	109.331(3)
$\beta$ (°)	100.031(3)	93.5920(10)
$\gamma$ (°)	90	91.766(2)
Volume (Å <sup>3</sup> )	4857.4(2)	91.766(2)
<i>Z</i>	4	4
$\rho$ (g cm <sup>-3</sup> )	1.497	1.607
$\mu$ (mm <sup>-1</sup> )	2.154	1.759
<i>F</i> (000)	2224.0	2368.0
Radiation	Mo Ka	MoK $\alpha$ ( $\lambda$ = 0.71073)
<i>hkl</i> range	12	14
	43	24
	22	32
No. of reflections collected	43521	59859
Independent reflections	11584 ( <i>R</i> <sub>int</sub> = 0.0620)	22150 ( <i>R</i> <sub>int</sub> = 0.0369)
No. of parameters	556	1147
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.024	1.034
Final <i>R</i> indexes [ <i>I</i> ≥ 2σ ( <i>I</i> )]	w <i>R</i> <sub>2</sub> =0.1069, <i>R</i> <sub>1</sub> =0.0503	<i>R</i> <sub>1</sub> = 0.0335, w <i>R</i> <sub>2</sub> = 0.0771
CCDC Numbers	2297786	2297788

#### 4. RCM with DEDAM at different wavelengths

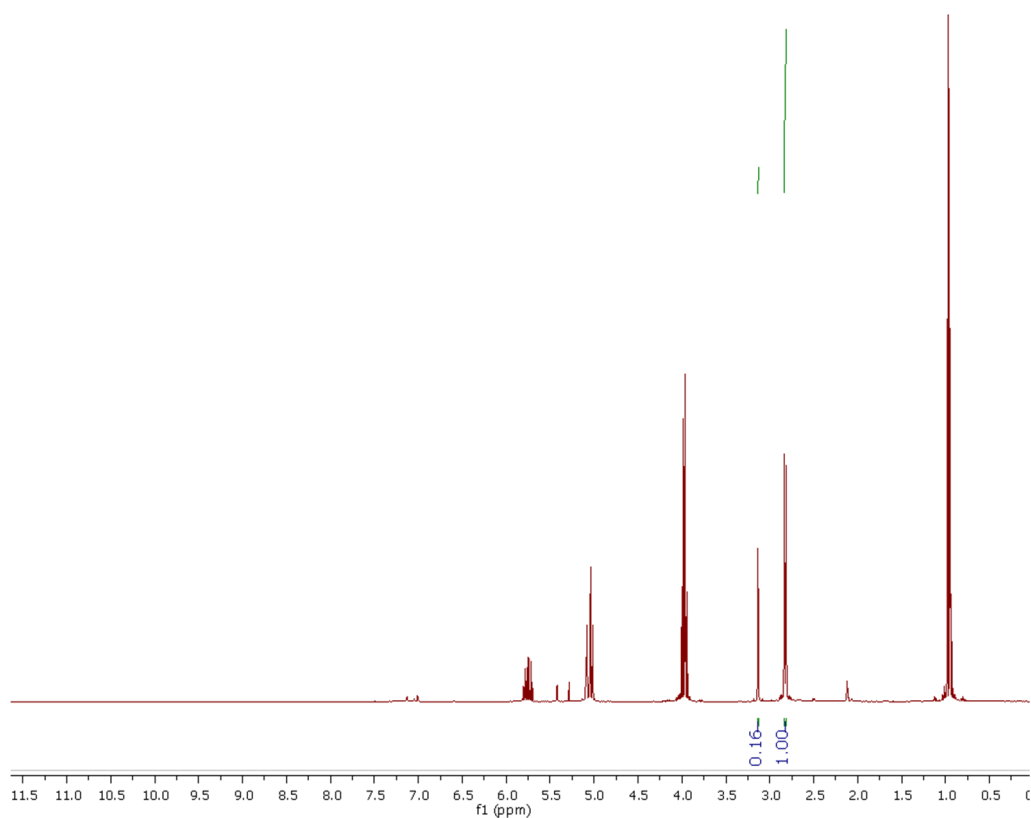


**Figure S8.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Cl<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 254 nm for 2 h.

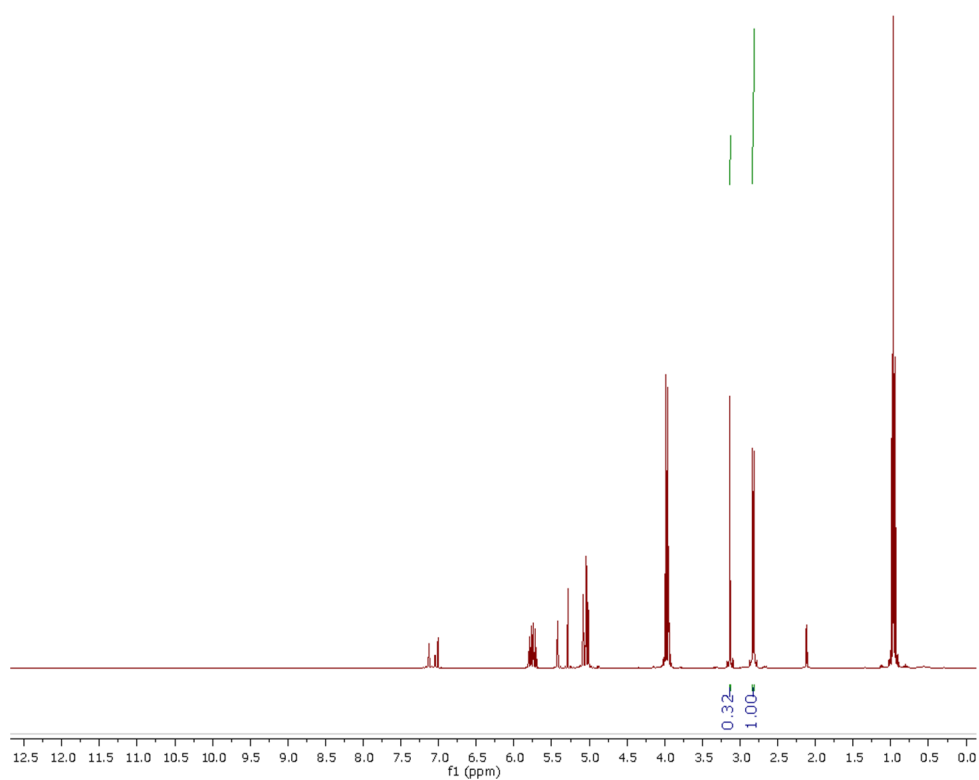


**Figure S9.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 254 nm for 2 h.

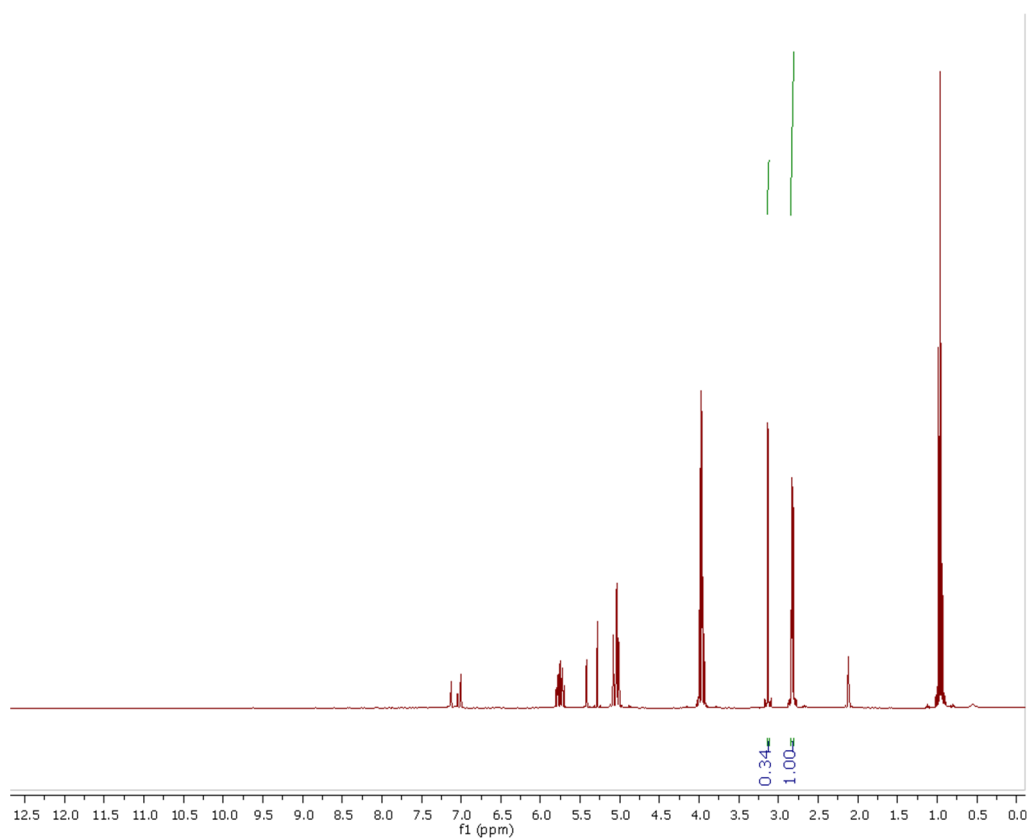




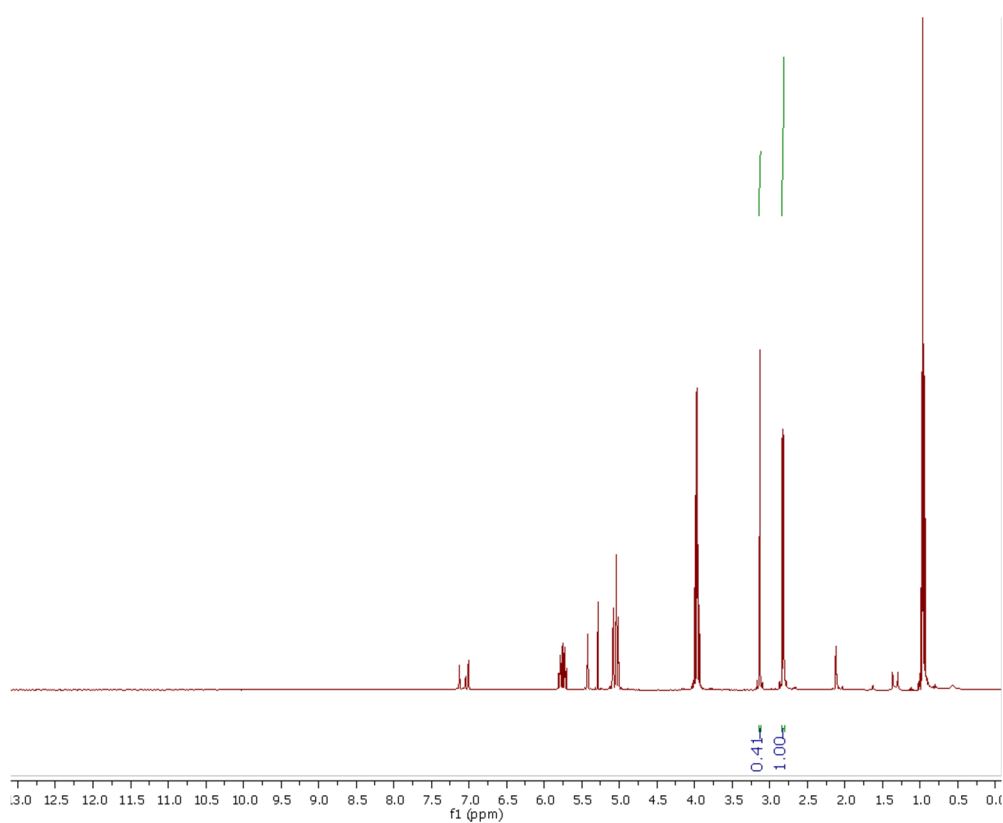
**Figure S10.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos- $\text{I}_2$  in 0.1 M toluene- $d_8$  at 254 nm for 2 h.



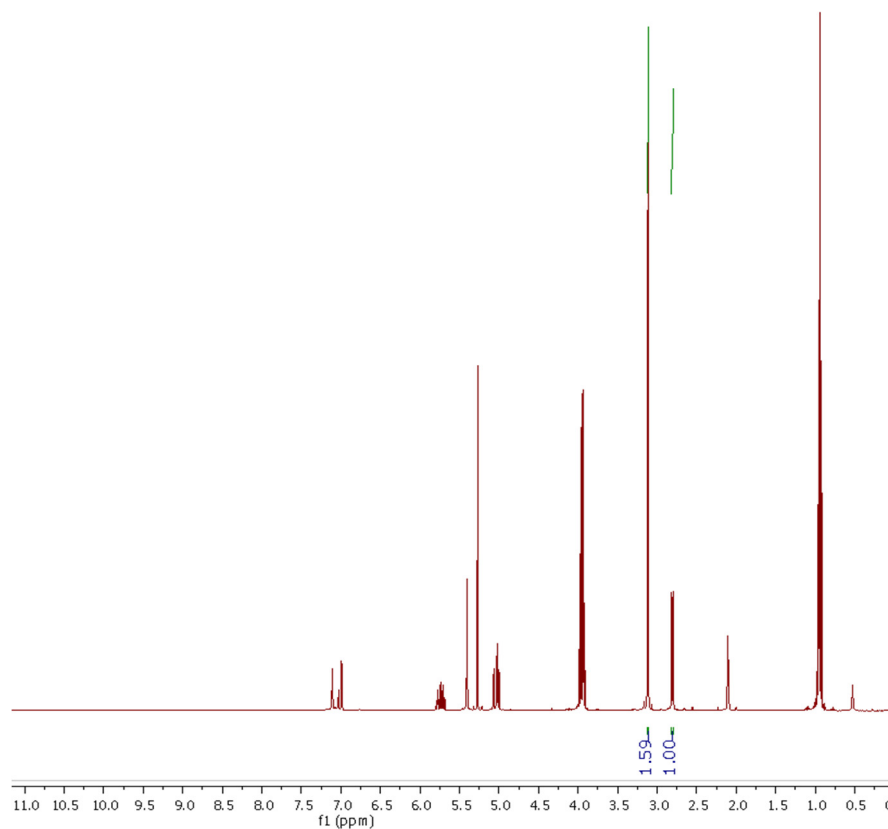
**Figure S11.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-PhosTB-Cl<sub>2</sub> in 0.1M toluene-*d*<sub>8</sub> at 313 nm for 2 h.



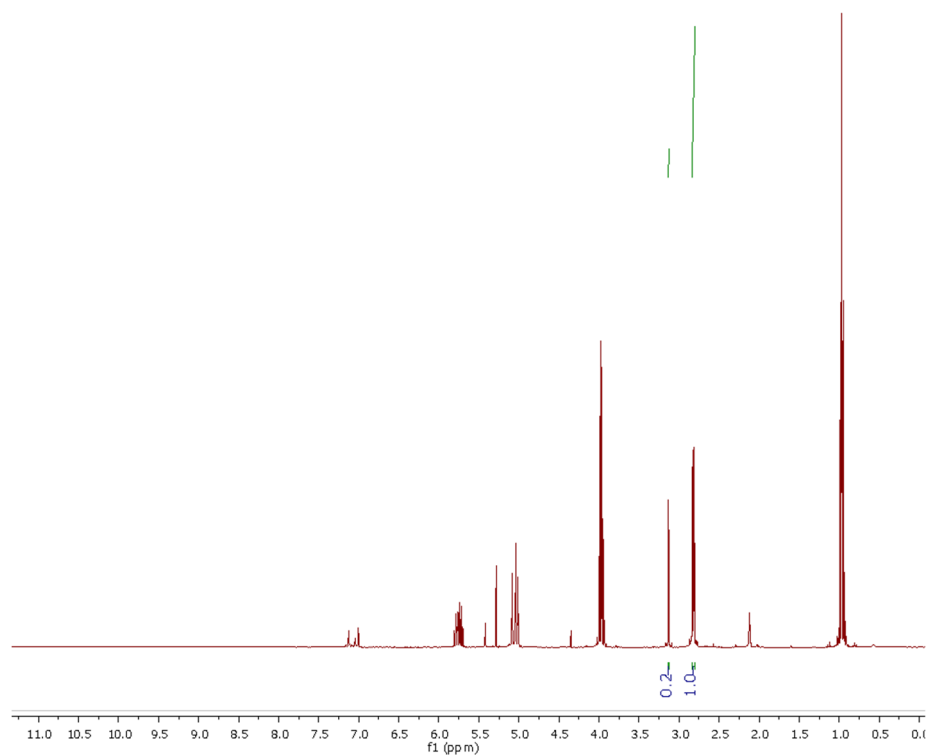
**Figure S12.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-PhosTB-Br<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 313 nm for 2 h.



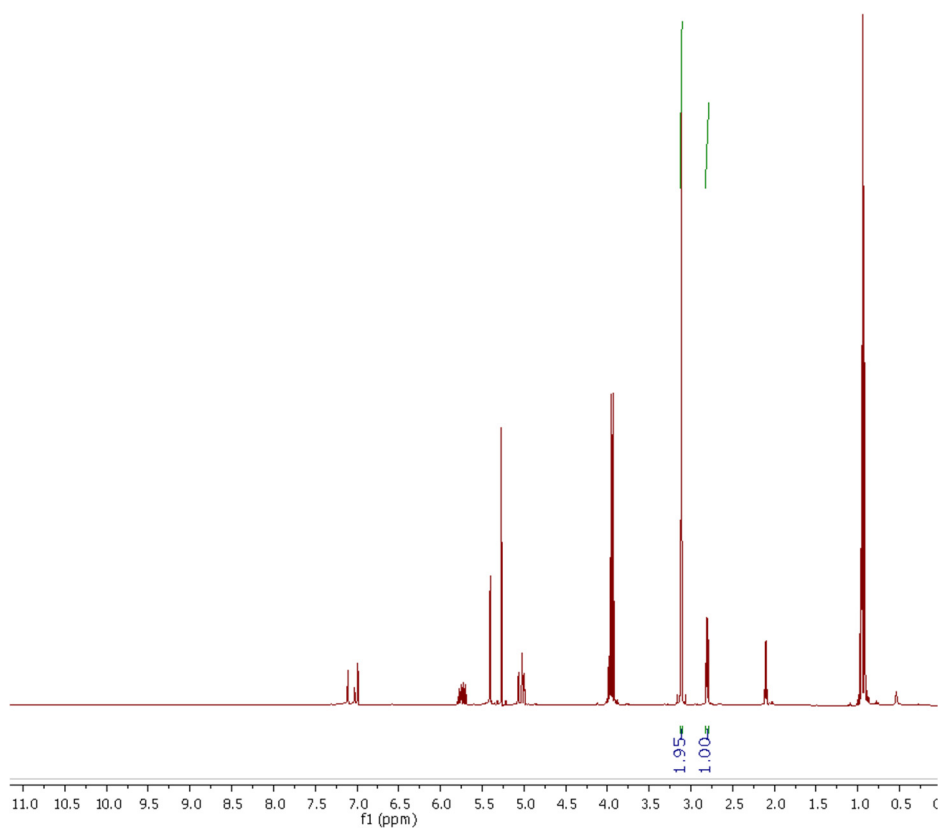
**Figure S13.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-PhosTB-I<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 313 nm for 2 h.



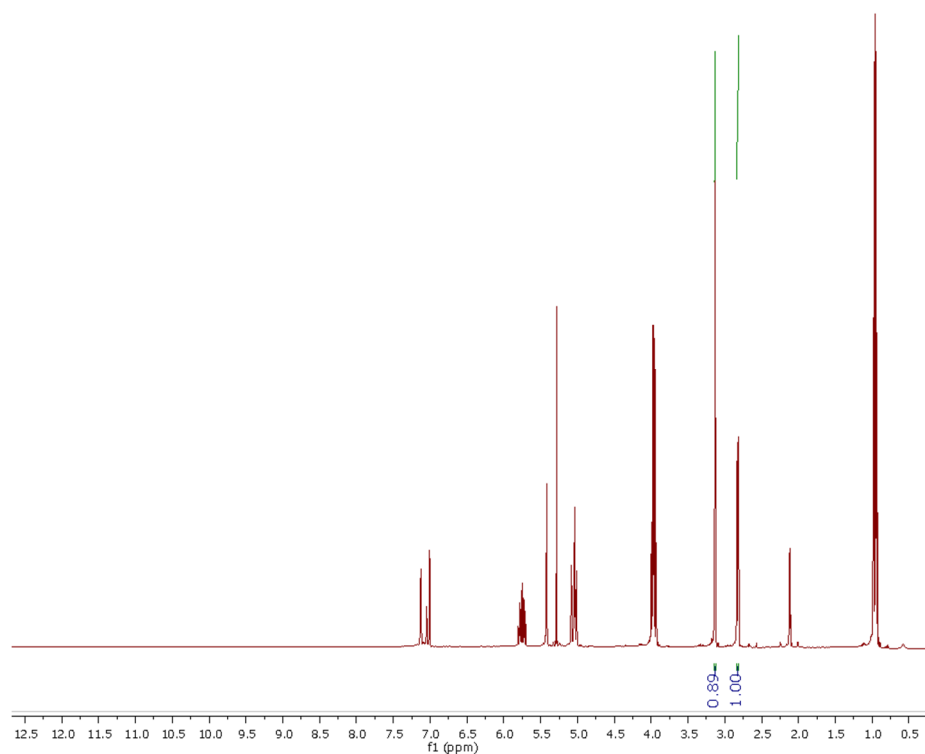
**Figure S14.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Cl<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 350 nm for 2 h.



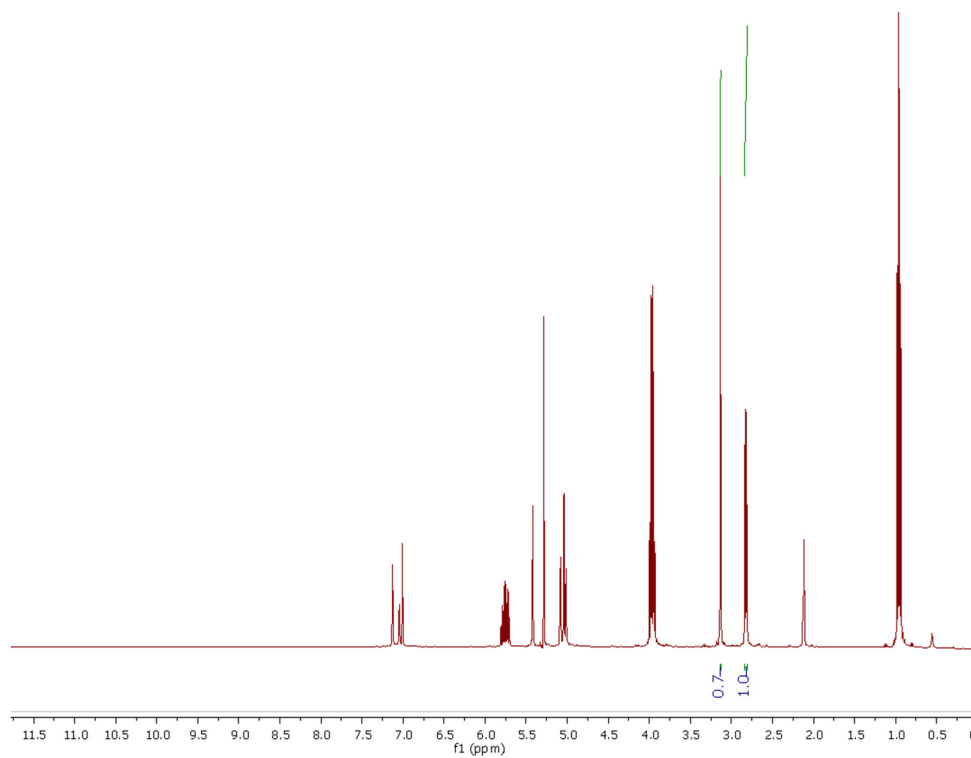
**Figure S15.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 350 nm for 2 h.



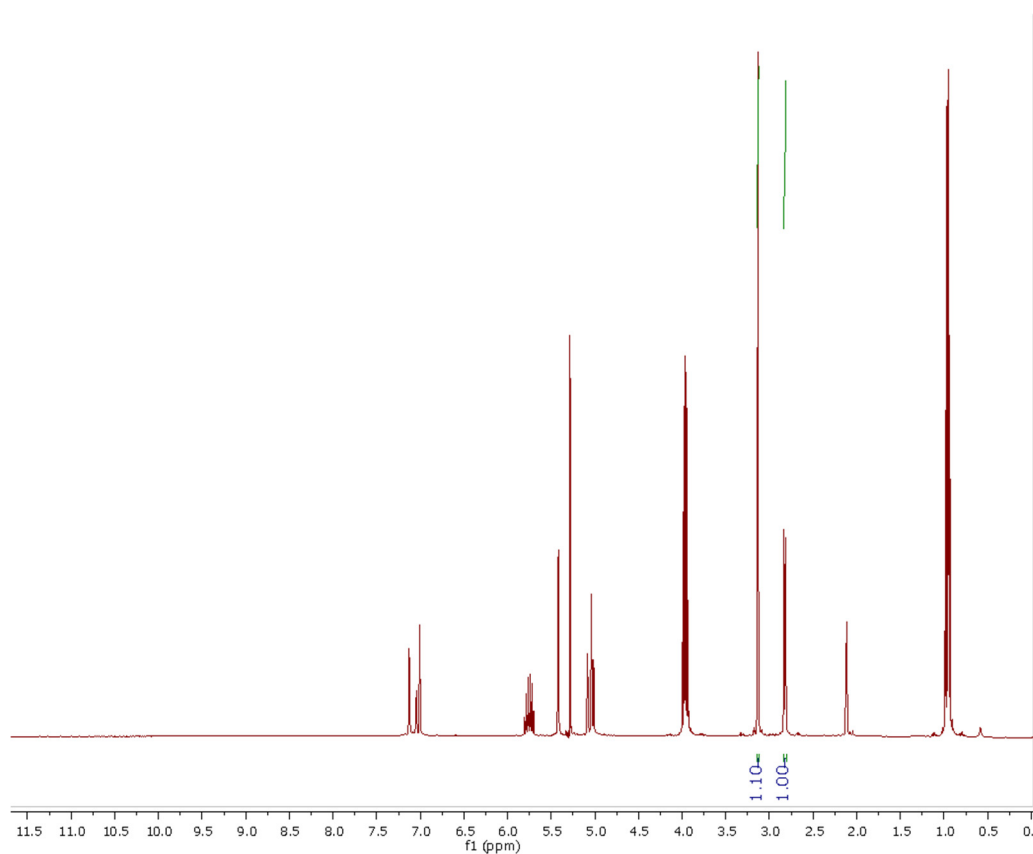
**Figure S16.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-I<sub>2</sub> in 0.1M toluene-*d*<sub>8</sub> at 350 nm for 2 h.



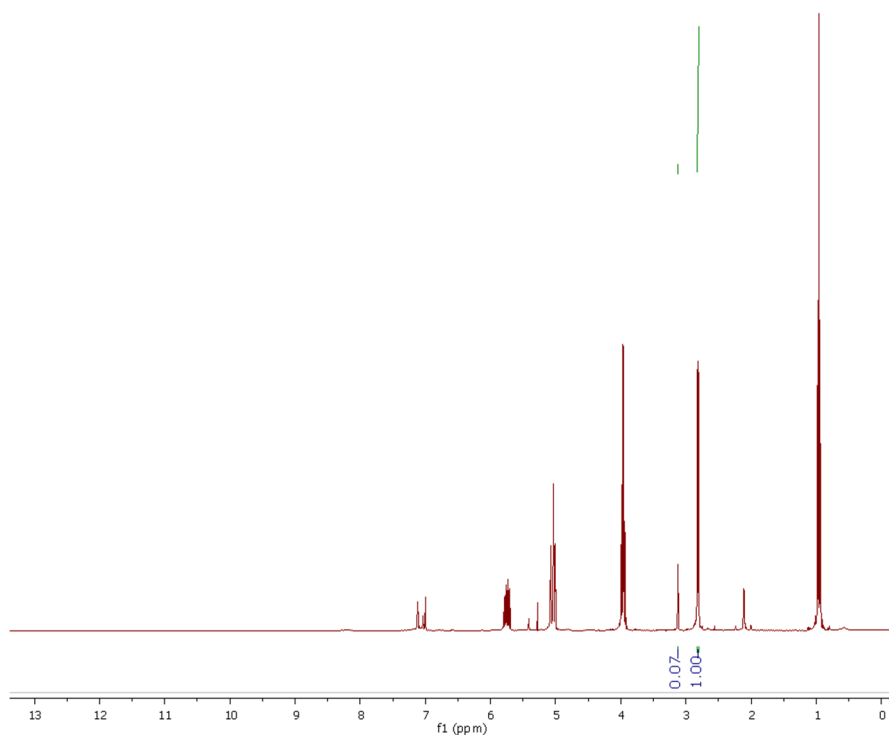
**Figure S17.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Cl<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 420 nm for 2 h.



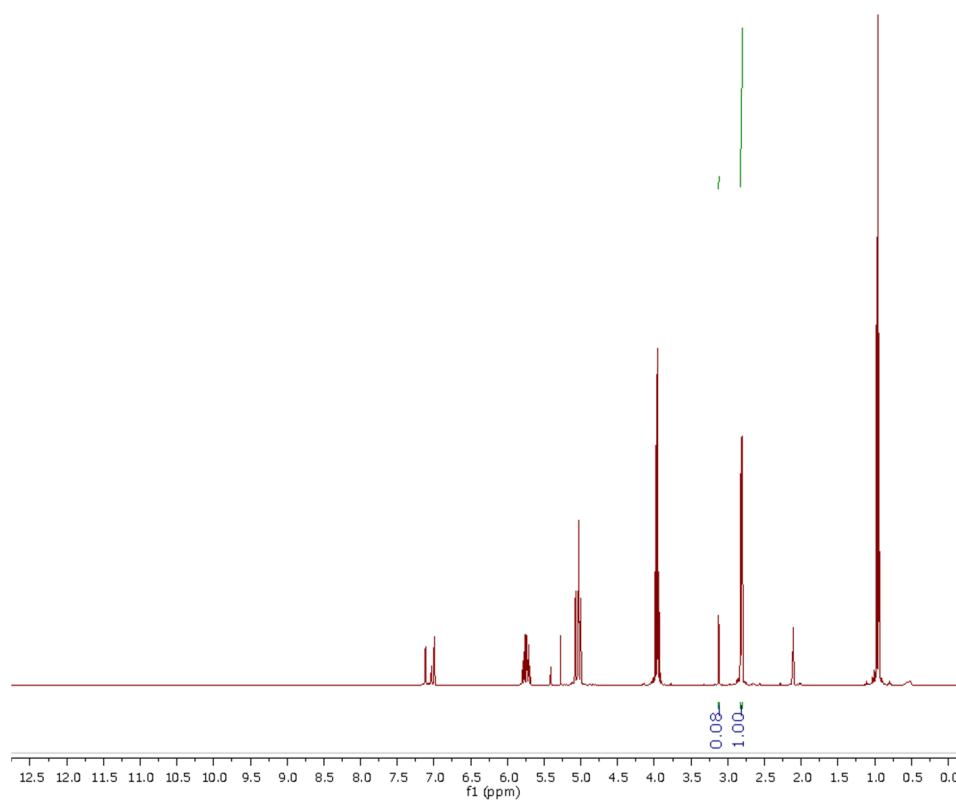
**Figure S18.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 420 nm for 2 h.



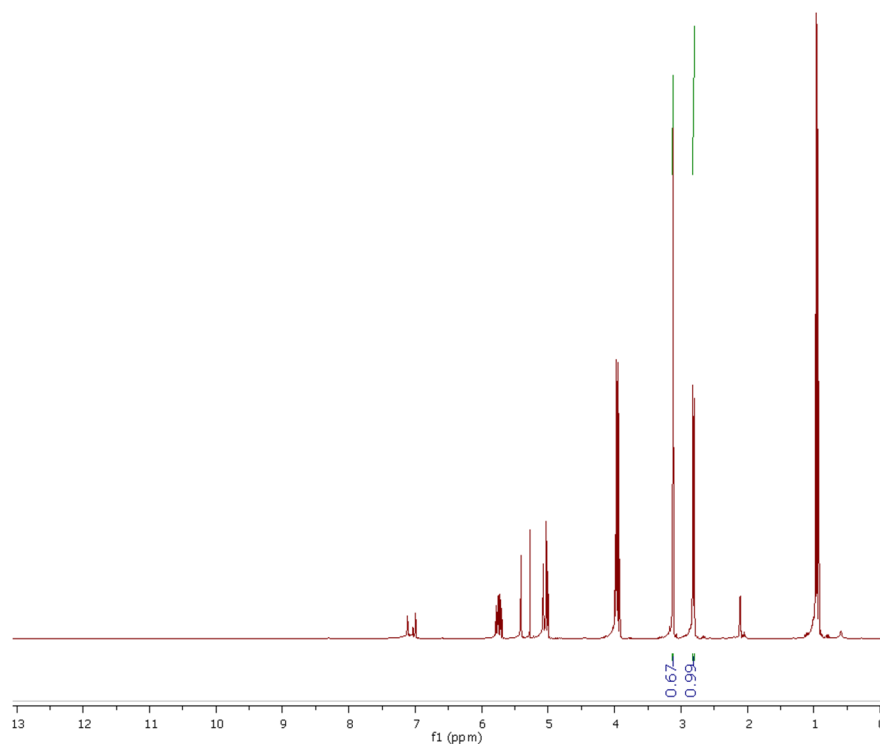
**Figure S19.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos- $\text{I}_2$  in 0.1 M toluene- $d_8$  at 420 nm for 2 h.



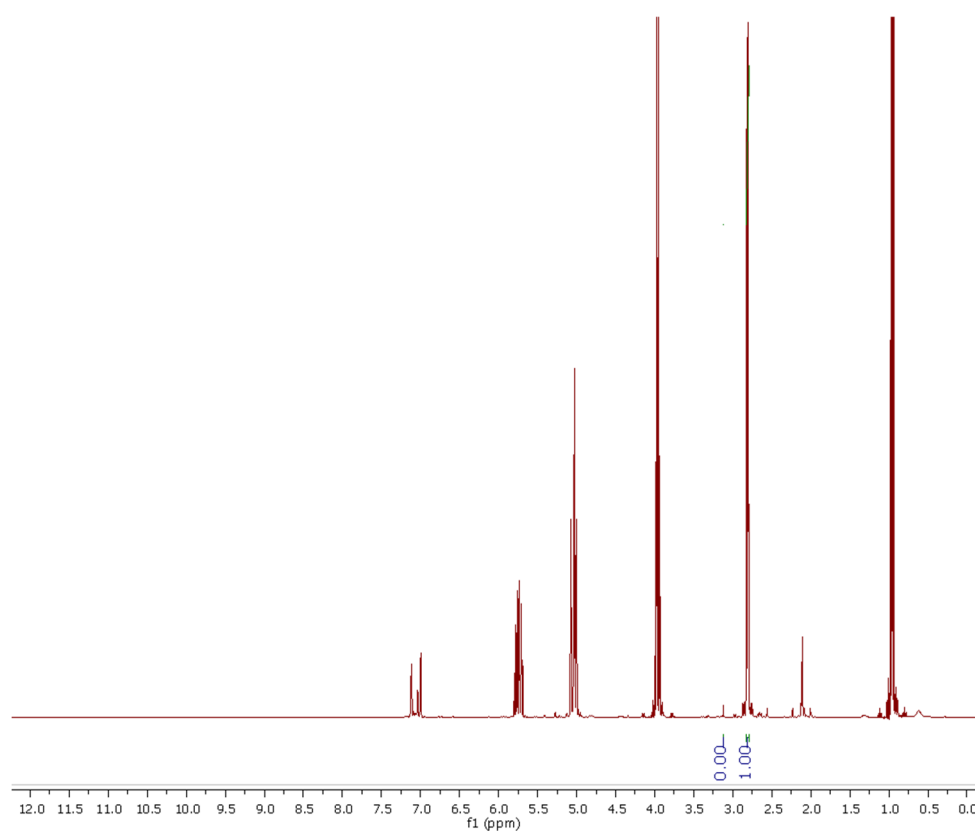
**Figure S20.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos- $\text{Cl}_2$  in 0.1 M toluene- $d_8$  at blue LED for 2 h.



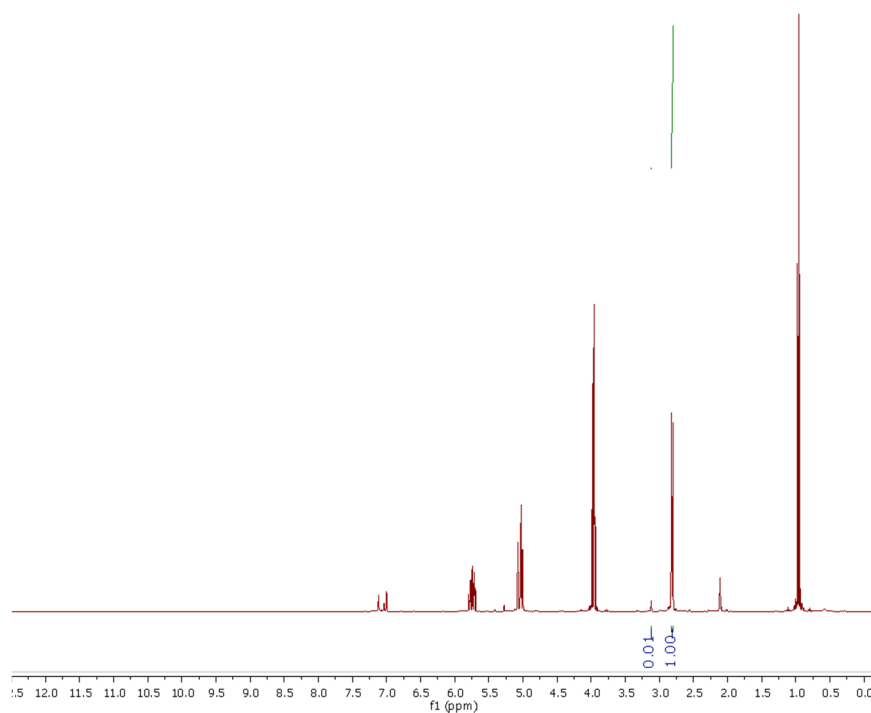
**Figure S21.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at blue LED for 2 h.



**Figure S22.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-I<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at blue LED for 2 h.

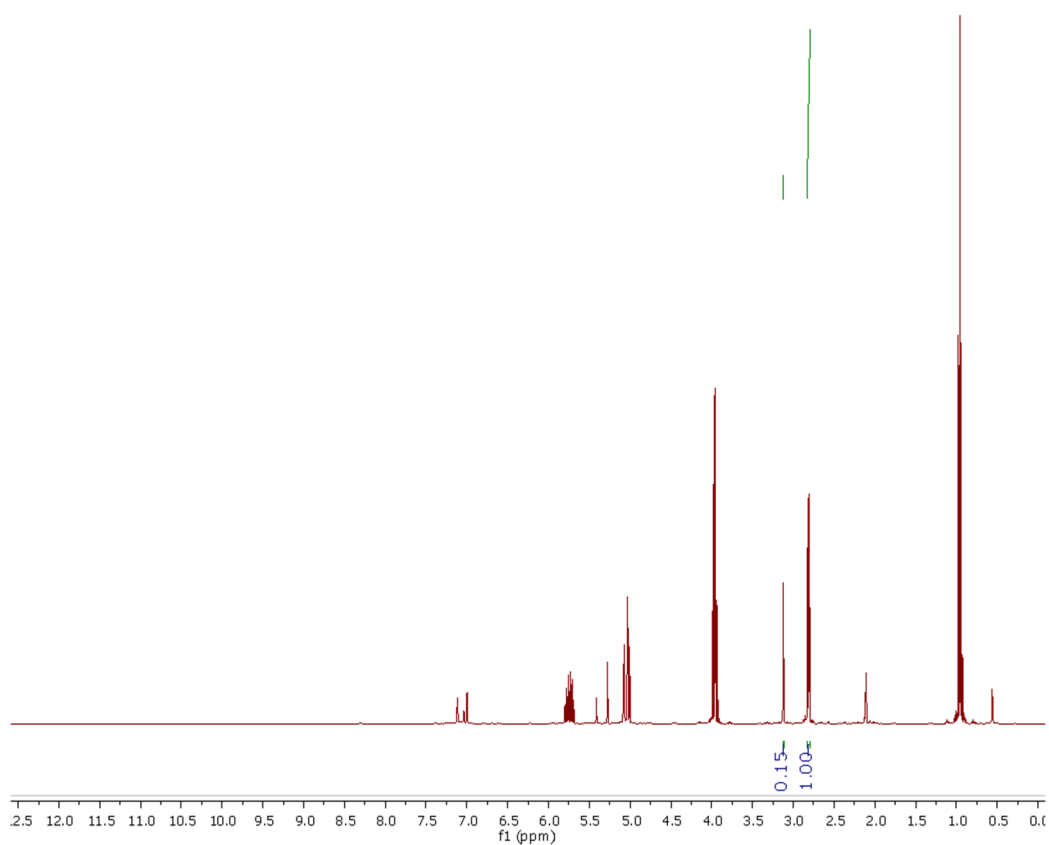


**Figure S23.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Cl<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 510 nm for 2 h.



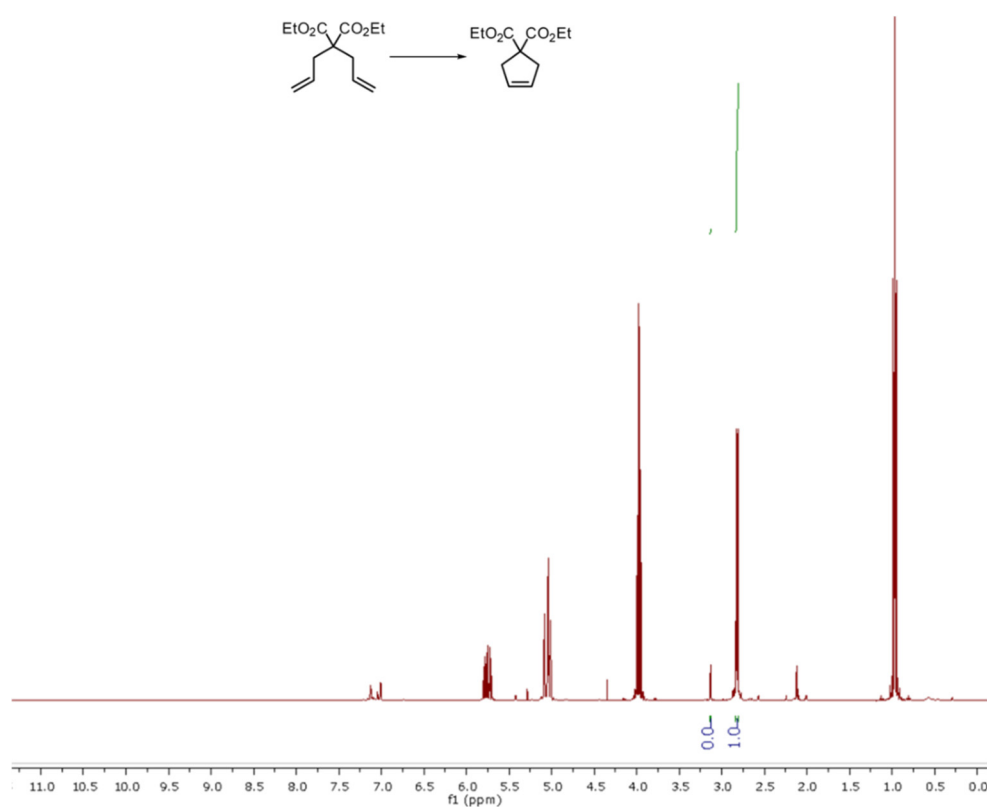
**Figure S24.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 510 nm for 2 h.



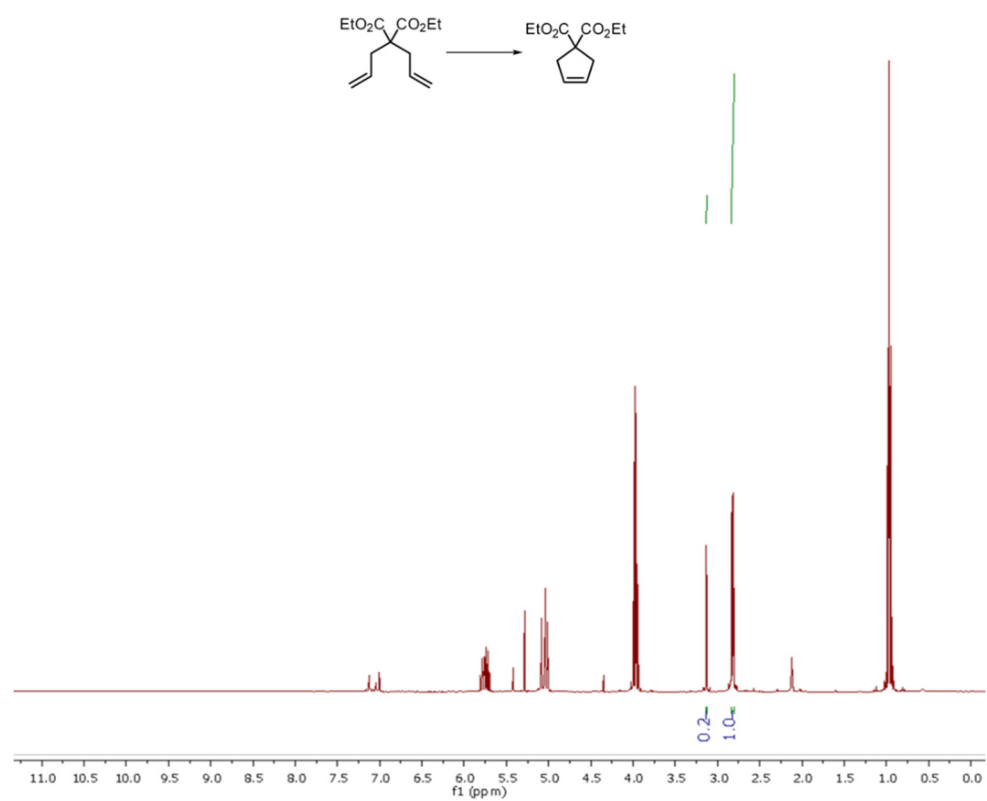


**Figure S25.** RCM reaction of DEDAM with 1 mol% of *cis*-Ru-Phos-I<sub>2</sub> in 0.1 M toluene-*d*<sub>8</sub> at 510 nm for 2 h.

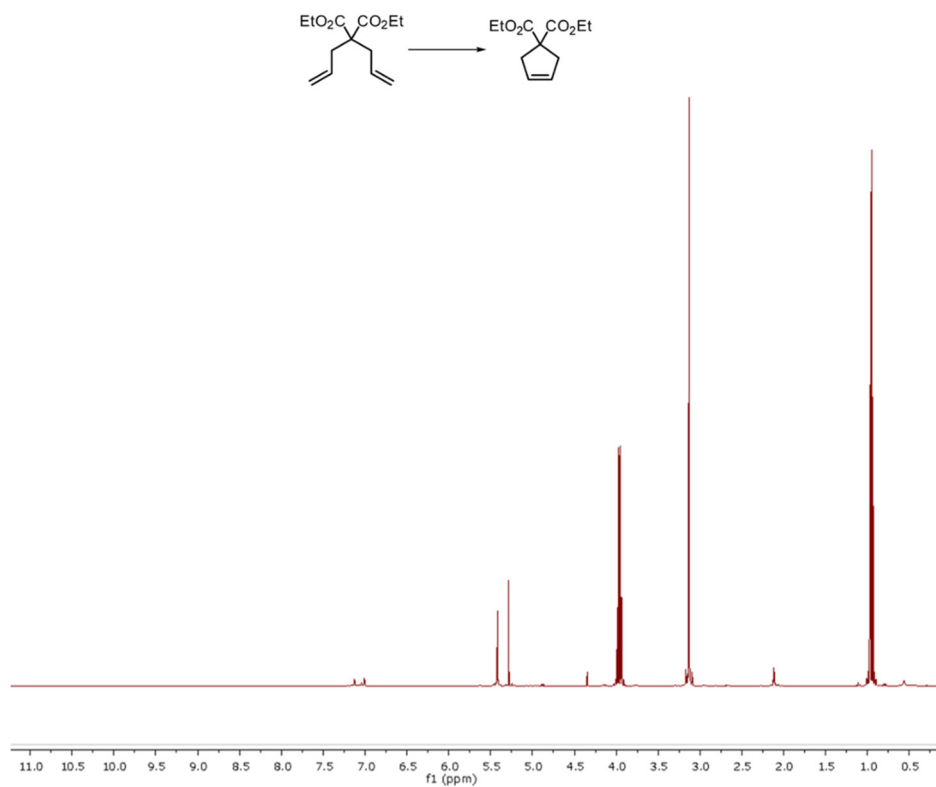
## 5. RCM with different substrates at 80 °C



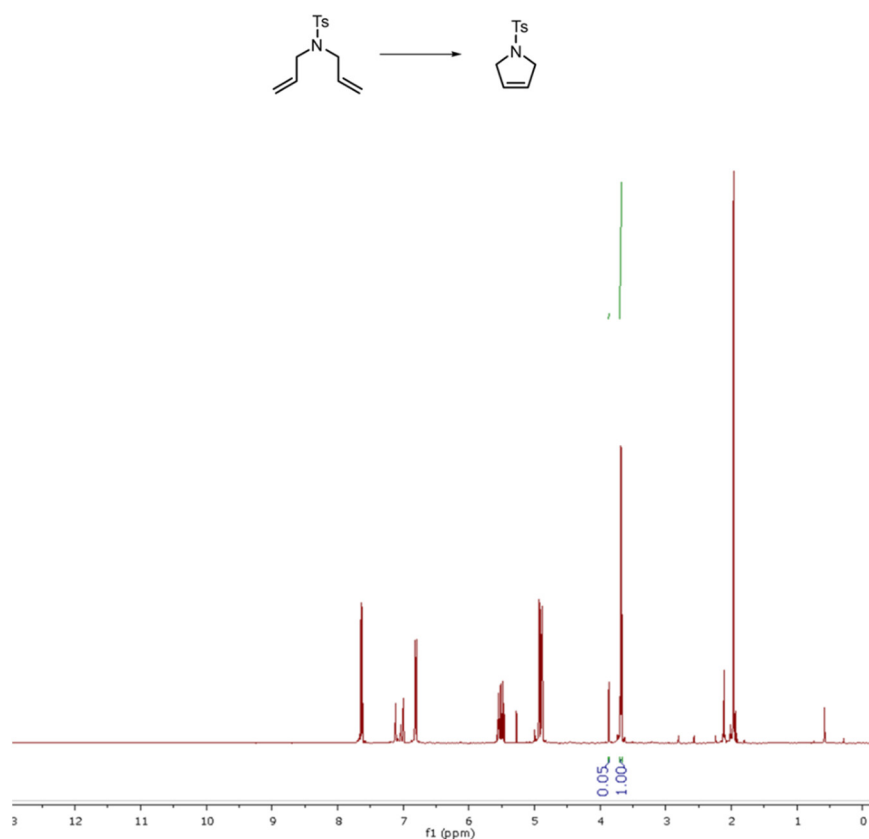
**Figure S26.** RCM of DEDAM. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> heating at 80 °C for 10 minutes.



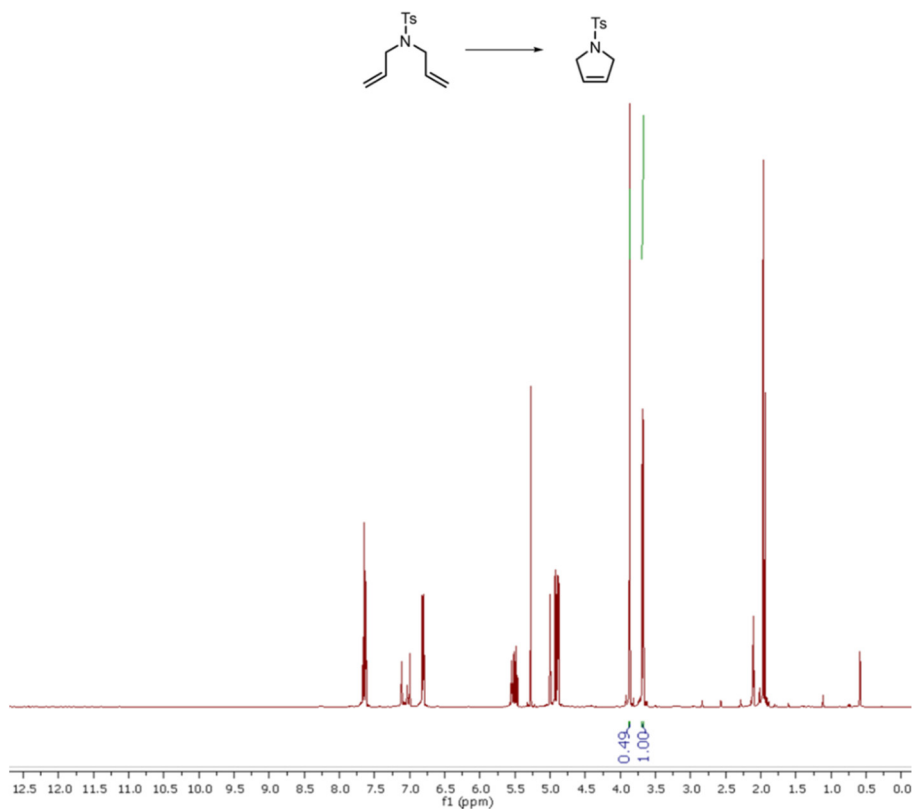
**Figure S27.** RCM of DEDAM. Reaction conditions: toluene- $d_8$ , 0.1 M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> heating at 80 °C for 10 minutes.



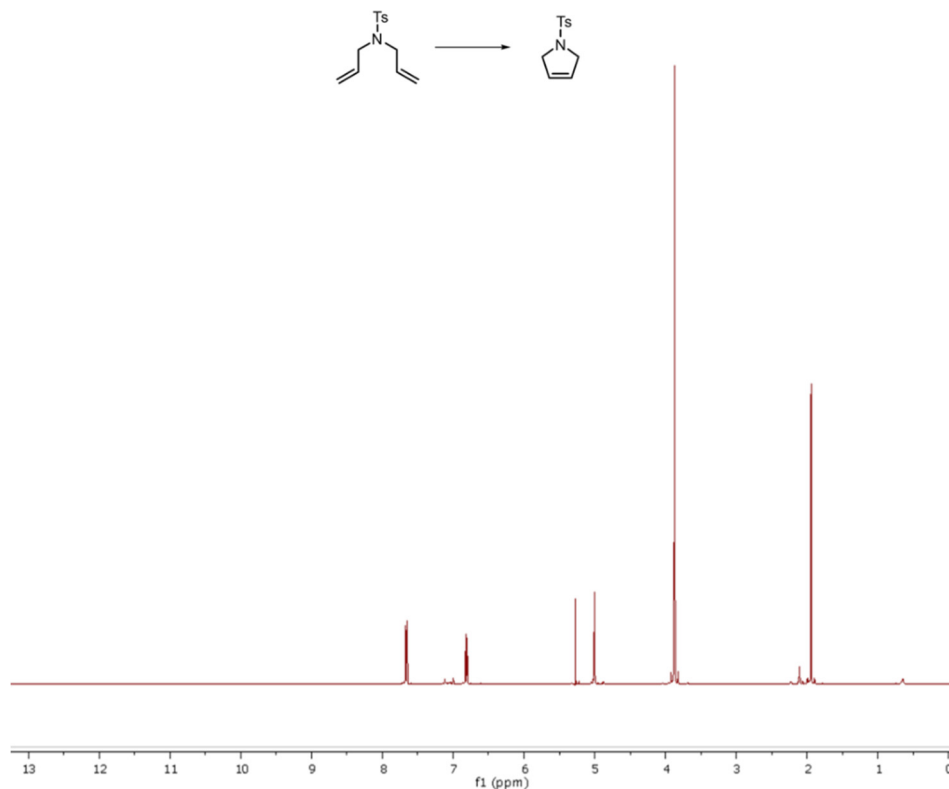
**Figure S28.** RCM of DEDAM. Reaction conditions: toluene- $d_8$ , 0.1 M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> heating at 80 °C for 10 minutes.



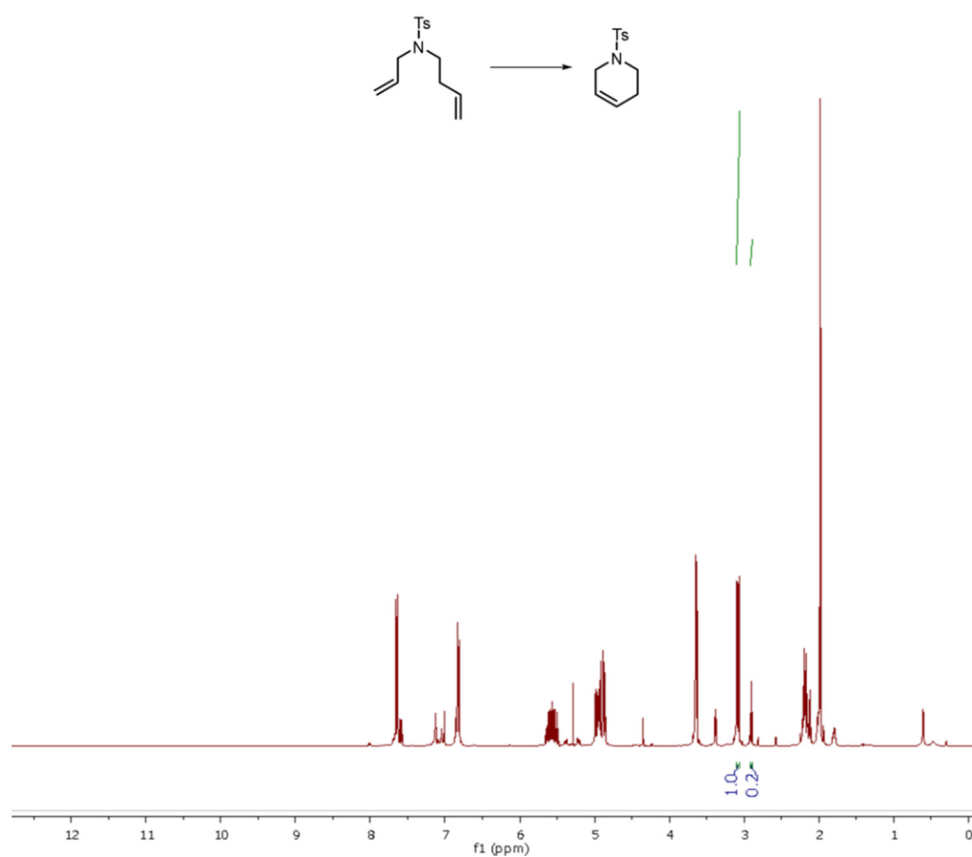
**Figure S29.** RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> heating at 80 °C for 10 minutes.



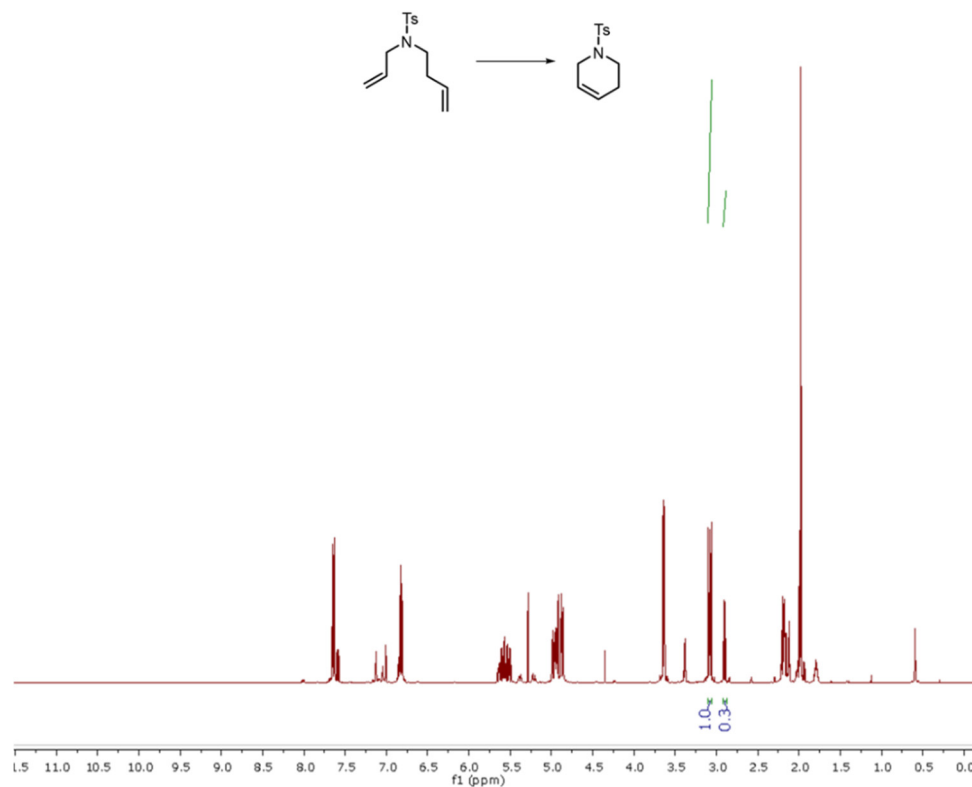
**Figure S30.** RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> heating at 80 °C for 10 minutes.



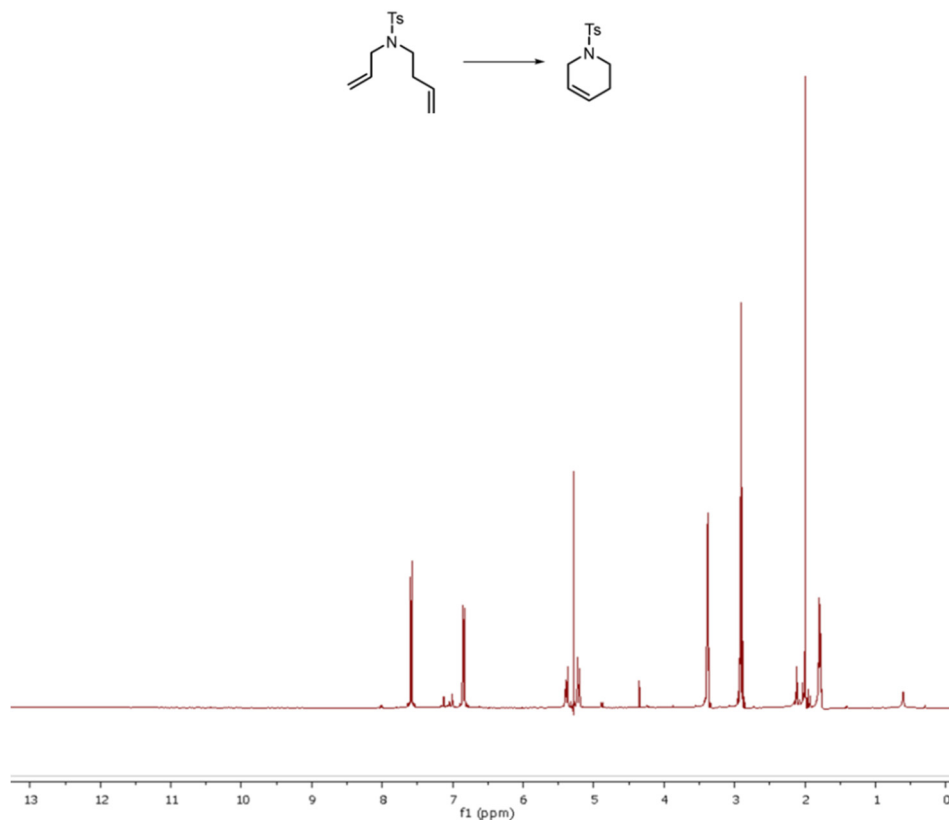
**Figure S31.** RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> heating at 80 °C for 10 minutes.



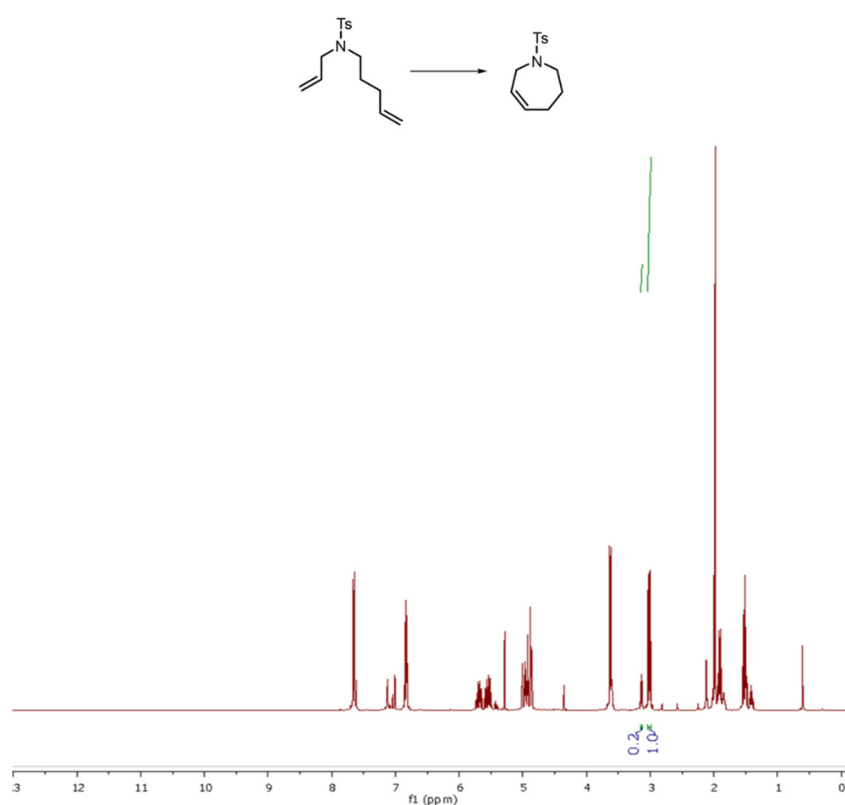
**Figure S32.** RCM of *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-Cl**<sub>2</sub> heating at 80 °C for 10 minutes.



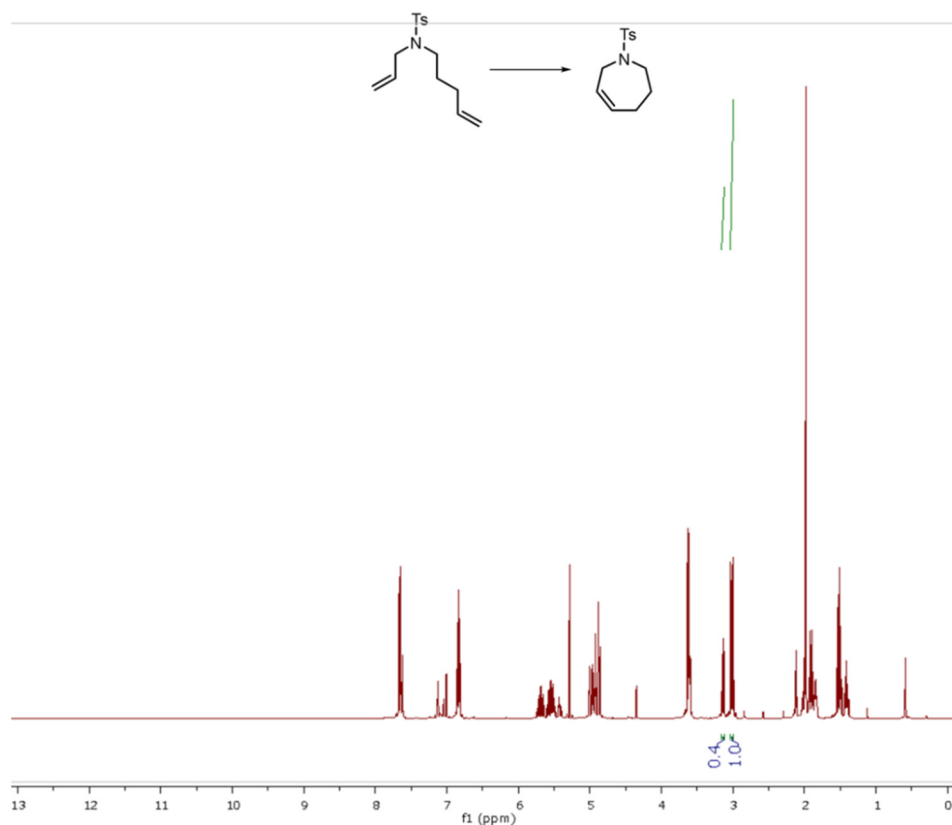
**Figure S33.** RCM of *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-Br**<sub>2</sub> heating at 80 °C for 10 minutes.



**Figure S34.** RCM of *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-I**<sub>2</sub> heating at 80 °C for 10 minutes.

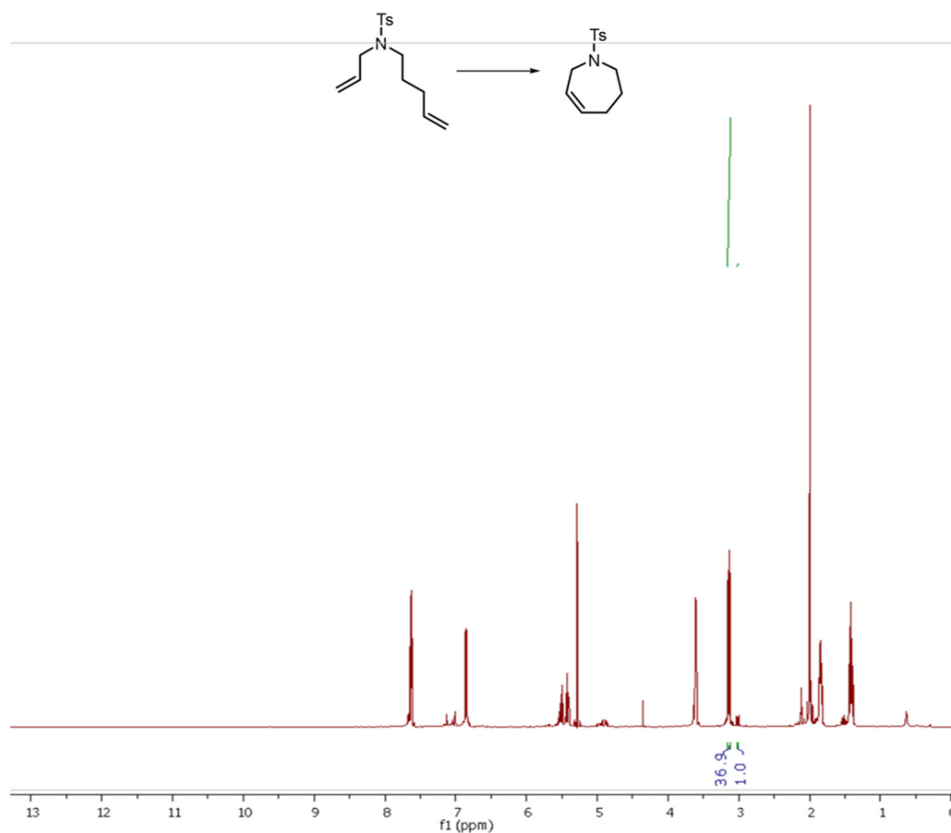


**Figure S35.** RCM of *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> heating at 80 °C for 10 minutes.

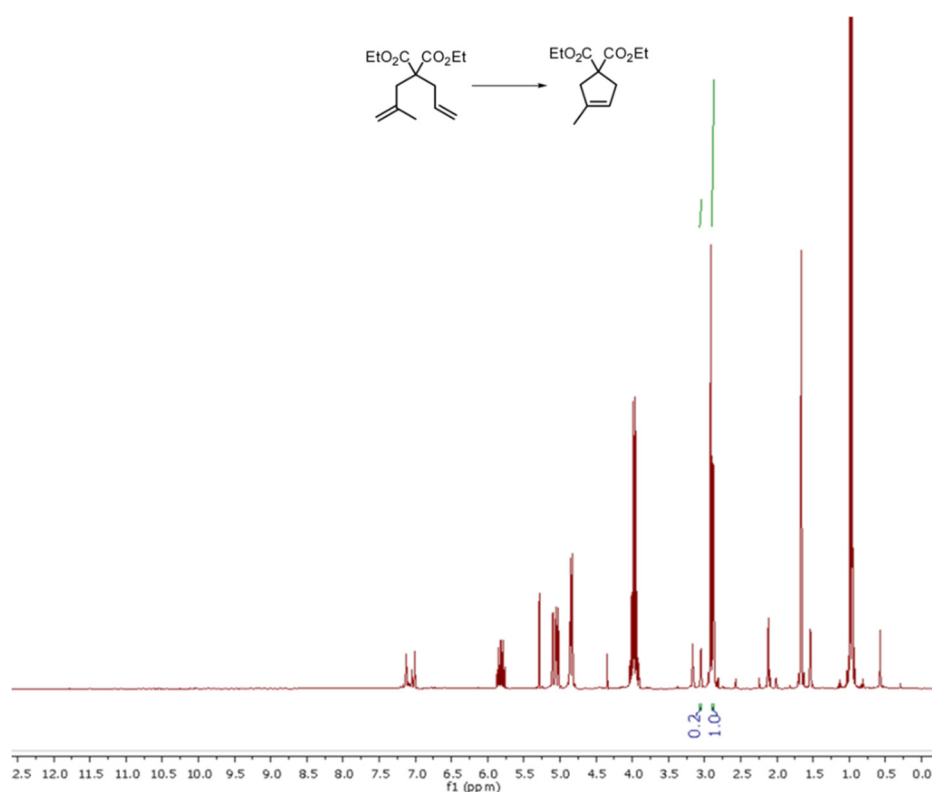




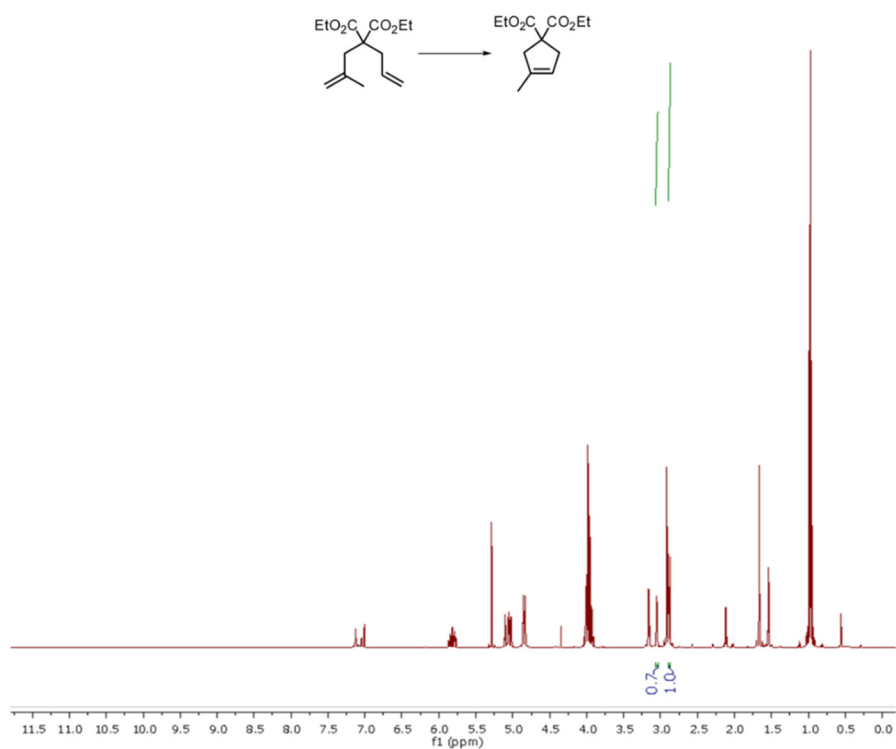
**Figure S36.** RCM of *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% ***cis*-Ru-Phos-Br<sub>2</sub>** heating at 80 °C for 10 minutes.



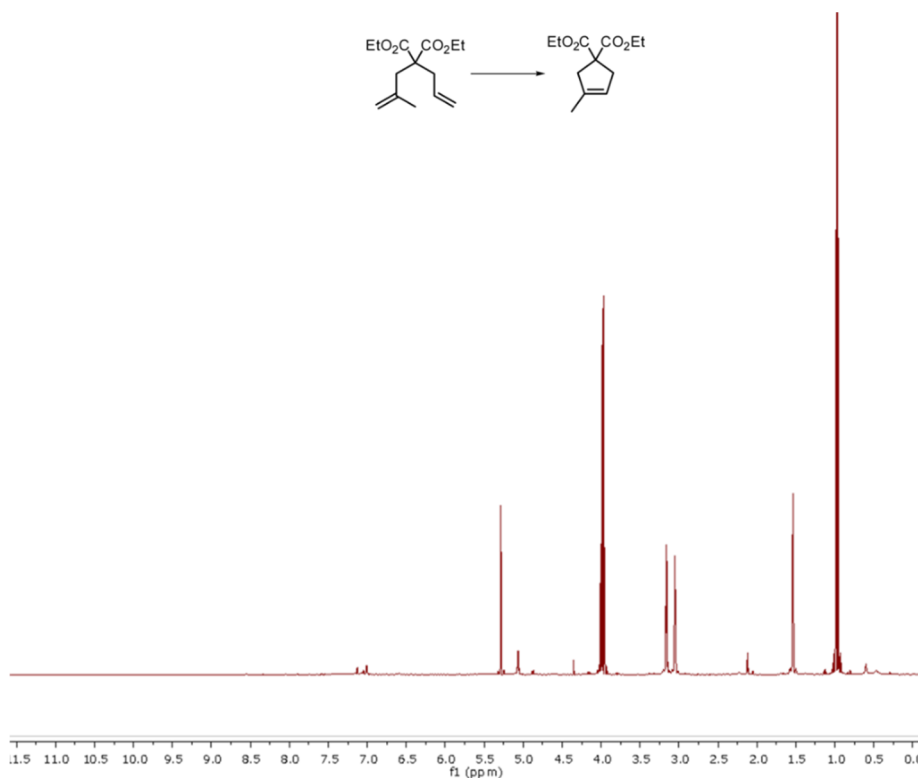
**Figure S37.** RCM of *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% ***cis*-Ru-Phos-I<sub>2</sub>** heating at 80 °C for 10 minutes.



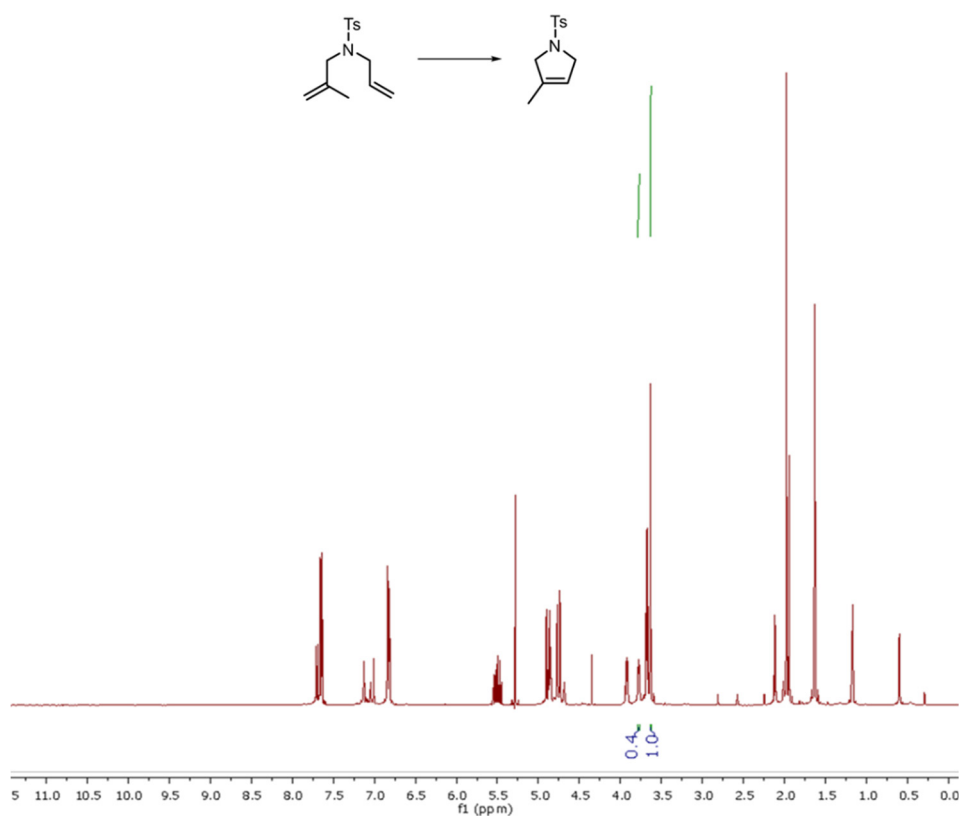
**Figure S38.** RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> heating at 80 °C for 10 minutes.



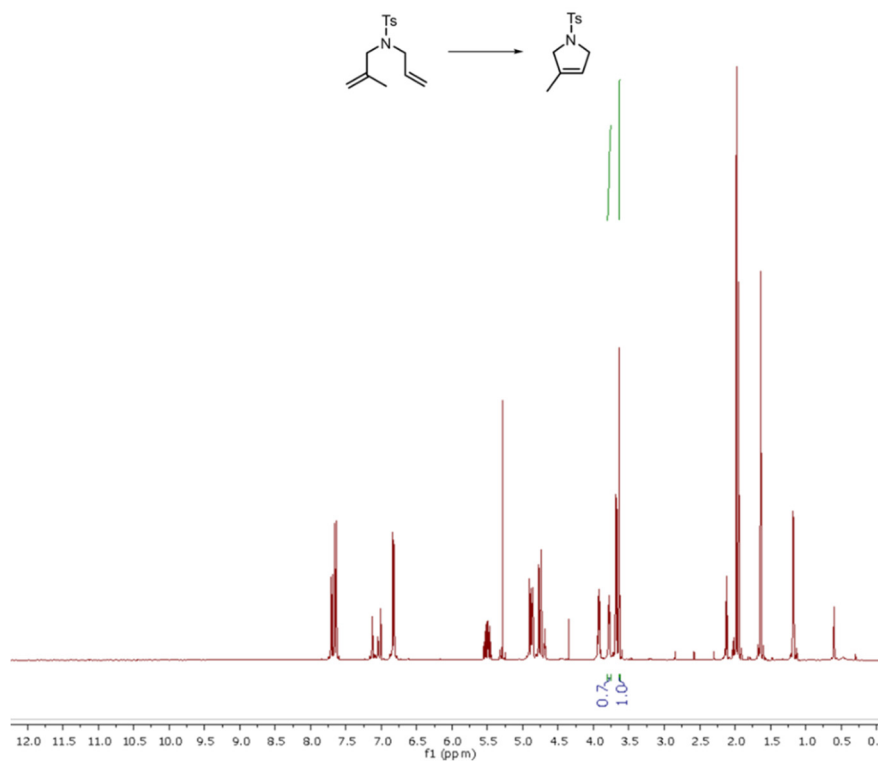
**Figure S39.** RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> heating at 80 °C for 10 minutes.



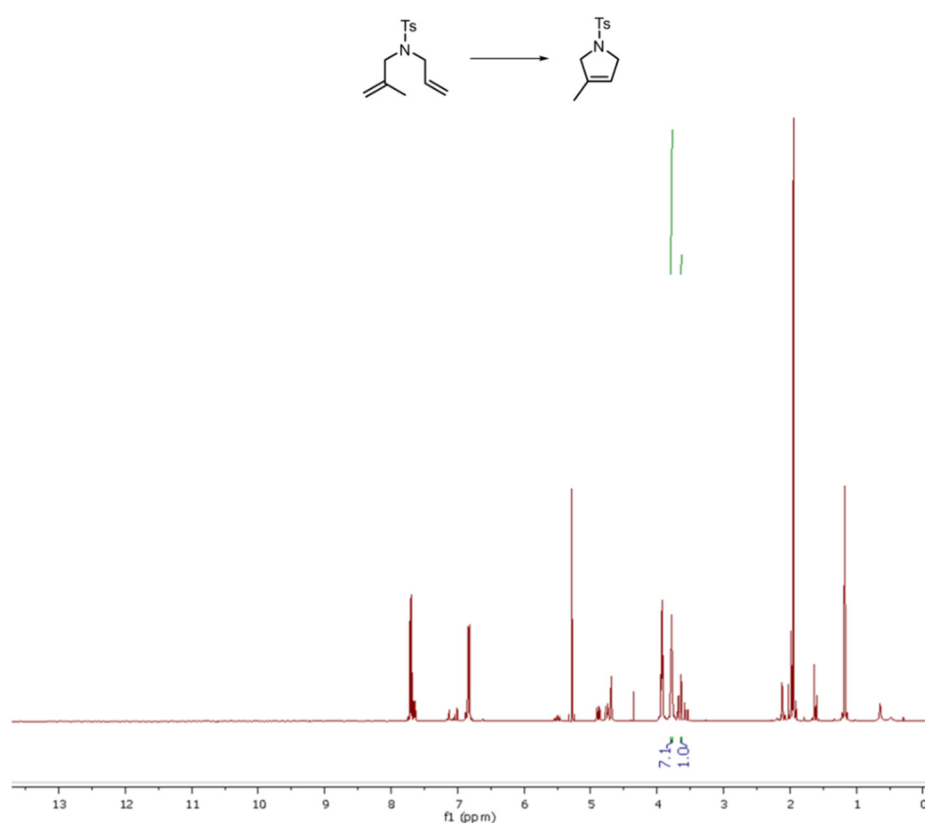
**Figure S40.** RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> heating at 80 °C for 10 minutes.



**Figure S41.** RCM of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> heating at 80 °C for 10 minutes.

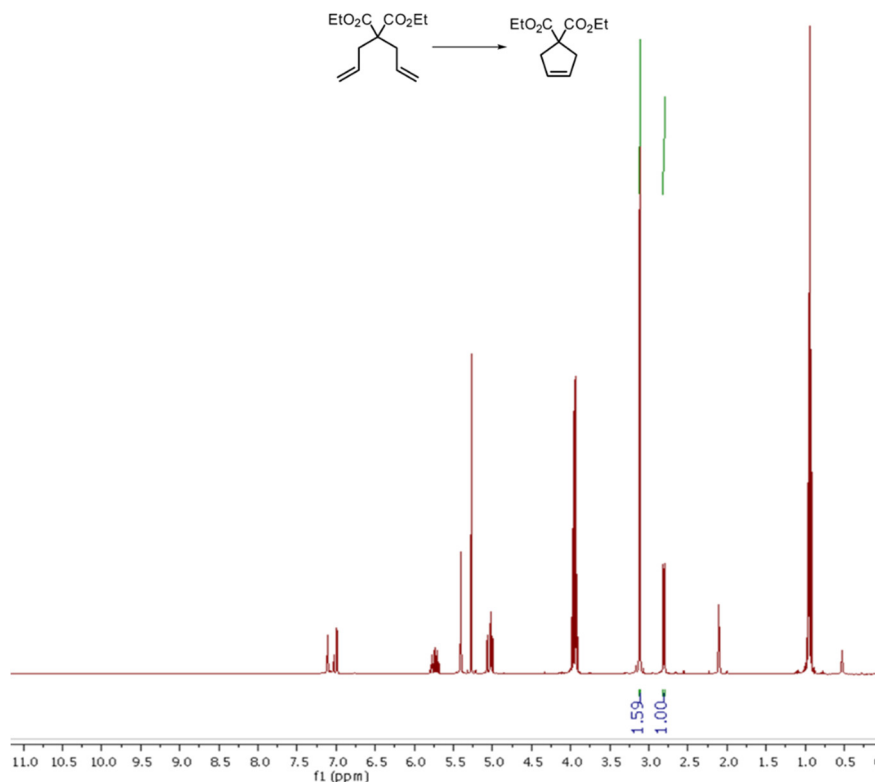


**Figure S42.** RCM of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> heating at 80 °C for 10 minutes.

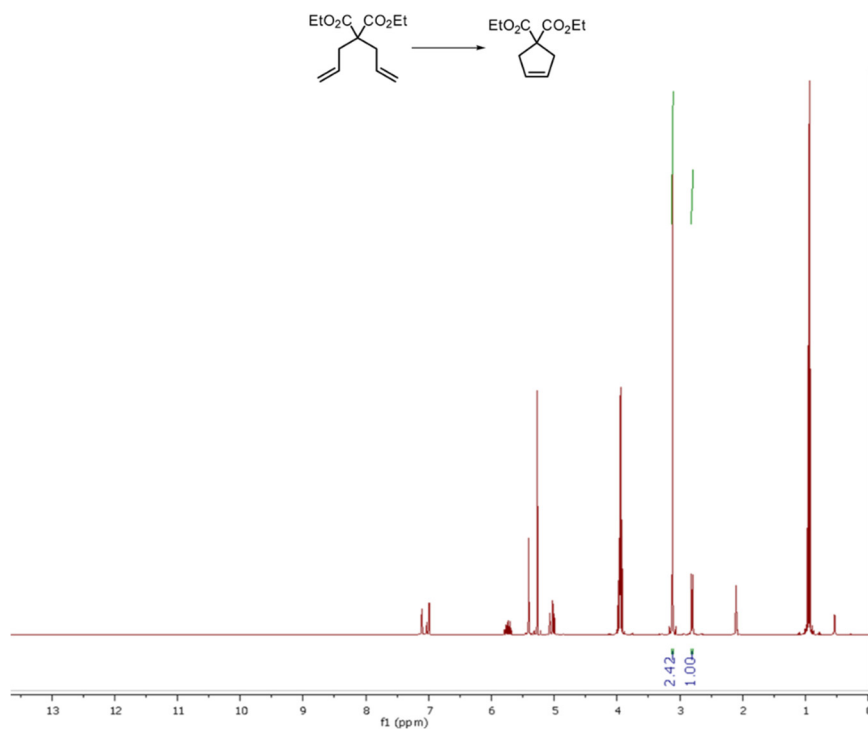


**Figure S43.** RCM of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-Ru-PhosTB-I<sub>2</sub> heating at 80 °C for 10 minutes.

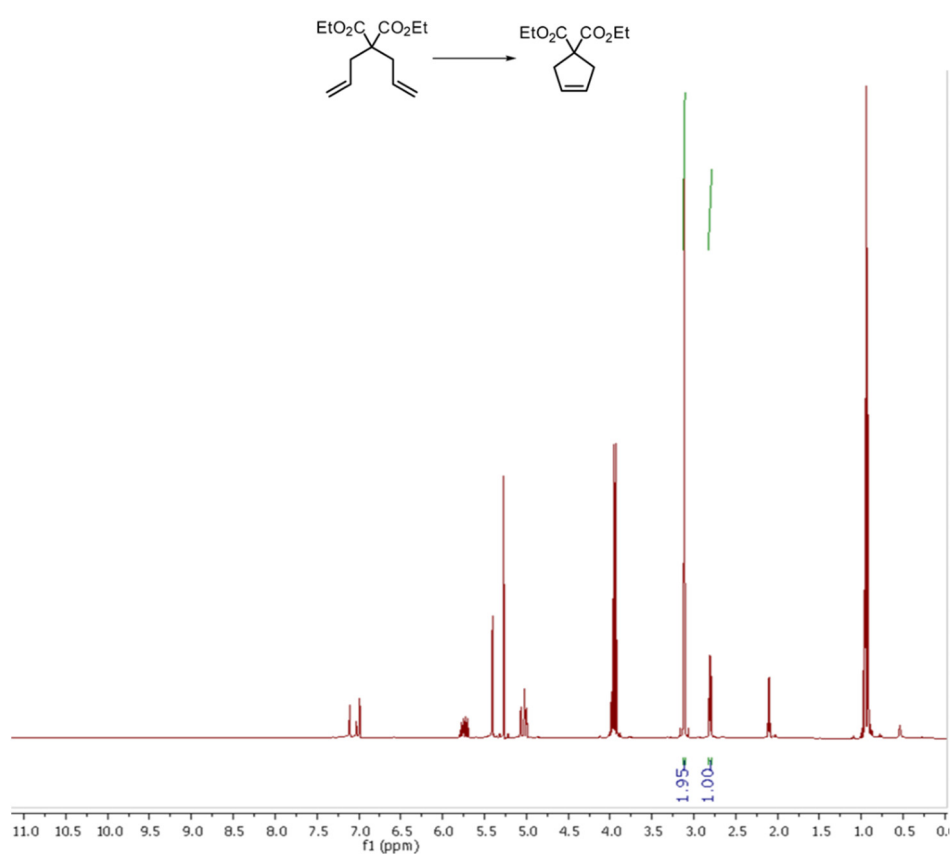
## 6. RCM with different substrates at 350 nm



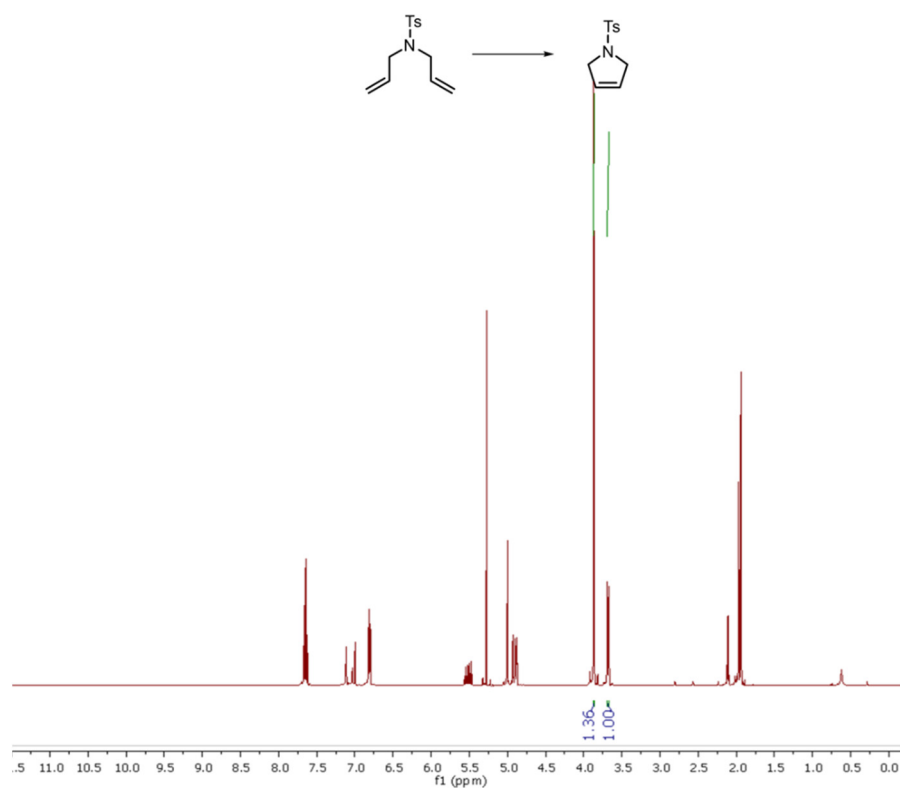
**Figure S44.** RCM of DEDAM. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> irradiation at 350 nm for 2 h.



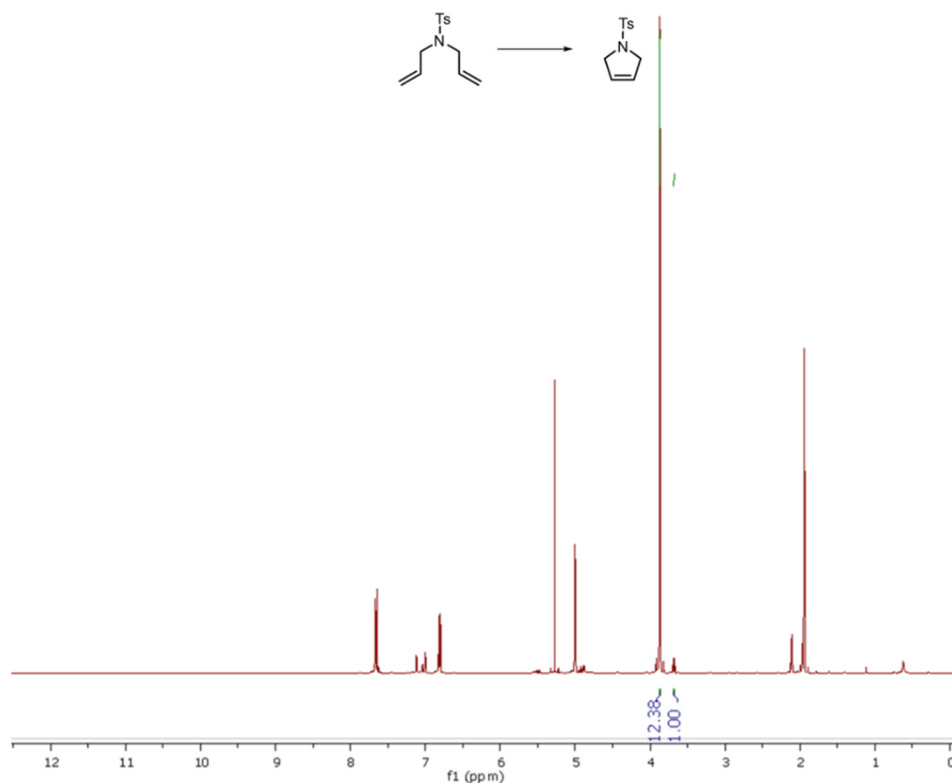
**Figure S45.** RCM of DEDAM. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> irradiation at 350 nm for 2 h.



**Figure S46.** RCM of DEDAM. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> irradiation at 350 nm for 2 h.

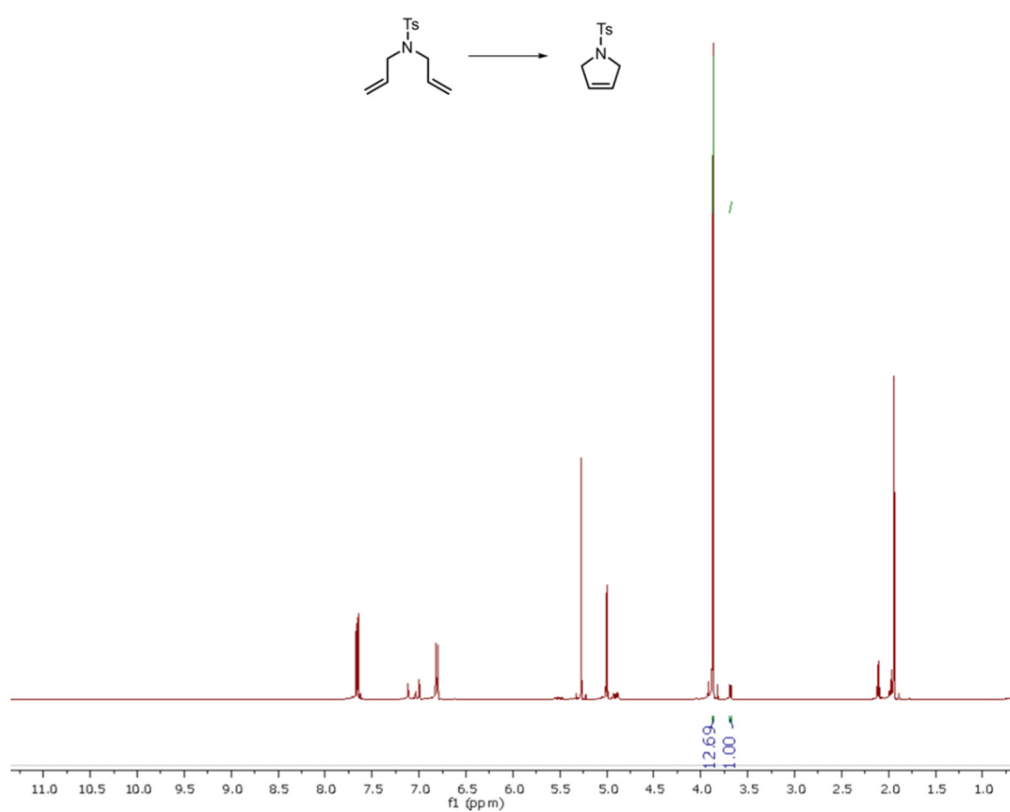


**Figure S47.** RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> irradiation at 350 nm for 2 h.

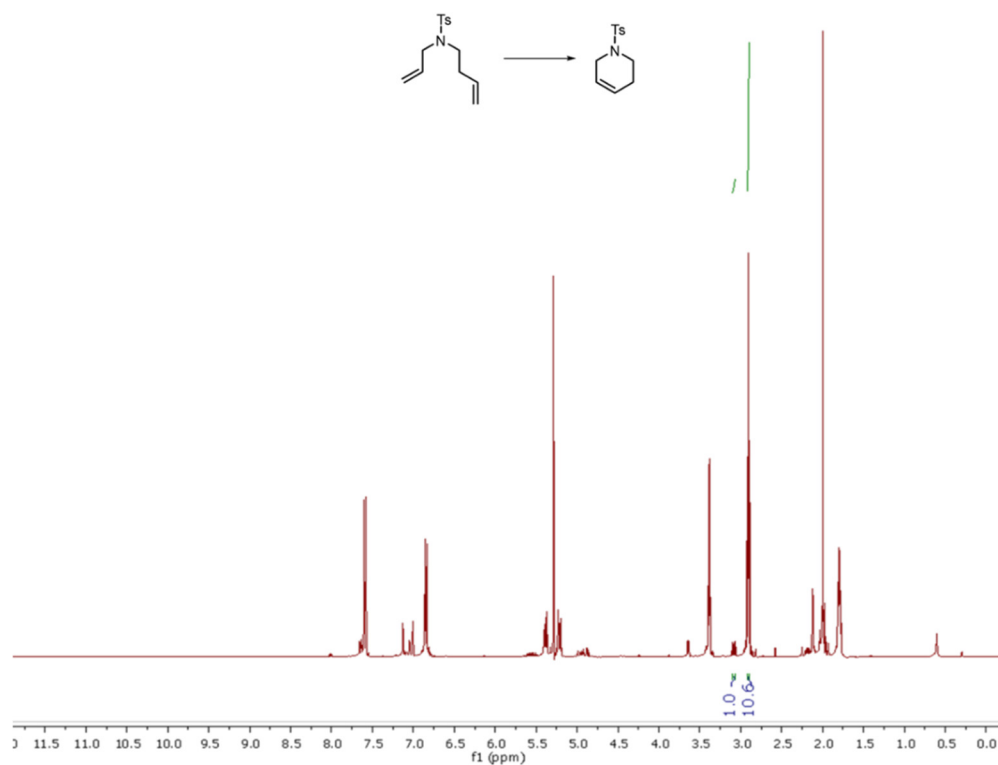


**Figure S48.** RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> irradiation at 350 nm for 2 h.

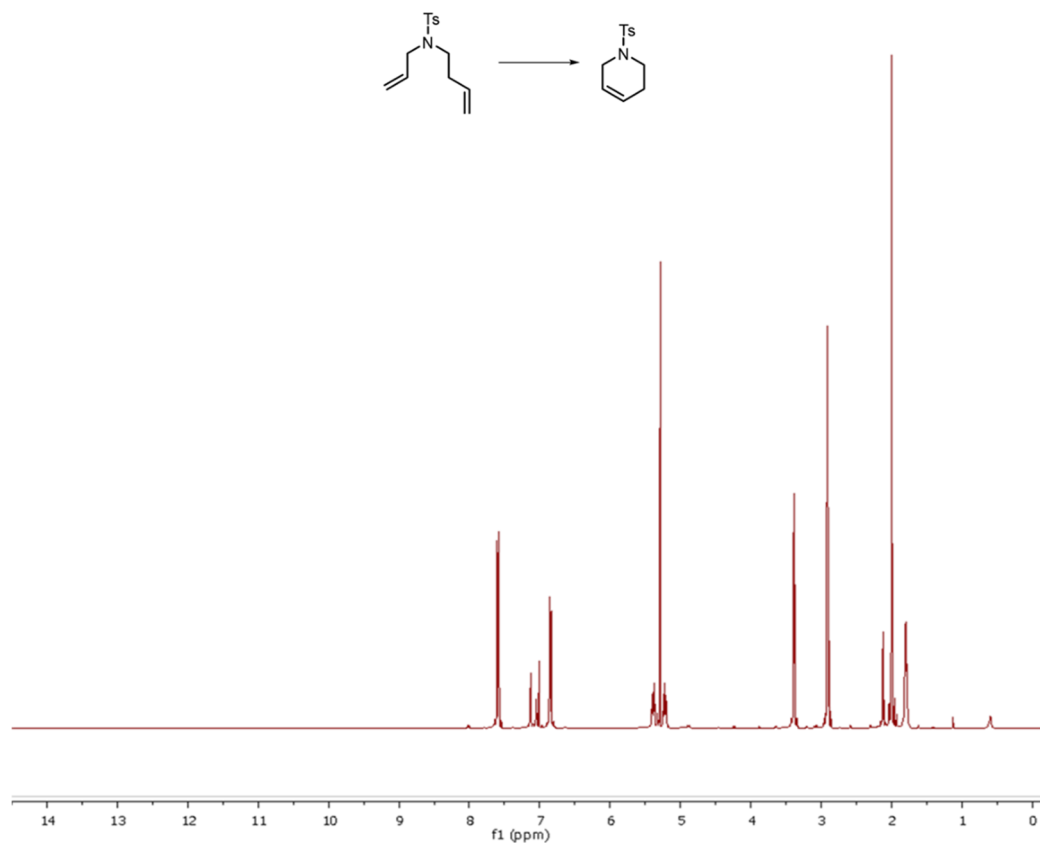




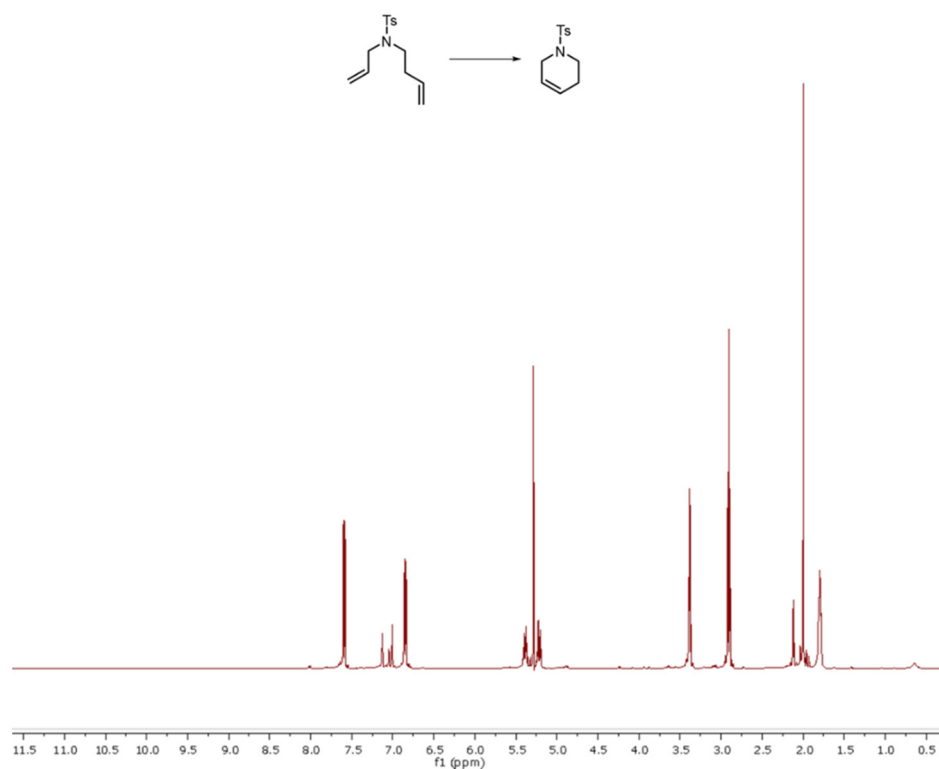
**Figure S49.** RCM of *N,N*-diallyl-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> irradiation at 350 nm for 2 h.



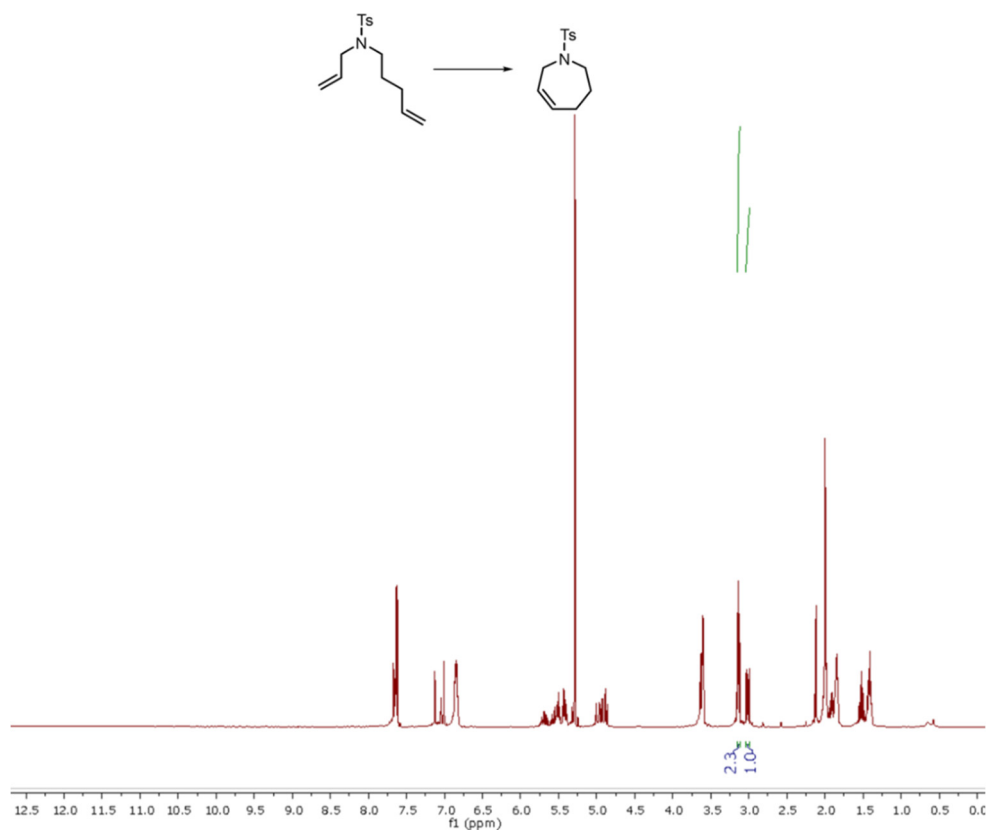
**Figure S50.** RCM of *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-Cl**<sub>2</sub> irradiation at 350 nm for 2 h.



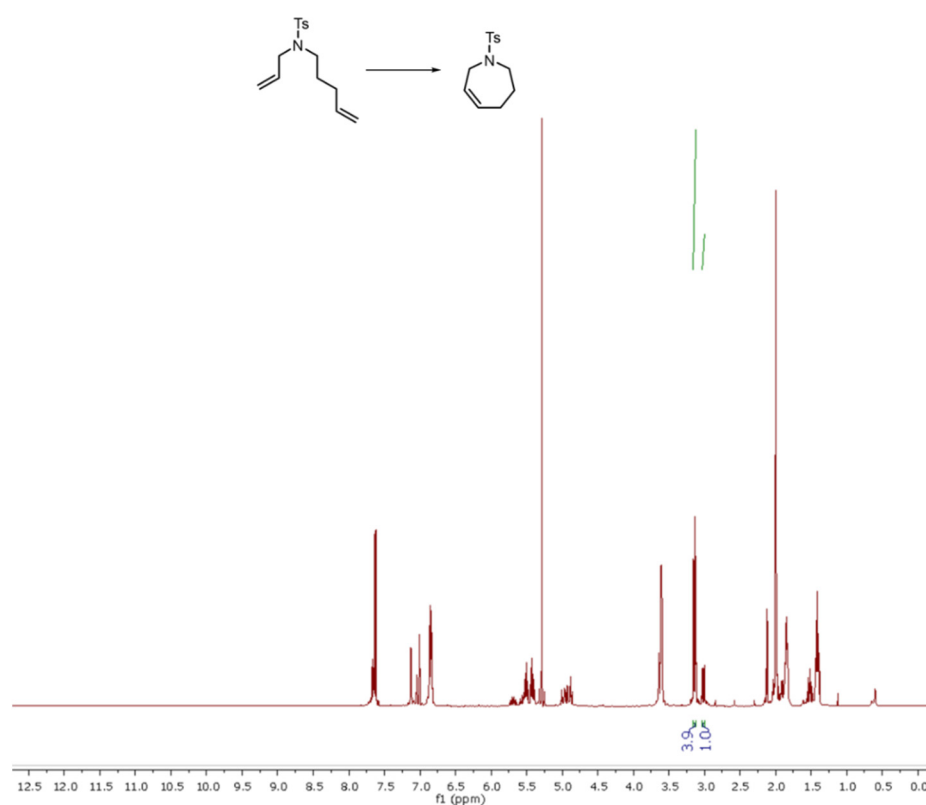
**Figure S51.** RCM of *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-**Ru-Phos-Br**<sub>2</sub> irradiation at 350 nm for 2 h.



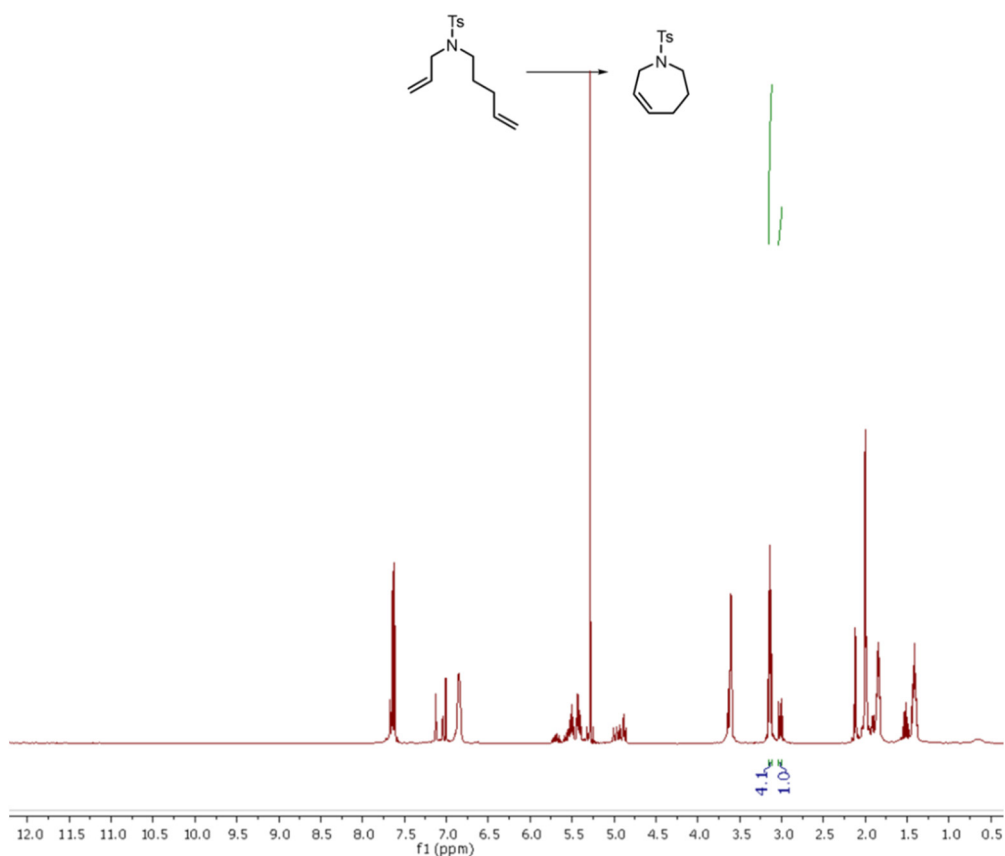
**Figure S52.** RCM of *N*-allyl-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> irradiation at 350 nm for 2 h.



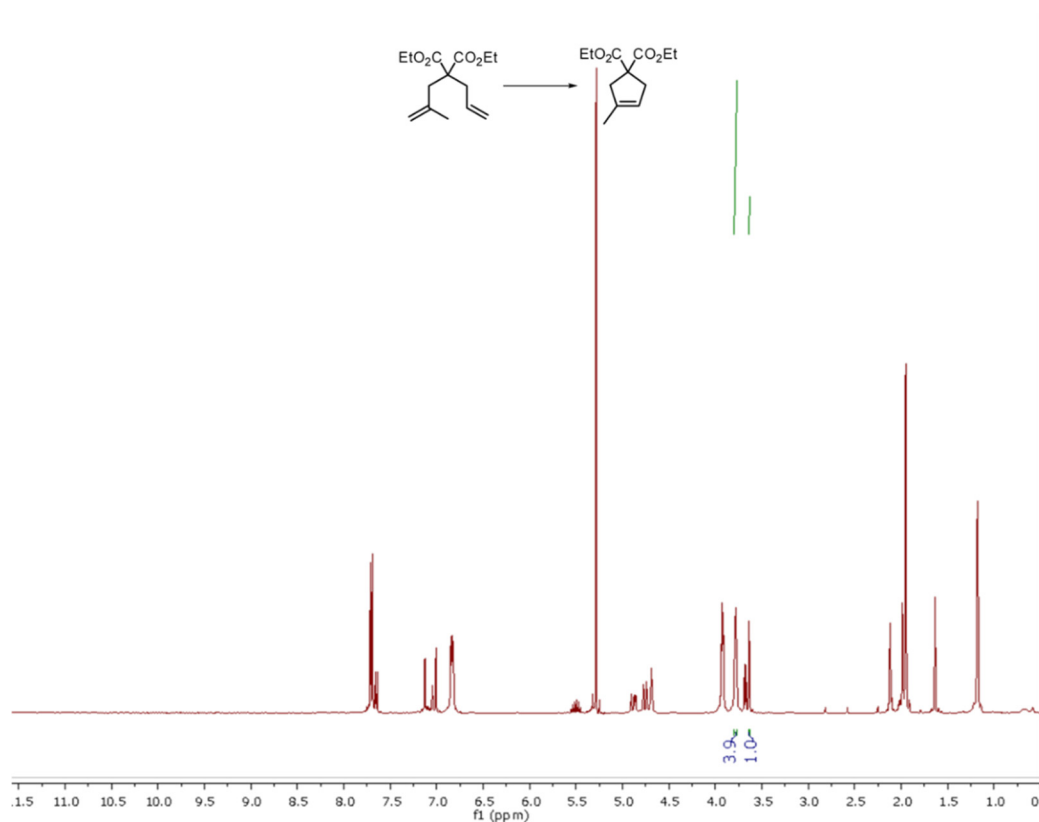
**Figure S53.** RCM of *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> irradiation at 350 nm for 2 h.



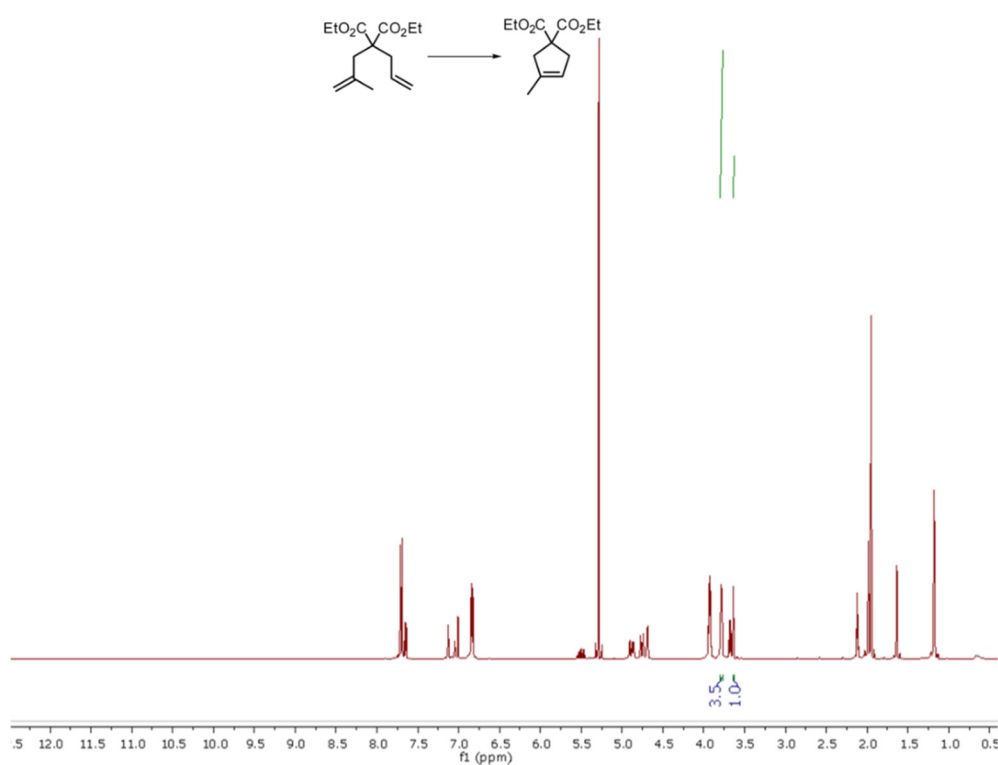
**Figure S54.** RCM of *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> irradiation at 350 nm for 2 h.



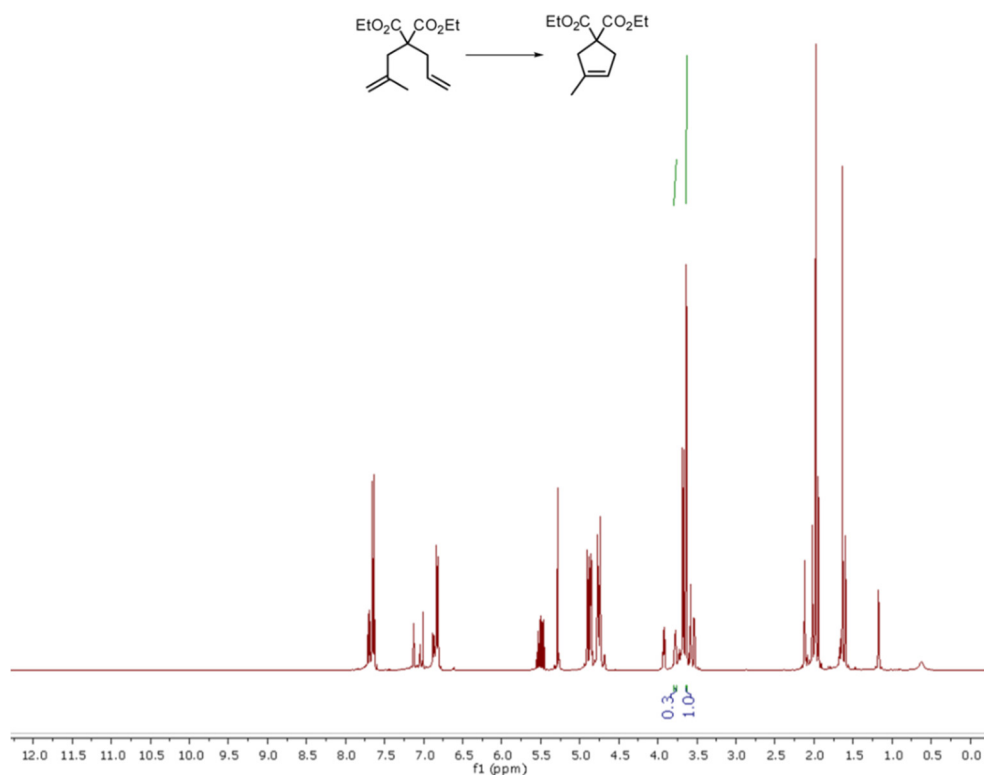
**Figure S55.** RCM of *N*-allyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-I**<sub>2</sub> irradiation at 350 nm for 2 h.



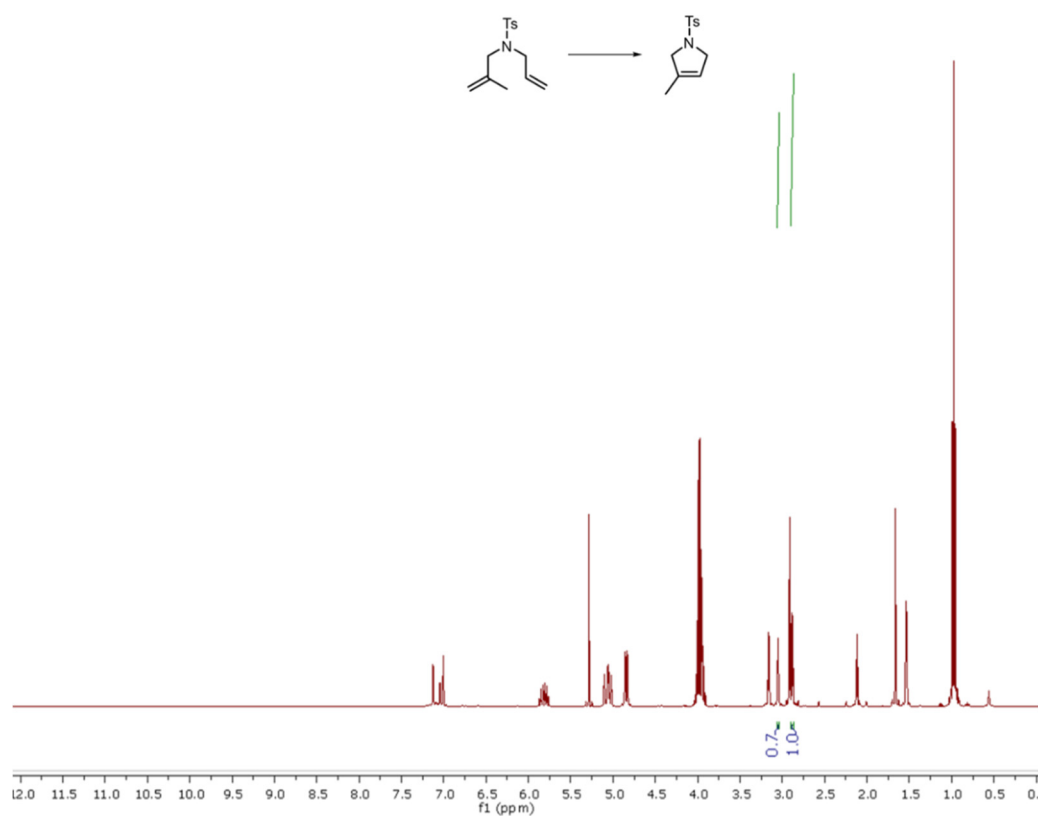
**Figure S56.** RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-Cl**<sub>2</sub> irradiation at 350 nm for 2 h.



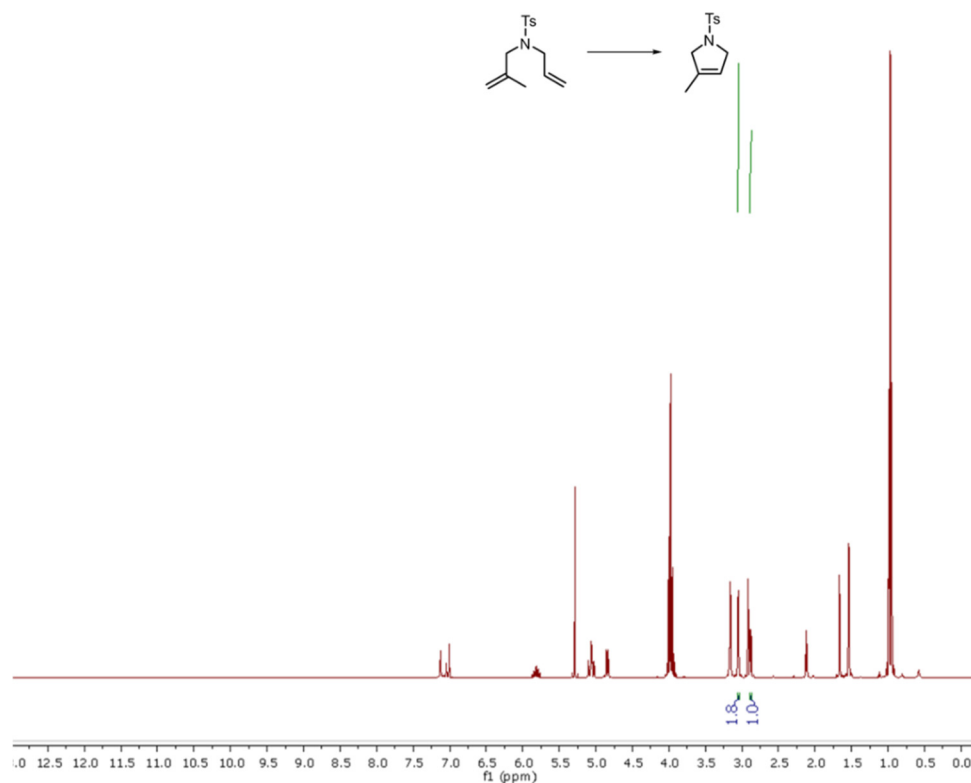
**Figure S57.** RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> irradiation at 350 nm for 2 h.



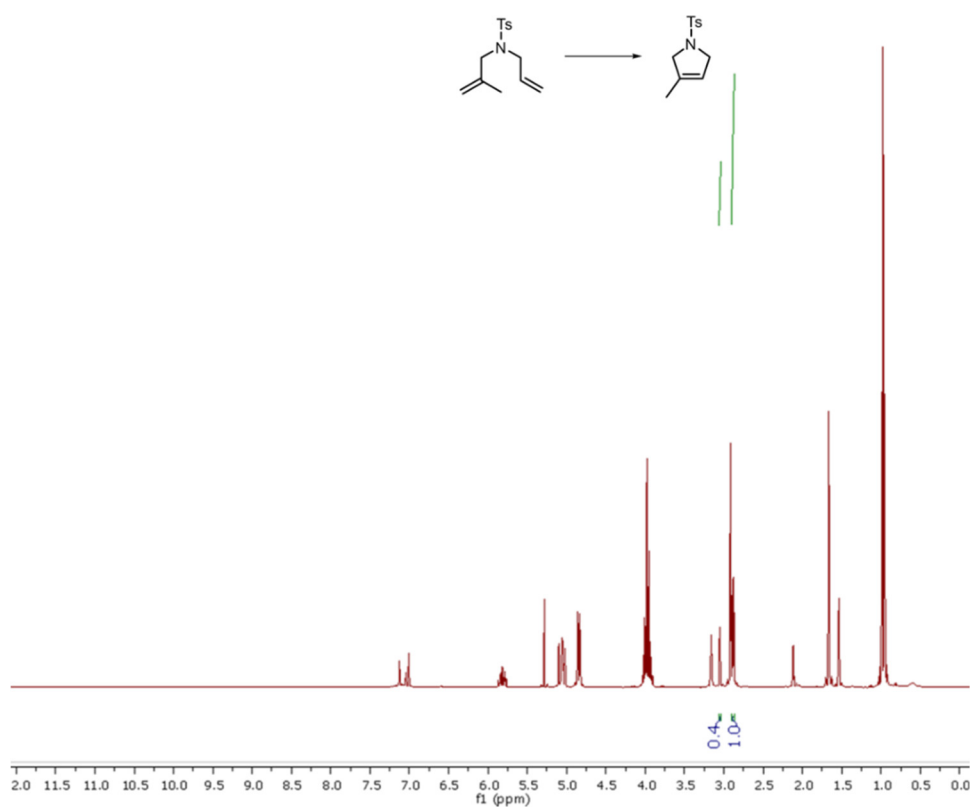
**Figure S58.** RCM of diethyl 2-allyl-2-(2-methylallyl)malonate. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-I<sub>2</sub> irradiation at 350 nm for 2 h.



**Figure S59.** RCM of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Cl<sub>2</sub> irradiation at 350 nm for 2 h.



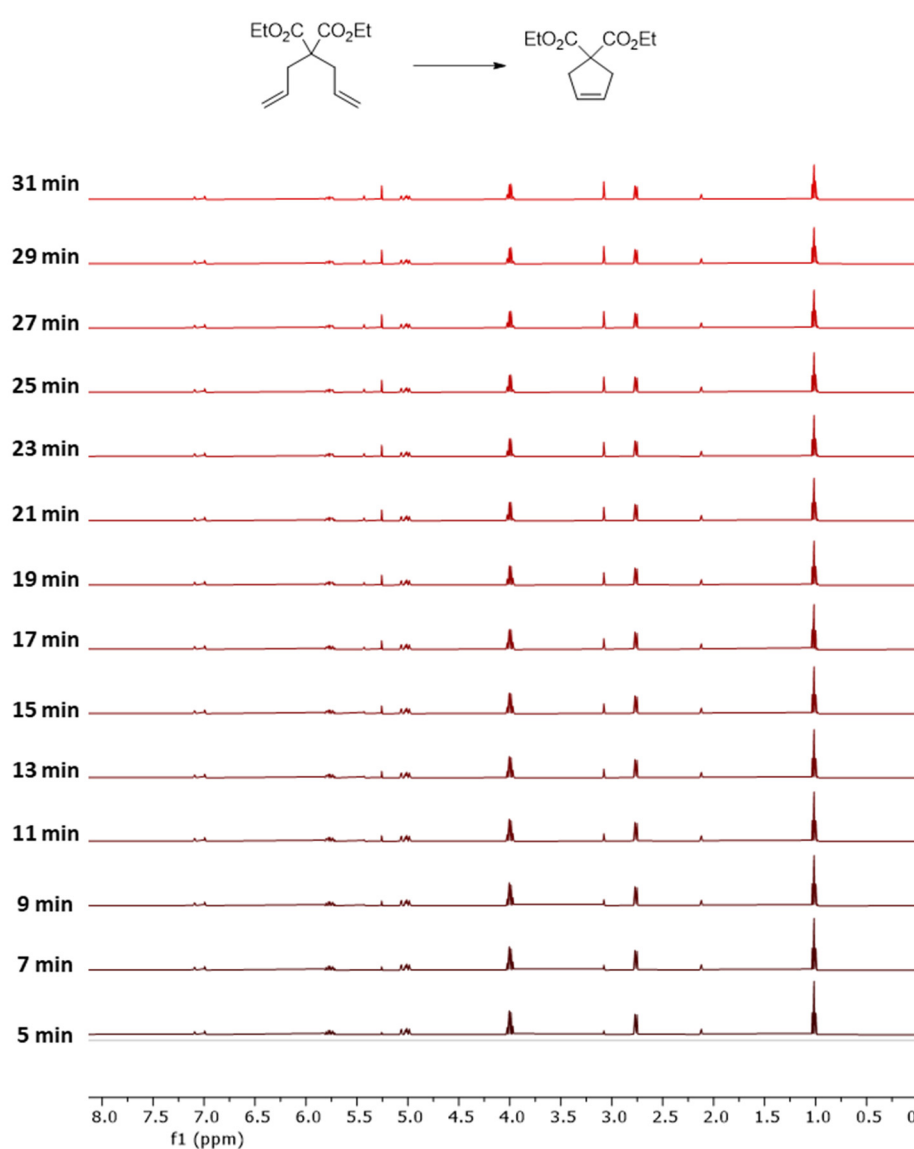
**Figure S60.** RCM of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-Ru-Phos-Br<sub>2</sub> irradiation at 350 nm for 2 h.



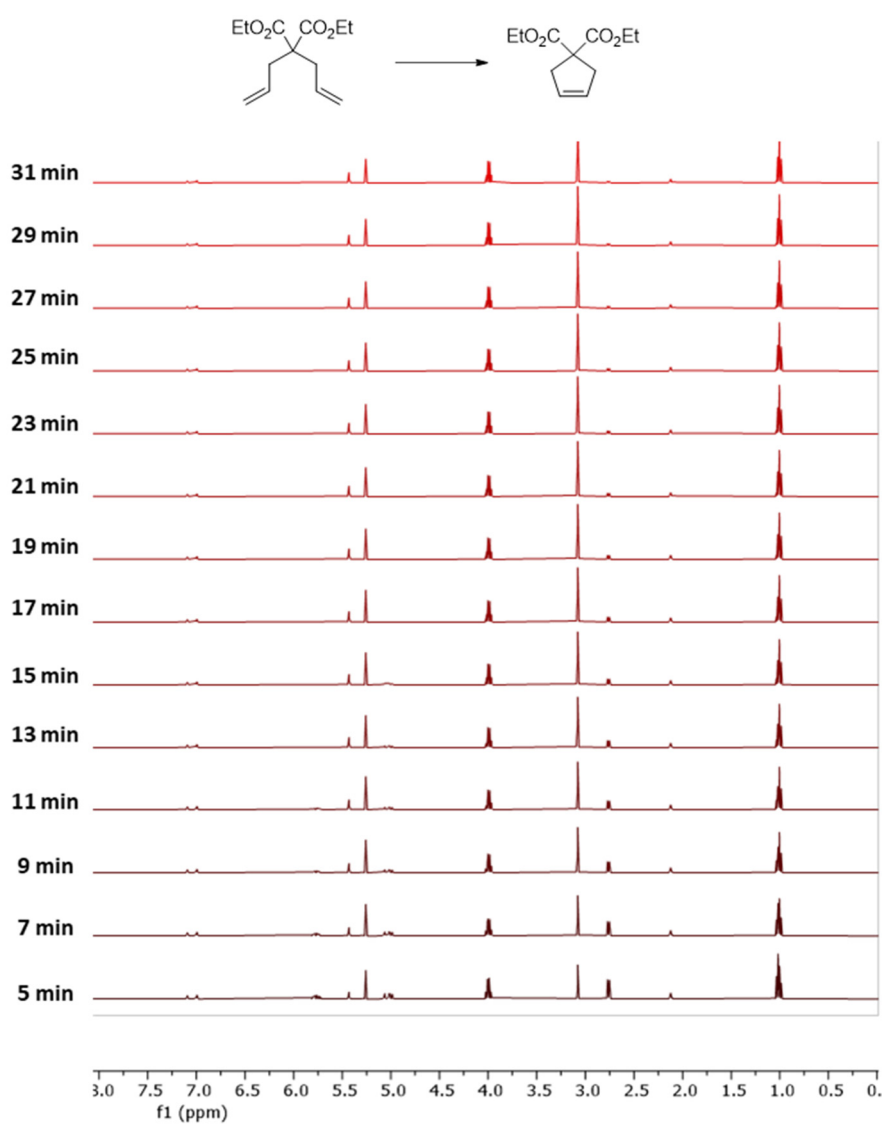
**Figure S61.** RCM of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide. Reaction conditions: toluene-*d*<sub>8</sub>, 0.1 M, 1 mol% *cis*-**Ru-Phos-I**<sub>2</sub> irradiation at 350 nm for 2 h.

## 7. Kinetic profile study with different substrates

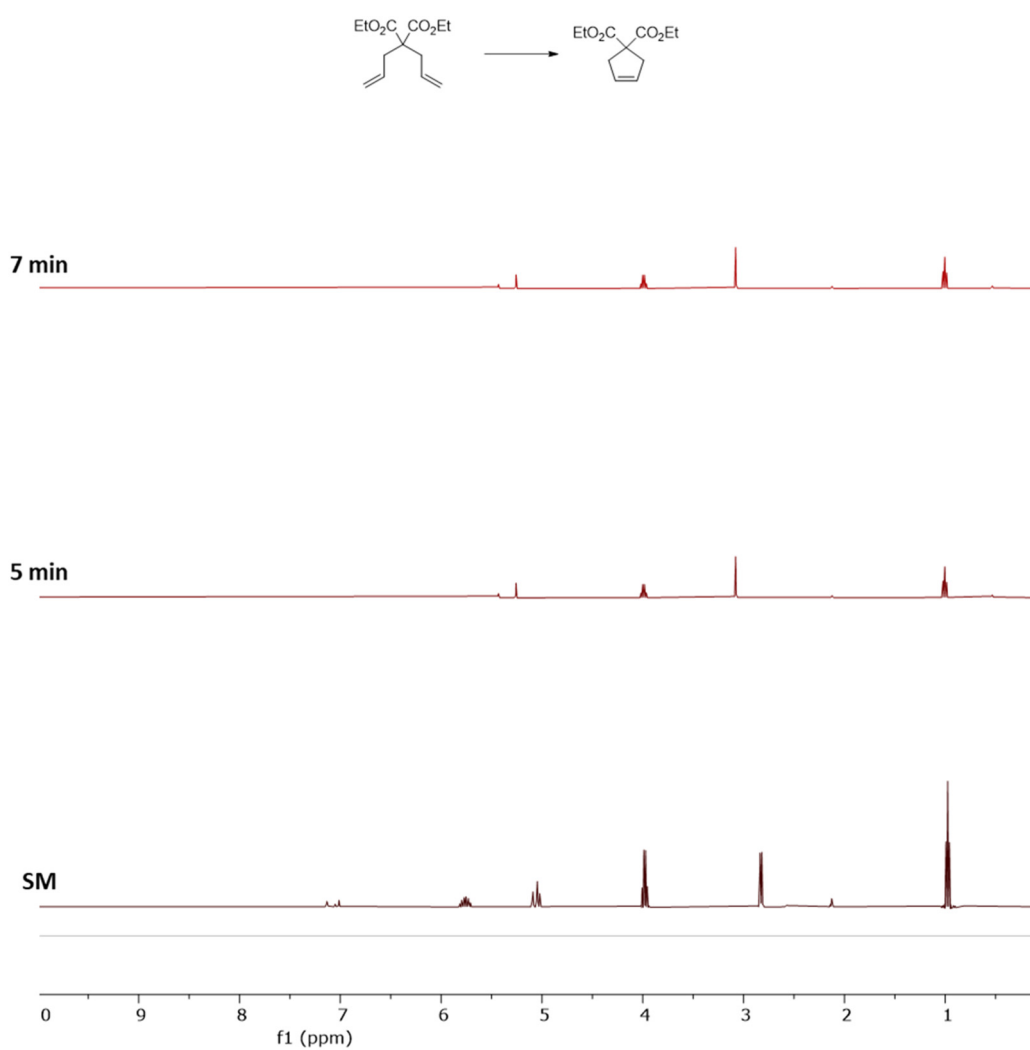




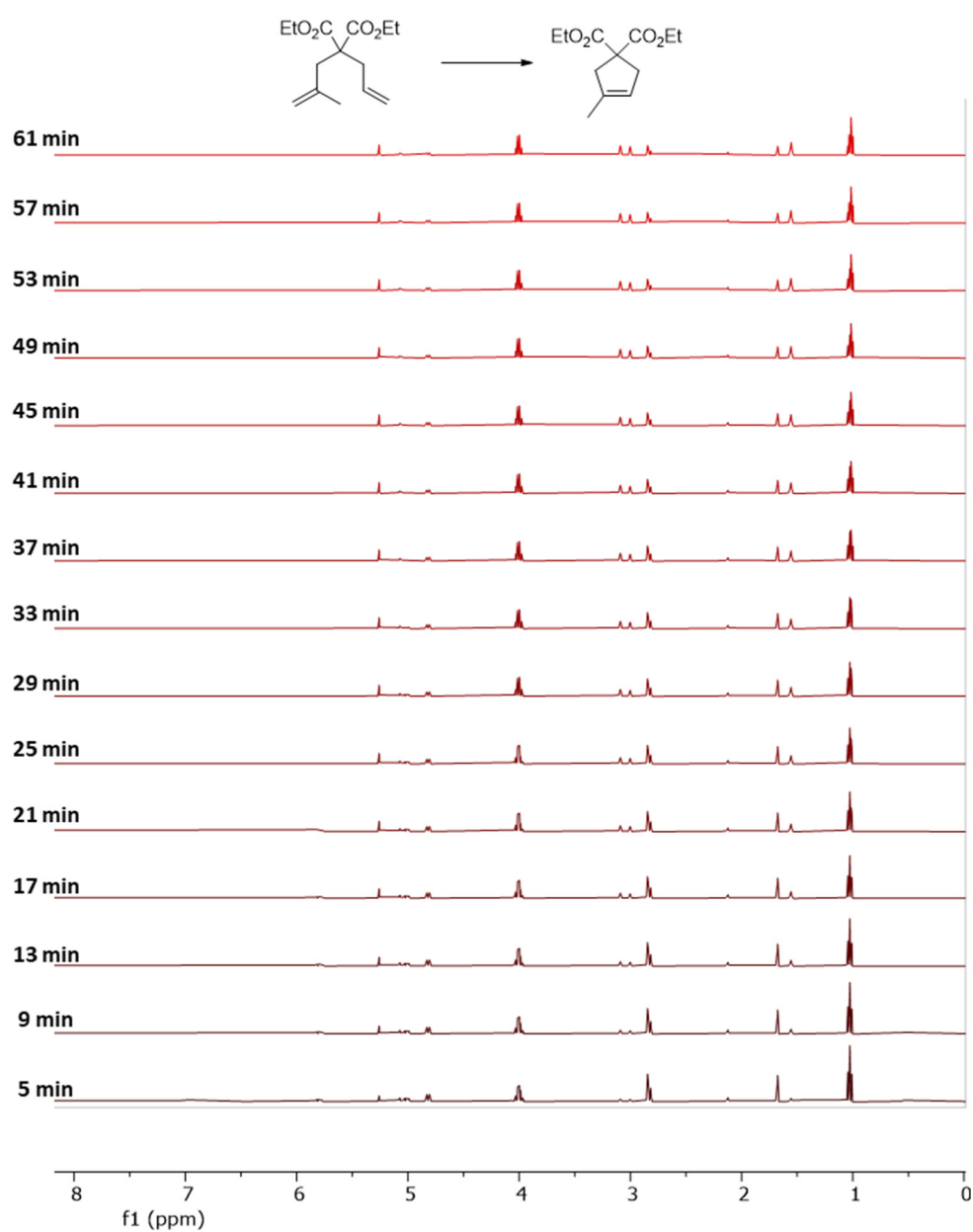
**Figure S62.** <sup>1</sup>H-NMR spectra of the kinetic profile of RCM reaction of DEDAM in toluene-*d*<sub>8</sub>, 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-Cl<sub>2</sub>.



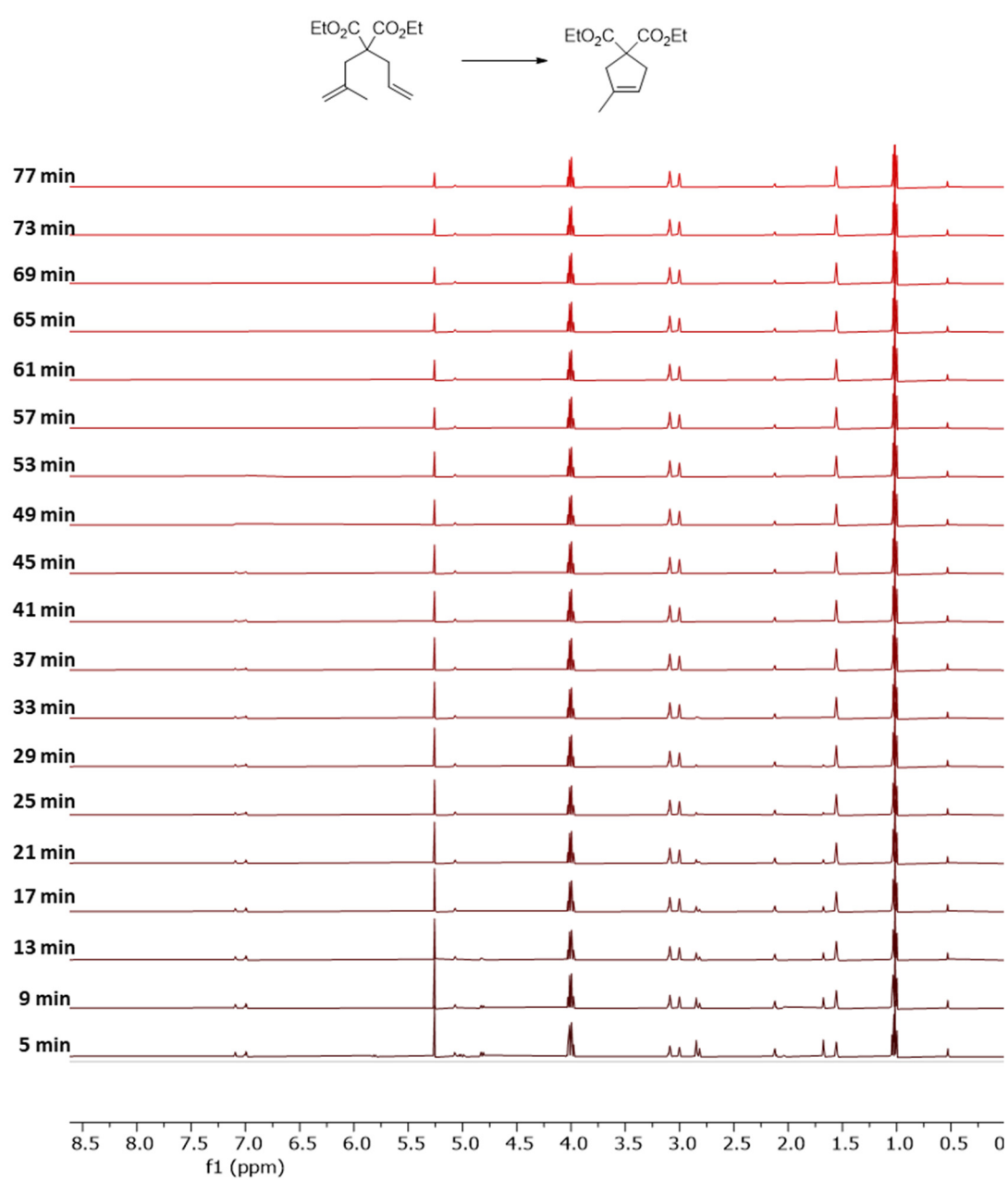
**Figure S63.** <sup>1</sup>H-NMR spectra of the kinetic profile of RCM reaction of DEDAM in toluene-*d*<sub>8</sub>, 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub>.



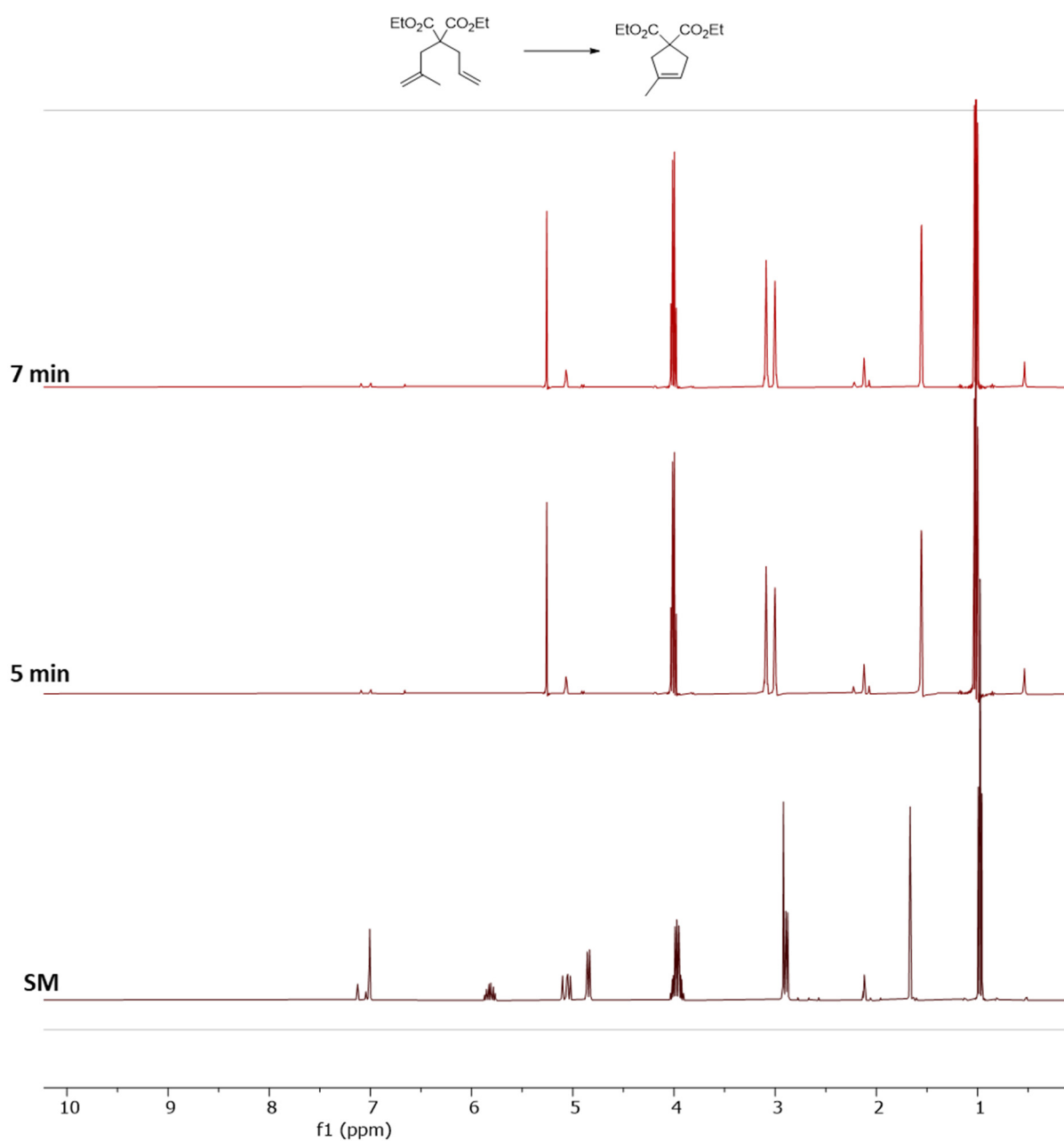
**Figure S64.**  $^1\text{H}$ -NMR spectra of the kinetic profile of RCM reaction of DEDAM in toluene- $d_8$ , 0.1M, 100  $^\circ\text{C}$ , 1 mol% of *cis*-Ru-Phos- $\text{I}_2$ .



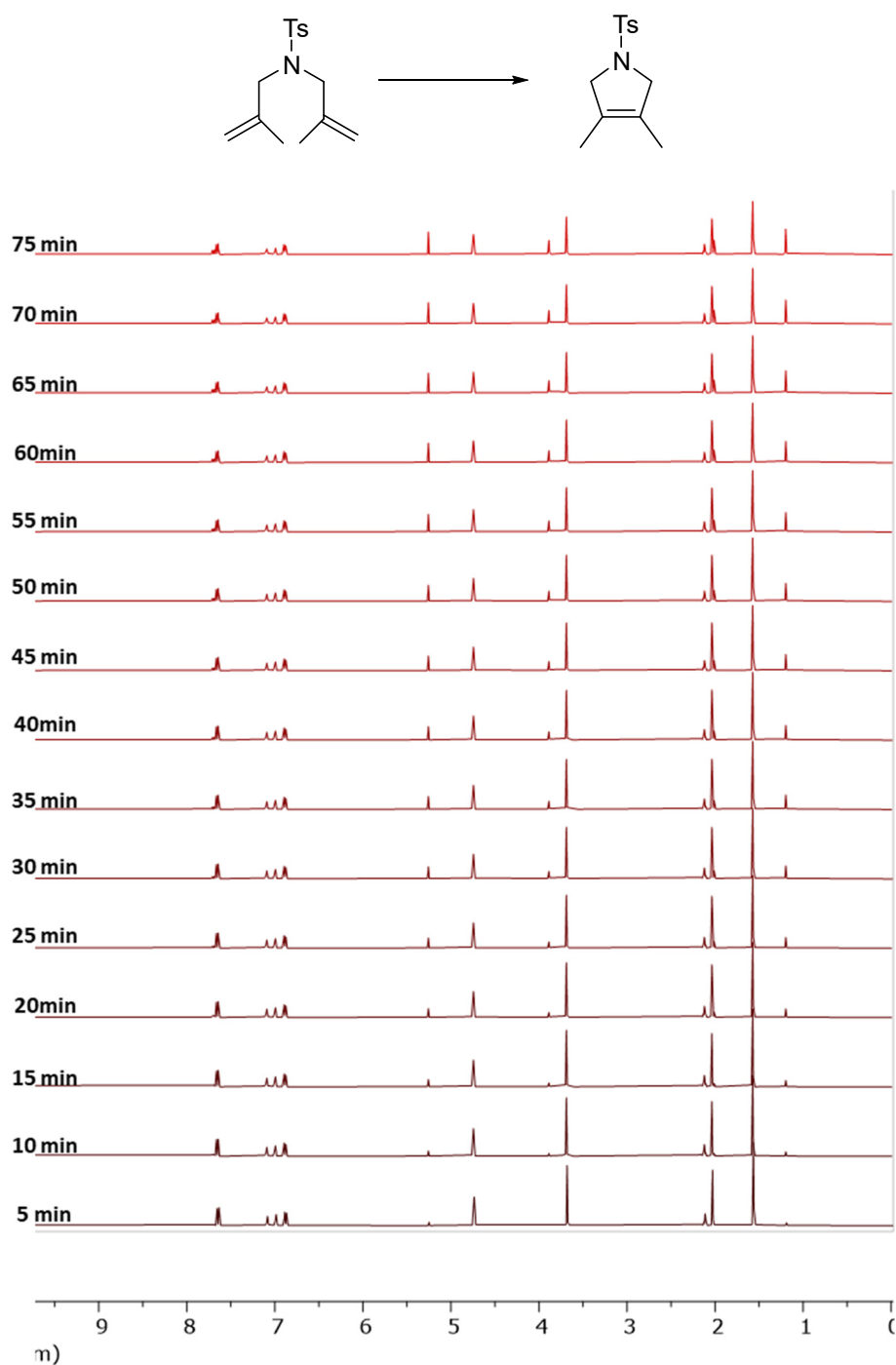
**Figure S65.**  $^1\text{H}$ -NMR spectra of the kinetic profile of RCM reaction of diethyl 2-allyl-2-(2-methylallyl)malonate in toluene- $d_8$ , 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos- $\text{Cl}_2$ .



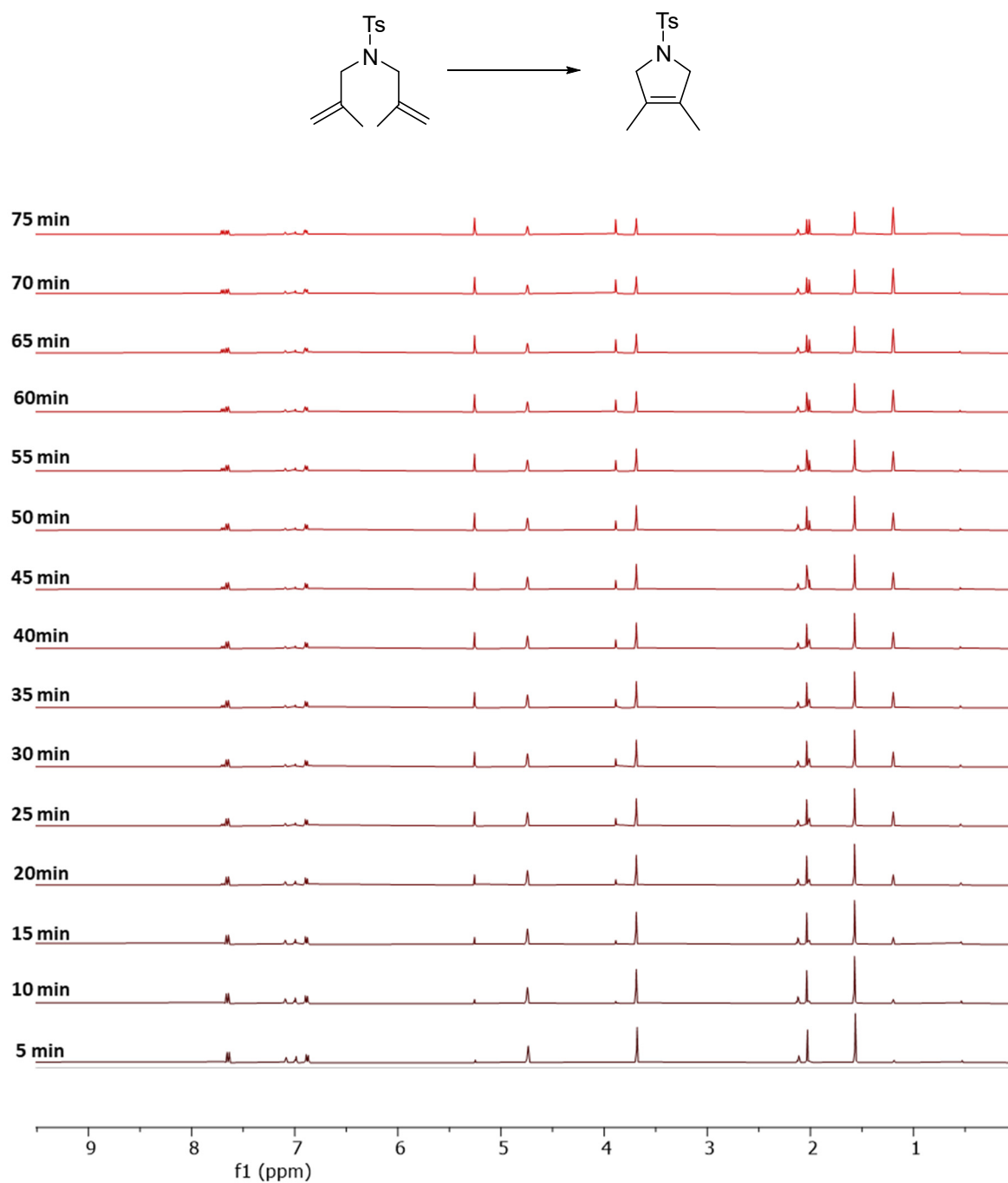
**Figure S66.** <sup>1</sup>H-NMR spectra of the kinetic profile of RCM reaction of diethyl 2-allyl-2-(2-methylallyl)malonate in toluene-*d*<sub>8</sub>, 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub>.



**Figure S67.**  $^1\text{H}$ -NMR spectra of the kinetic profile of RCM reaction of diethyl 2-allyl-2-(2-methylallyl)malonate in toluene- $d_8$ , 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-**I**<sub>2</sub>.

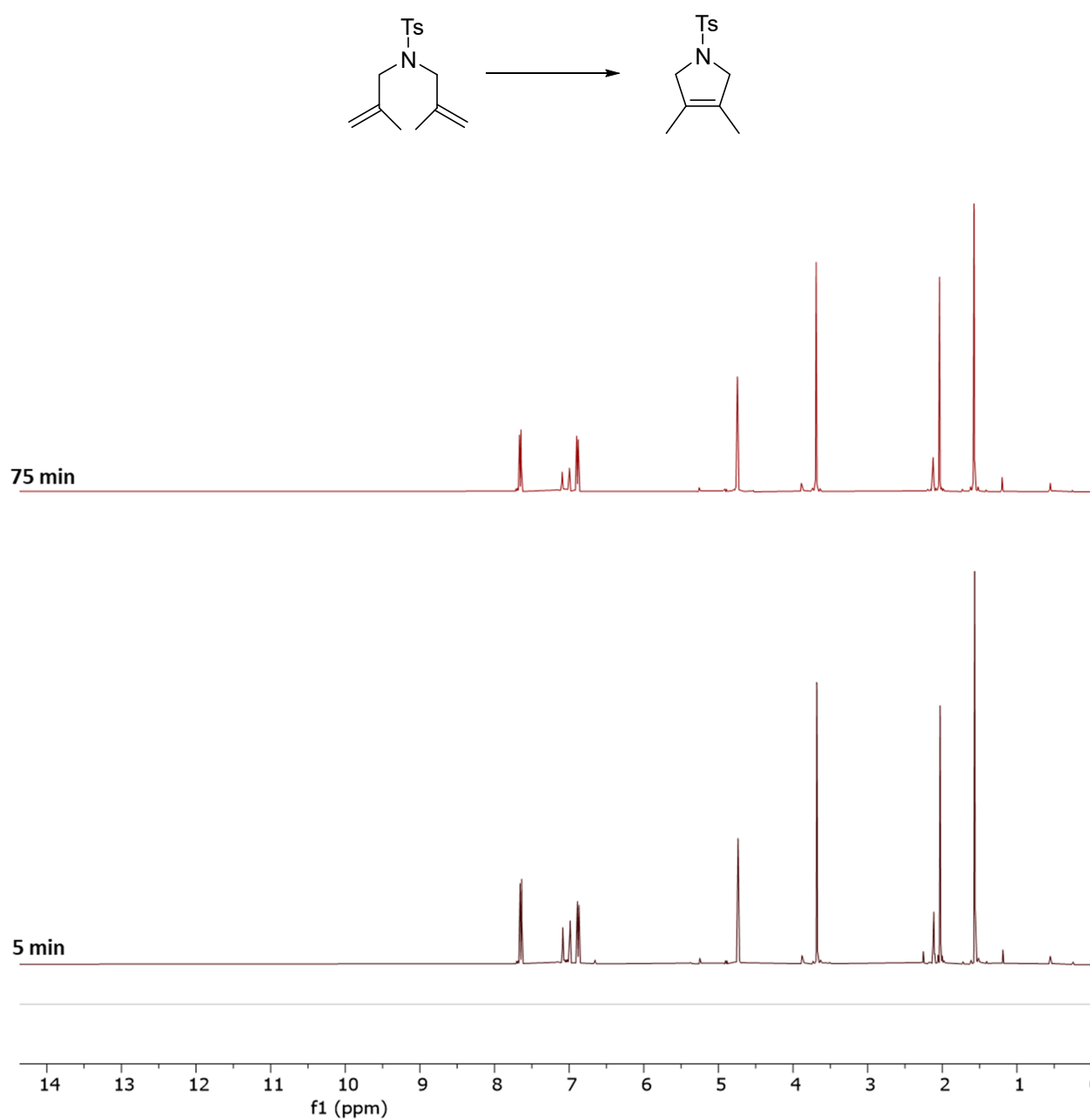


**Figure S68.** <sup>1</sup>H-NMR spectra of the kinetic profile of RCM reaction of 4-methyl-*N,N*-bis(2-methylallyl)benzenesulfonamide in toluene-*d*<sub>8</sub>, 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-Cl<sub>2</sub>.



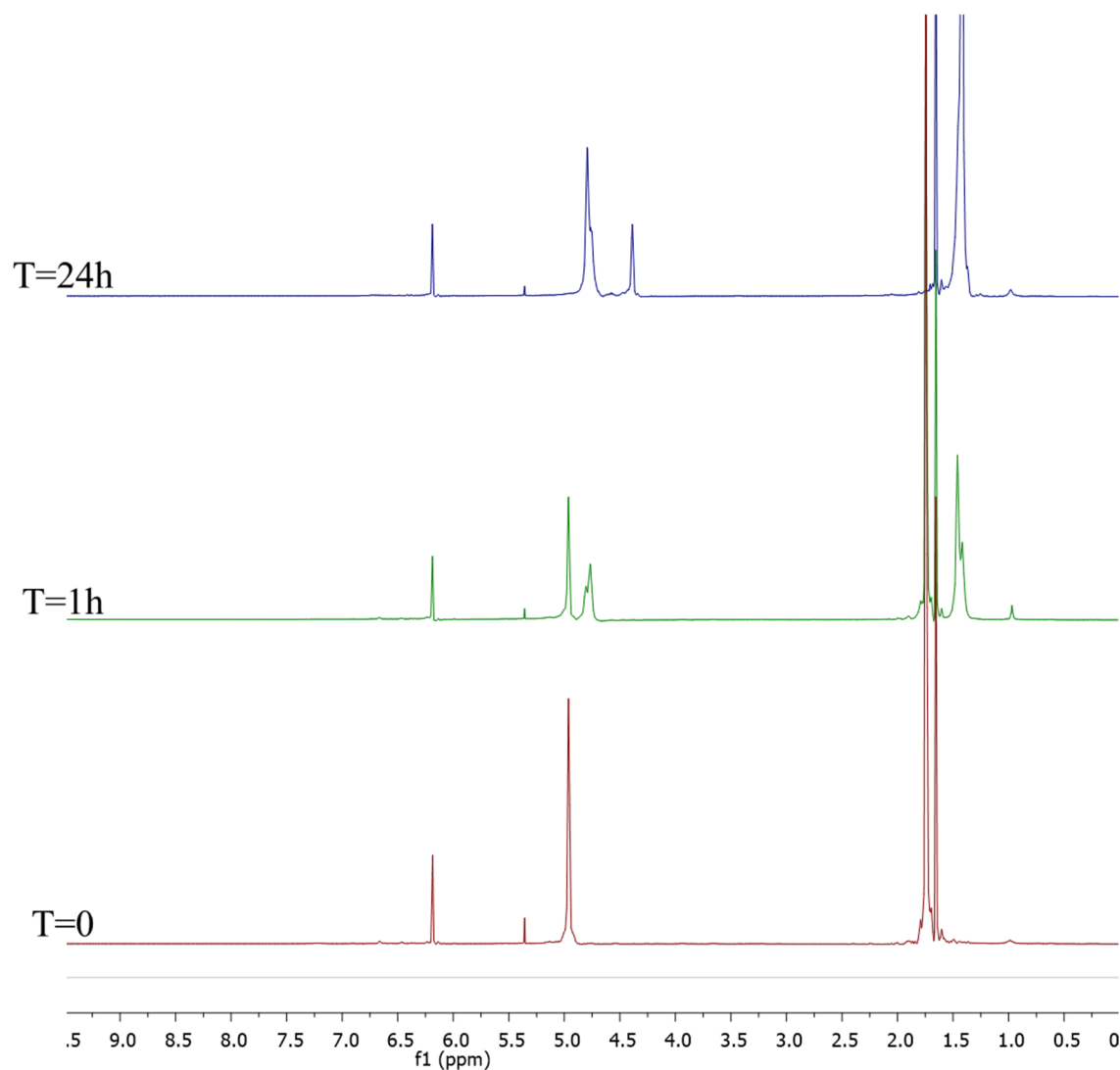
**Figure S69.** <sup>1</sup>H-NMR spectra of the kinetic profile of RCM reaction of 4-methyl-*N,N*-bis(2-methylallyl)benzenesulfonamide in toluene-*d*<sub>8</sub>, 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-Br<sub>2</sub>.



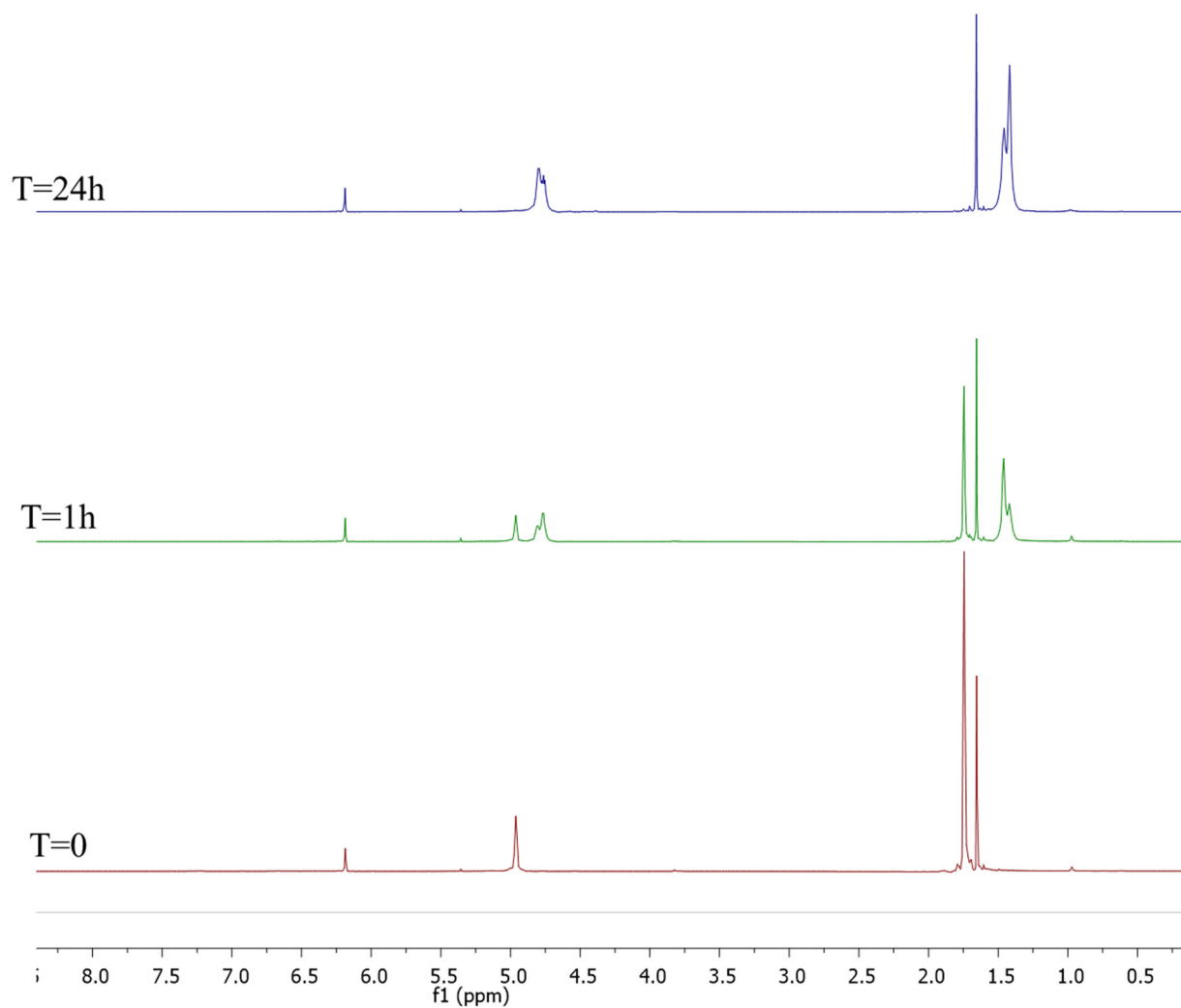


**Figure S70.** <sup>1</sup>H-NMR spectra of the kinetic profile of RCM reaction of 4-methyl-*N,N*-bis(2-methylallyl)benzenesulfonamide in toluene-*d*<sub>8</sub>, 0.1M, 100 °C, 1 mol% of *cis*-Ru-Phos-I<sub>2</sub>.

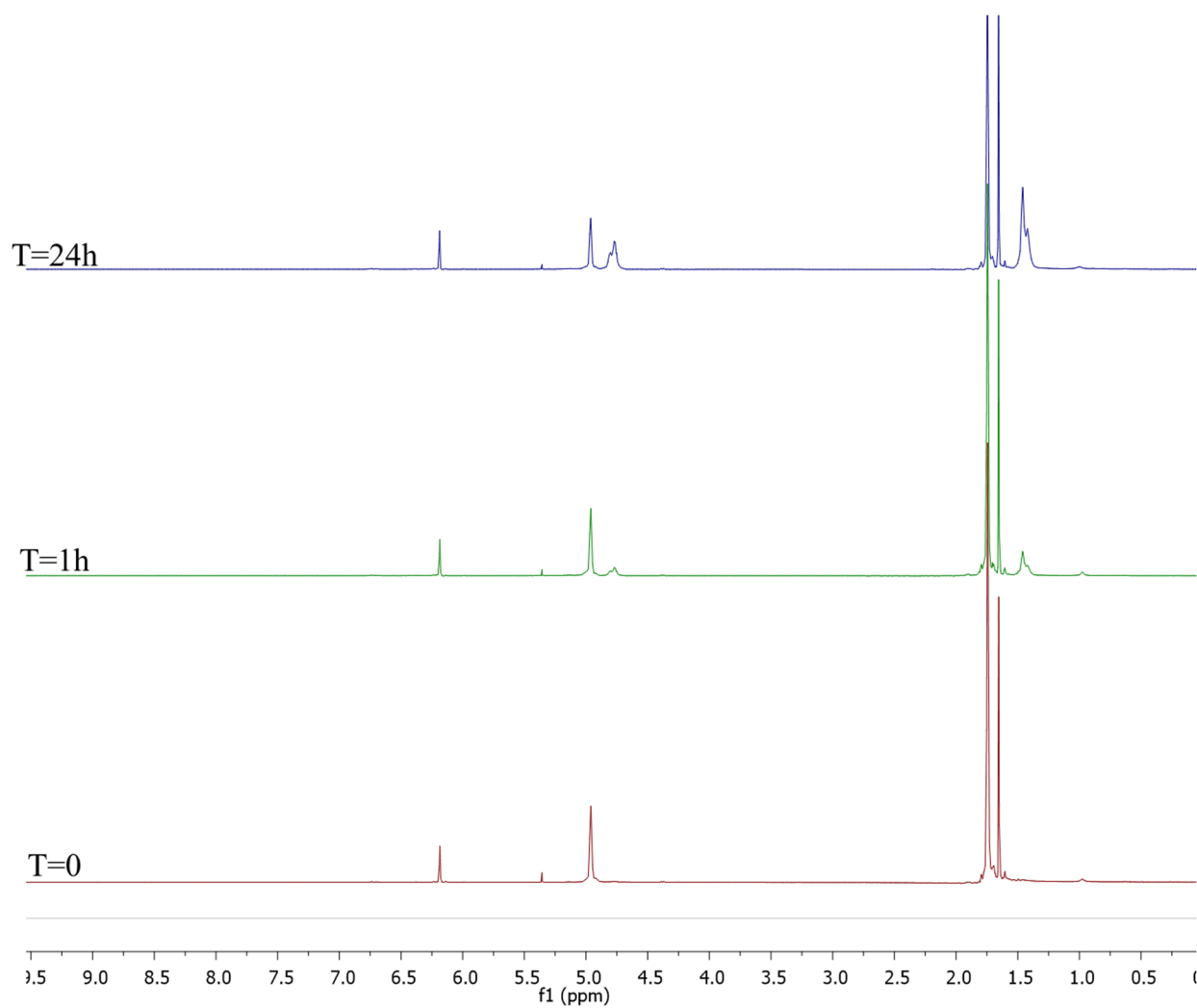
## 8. ROMP study with COD under thermal and photochemical conditions



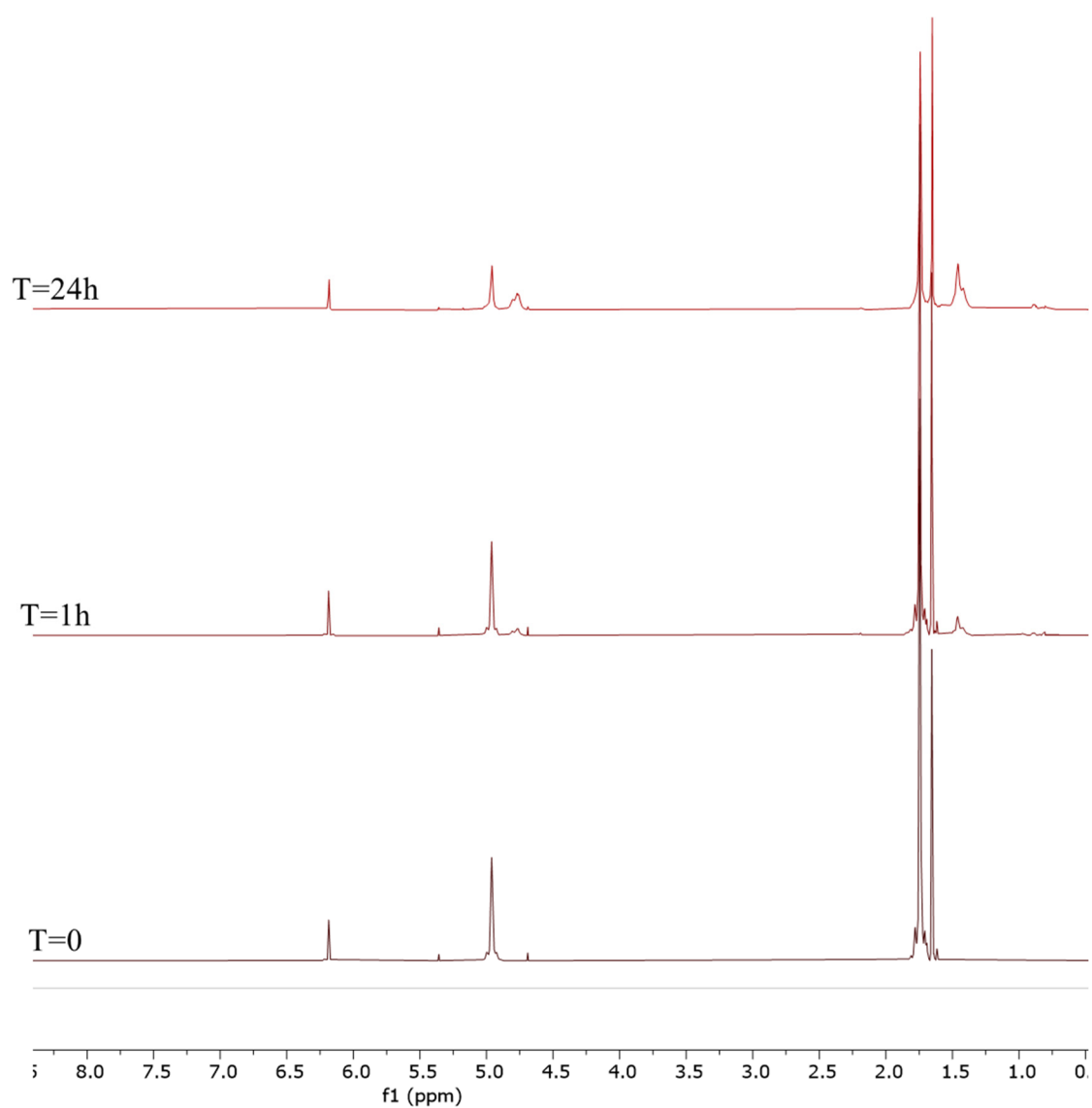
**Figure S71.** ROMP of *cis*-1,5-Cyclooctadiene. Reaction conditions: TCE-*d*<sub>2</sub>, 0.5 M, 0.2 mol% *cis*-Ru-Phos-Cl<sub>2</sub> irradiation at 350 nm.



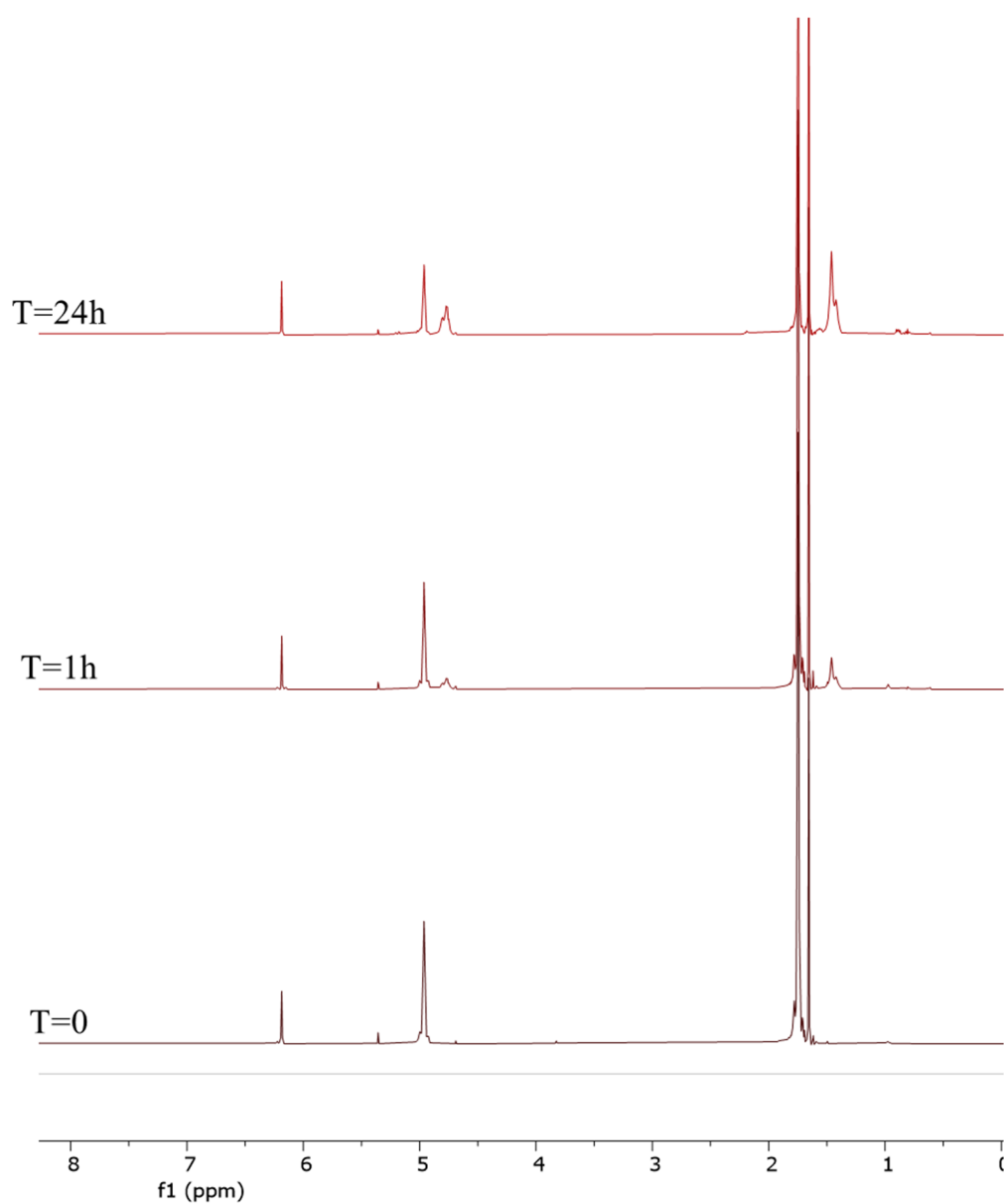
**Figure S72.** ROMP of *cis*-1,5-Cyclooctadiene. Reaction conditions: TCE-*d*<sub>2</sub>, 0.5 M, 0.2 mol% *cis*-Ru-Phos-Br<sub>2</sub> irradiation at 350 nm.



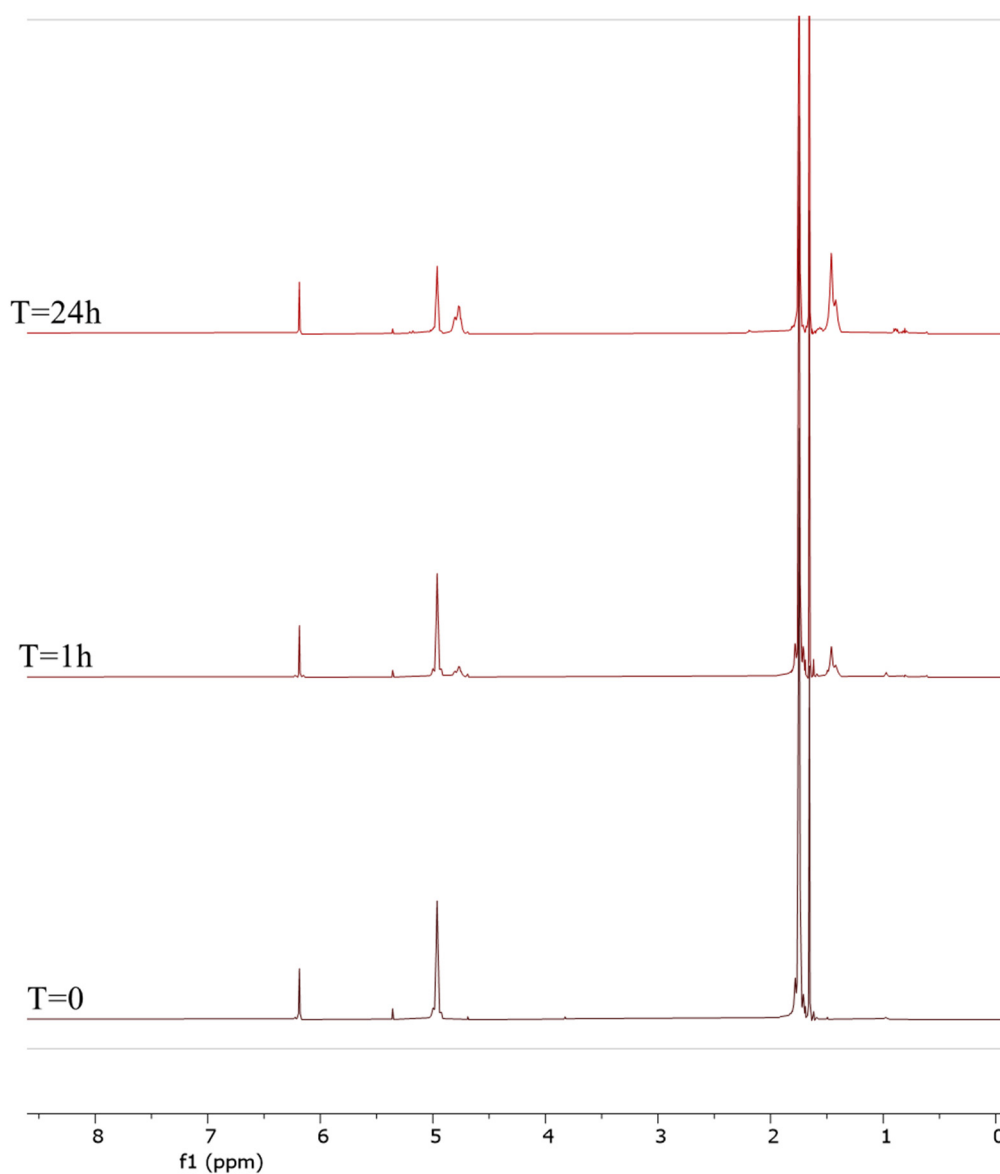
**Figure S73.** ROMP of *cis*-1,5-Cyclooctadiene. Reaction conditions: TCE-*d*<sub>2</sub>, 0.5 M, 0.2 mol% *cis*-Ru-Phos-**I**<sub>2</sub> irradiation at 350 nm.



**Figure S74.** ROMP of *cis*-1,5-Cyclooctadiene. Reaction conditions: TCE-*d*<sub>2</sub>, 0.5 M, 0.2 mol% *cis*-Ru-Phos-Cl<sub>2</sub> at 80 °C.



**Figure S75.** ROMP of *cis*-1,5-Cyclooctadiene. Reaction conditions: TCE-*d*<sub>2</sub>, 0.5 M, 0.2 mol% *cis*-Ru-Phos-Br<sub>2</sub> at 80 °C.



**Figure S76.** ROMP of *cis*-1,5-Cyclooctadiene. Reaction conditions: TCE-*d*<sub>2</sub>, 0.5 M, 0.2 mol% *cis*-Ru-Phos-I<sub>2</sub> at 80 °C.