

## Supporting Information

### A Tandem Approach to Photoactive Metathesis: Combining a Photoacid Generator with an Acid Activated Catalyst

Benjamin K. Keitz and Robert H. Grubbs

#### General Information.

All reactions unless otherwise specified were carried out in dry glassware under argon using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere. All solvents were purified by passage through solvent purification columns and further degassed with bubbling argon.<sup>1</sup> NMR solvents were dried over CaH<sub>2</sub> and vacuum transferred to a dry Schlenk flask and subsequently degassed with argon. Commercially available reagents were used as received with the following exceptions. Triphenylsulfonium chloride (**3**) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, passed through a column of basic alumina and concentrated *in vacuo*. Diethyldiallylmalonate (**6**), Cyclooctene (**16**), *t*-butyldiallyl carbamate (**9**), dicyclopentadiene, and diethyl 2-allyl-2-(2-methylallyl)malonate (**7**) were distilled prior to use. Norbornene monomers were prepared by modification of literature procedures.<sup>2</sup> Monomer **16** was isolated as a complex mixture of stereoisomers. Triphenylsulfonium nonaflate was acquired from Midori Kagaku Inc. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P spectra were recorded on a Varian Mercury 300 Spectrometer and the chemical shifts are reported in ppm relative to the appropriate solvent. Reaction conversions were obtained by comparing the integral values of starting material and product, no internal standard was used.

High resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility.

Gel Permeation Chromatography was carried out in THF on two I-Series MBLMW ViscoGel columns (Viscotek) connected in series with a DAWN EOS multi-angle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer. No standards were used, and  $dn/dc$  values were obtained for each injection by assuming 100% mass recovery from the columns.

Photoreactions were performed in quartz glassware using a 450 W medium pressure mercury arc lamp (Hanovia PC4510-50) surrounded by a water cooled quartz jacket. The reaction vessel was positioned ca. 5 cm from the center of the irradiating lamp.

### Synthesis of **2a**.

**1a** (69 mg, .084 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedionato thallium (65.6 mg, .168 mmol) were combined in a 20 mL scintillation vial and dissolved in 5 mL of benzene. The resulting green solution was stirred at RT for 24 hours after which it was filtered through a plug of celite. CuCl (115 mg, 1.16 mmol) was added to the filtered solution and stirred for 2 h at room temperature. The solution was frozen at  $-30^{\circ}\text{C}$  and the solvent sublimed off under vacuum after which the resulting green residue was dissolved in pentane, filtered through celite, and concentrated *in vacuo* to yield **2a** (54 mg, 77%) as a green powder.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.03 (s, 9H), 1.26 (br s, 20H), 1.38 (d,  $J = 3.9$  Hz, 18H), 1.6-1.8 (m, 13H), 2.12 (br q, 9H), 5.32 (s, 1H), 5.99 (s, 1H), 7.24 (t,  $J = 9$  Hz, 2H), 7.42 (t,  $J = 9$  Hz, 1H), 8.46 (d,  $J = 9$  Hz, 2H), 19.27 (d,  $J = 12$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  27.1, 29.0, 34.8, 41.5, 87.9, 90.8, 127.7, 128.7, 131.9, 154.1, 193.6, 195.2, 196.8, 199.0.  $^{31}\text{P}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  39.12. HRMS (FAB+): calculated 838.4603, found 838.4617.

### Synthesis of **2b**.

**1b** (31 mg, 0.037 mmol) and 2,2,6,6-Tetramethyl-3,5-heptanedionato thallium (27 mg, 0.069 mmol) were combined in a 20 mL scintillation vial and dissolved in 5 mL of benzene. The vial was sealed and heated to 60°C for ca. 1 h at which point the solution had turned green and a white precipitate had formed. After filtration through celite, CuCl (40 mg, 0.404 mmol) was added and the solution stirred for 2 h at RT. The solution was frozen at -30°C and the solvent sublimed off under vacuum after which the resulting green residue was dissolved in pentane, filtered through celite, and concentrated *in vacuo* to yield **2b** (24 mg, 80%) as a green crystalline solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.89 (s, 9H), 1.15 (s, 9H), 1.37 (s, 9H), 1.61 (br s, 9H), 1.86 (s, 3H), 1.99 (s, 3H), 2.06 (s, 3H), 2.59 (s, 3H), 2.62 (s, 3H), 2.66 (s, 3H), 3.45 (m, 4H), 6.03 (s, 1H), 6.37 (s, 1H), 6.781 (s, 2H), 6.86 (s, 2H), 7.04 (t, J = 6 Hz, 2H), 7.28 (t, J = 6 Hz, 1H), 8.14 (d, J = 7.5 Hz, 2H), 17.82 (s, 1H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 18.7, 19.2, 20.2, 20.9, 21.4, 27.2, 28.5, 28.8, 29.6, 29.8, 31.0, 33.2, 41.2, 41.5, 41.9, 50.4, 51.9, 91.0, 129.0, 129.5, 130.0, 130.5, 131.0, 135.1, 137.1, 137.8, 138.2, 139.0, 140.6, 152.0, 197.2, 198.5, 222.4. HRMS (FAB+): calculated 864.4370, found 864.4397.

### Polymerization Procedure.

In a glovebox, a quartz NMR tube was charged with monomer **13** (13 mg), **2a** (2 mg, 5 mol %), and **3** (1.6 mg, 10 mol %). CD<sub>2</sub>Cl<sub>2</sub> (.1 M, relative to substrate, .5-.75 ml) was added and the NMR tube was capped with a rubber septum and irradiated for the duration indicated in Table 2 at RT during which time the solution changed color from green to orange/brown. The contents of

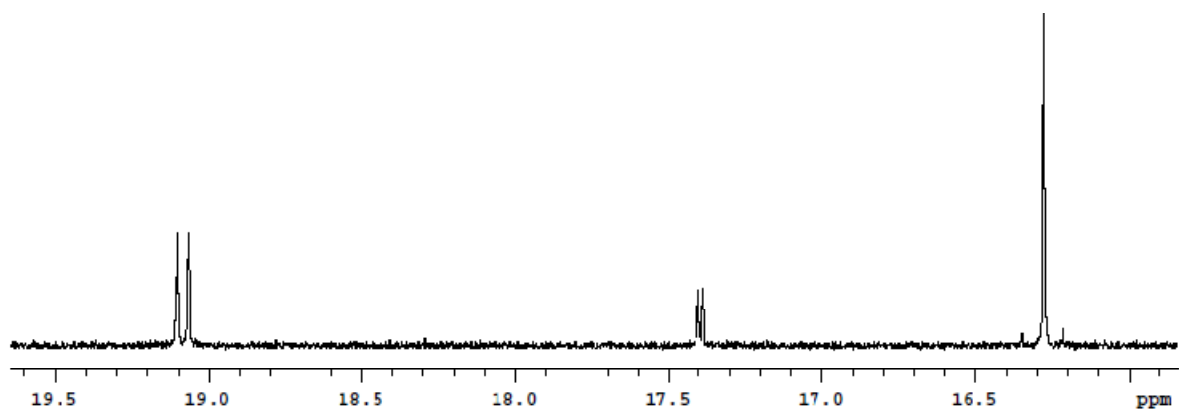
the NMR tube were emptied into a vial and concentrated, after which the residue was dissolved in a minimal amount of THF and precipitated into cold MeOH (poly-(cylcooctene)) or cold 1:1 Et<sub>2</sub>O/Hexanes (polynorbornenes). The precipitate was then collected by filtration and dried under vacuum for several hours.

### **Ring Closing Metathesis Procedure.**

In a glovebox, a quartz NMR tube was charged with substrate **5** (14 mg), **2a** (2 mg, 5 mol %), and **3** (1.6, 10 mol %). CD<sub>2</sub>Cl<sub>2</sub> (.1 M) was added and the NMR tube was capped with a rubber septum and irradiated for 1 h at RT after which the conversion was determined via NMR spectroscopy. The contents of the tube were emptied and concentrated before purifying the product by column chromatography on silica gel.

### **Trapping Experiment Procedure.**

In a glovebox, a 20 ml scintillation vial was charged with **2a** (12.7 mg, .015 mmol) and **3** (9 mg, .030 mmol). The contents of the vial were dissolved in .75 ml of CD<sub>2</sub>Cl<sub>2</sub> and loaded into a quartz NMR tube which was then capped with a rubber septum. **18** (53 mg, .3 mmol) was injected and the sample irradiated for 5 hours after which a <sup>1</sup>H-NMR spectrum revealed the presence of catalyst **19** (Figure 1). The presence of **19** was also confirmed by <sup>31</sup>P spectroscopy.



**Figure 1.** Trapping experiment <sup>1</sup>H spectrum in CD<sub>2</sub>Cl<sub>2</sub> showing precatalyst **2a** (ca. 19.1 ppm) and catalyst **19** (ca. 17.4 ppm)

#### References

- (1) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2002**, *41*, 4035-4037.
- (2) Matson, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 6731-6733.

Sample directory:

Pulse Sequence: s2pul

Solvent: C6D6

Temp. 22.0 C / 295.1 K

File: KKTI-205-H

INOVA-500 "nmr"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.998 sec

Width 30030.0 Hz

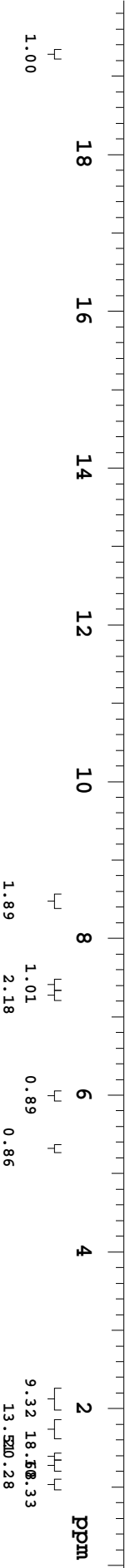
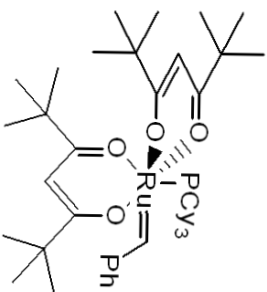
16 repetitions

OBSERVE H1, 299.8660878 MHz

DATA PROCESSING

FT size 131072

Total time 0 min, 48 sec

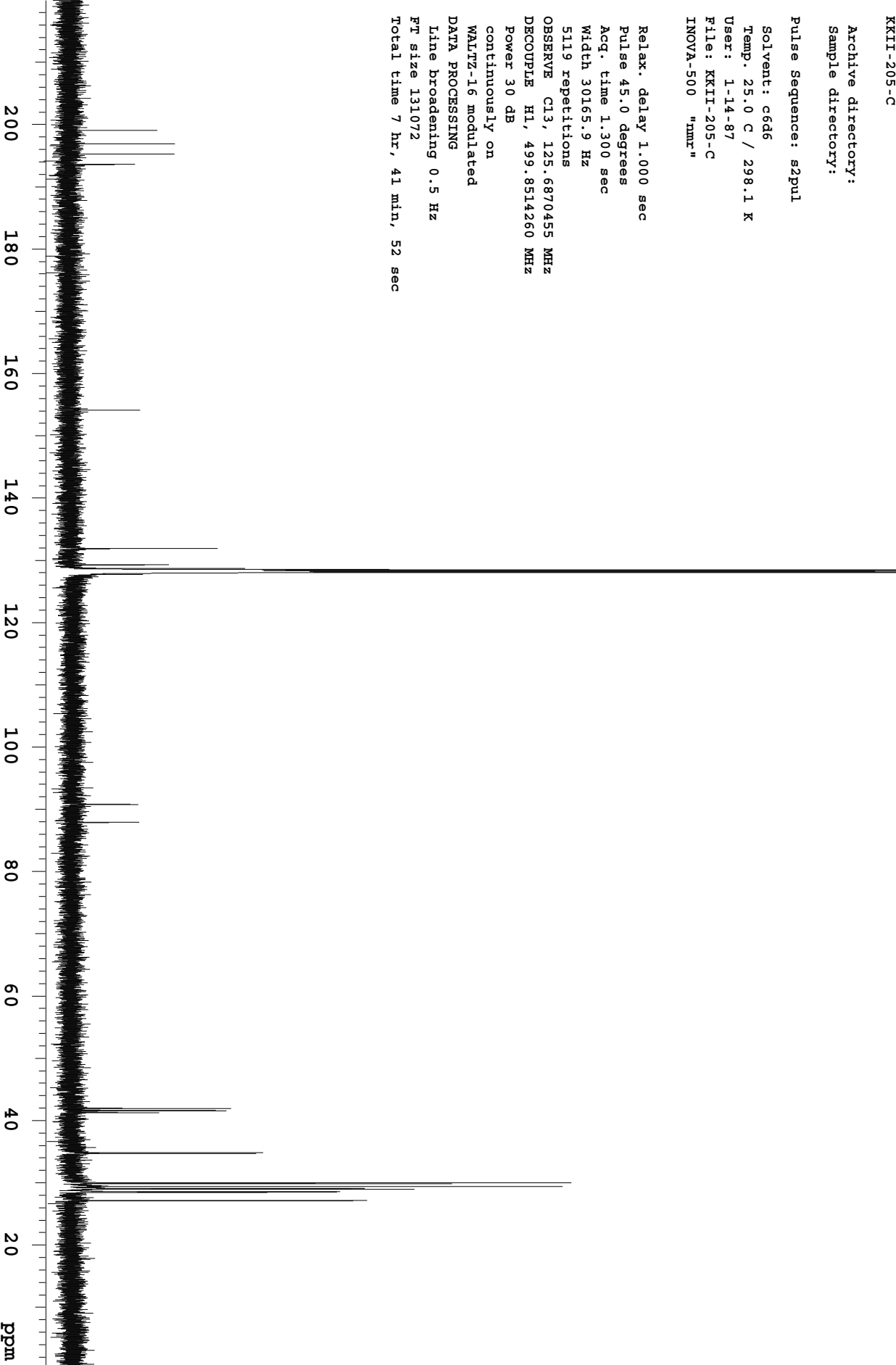


Archive directory:  
Sample directory:

Pulse Sequence: s2pul

Solvent: c6d6  
Temp. 25.0 C / 298.1 K  
User: 1-14-87  
File: KKII-205-C  
INOVA-500 "nmr"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 30165.9 Hz  
5119 repetitions  
OBSERVE C13, 125.6870455 MHz  
DECOUPLE H1, 499.8514260 MHz  
Power 30 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 7 hr, 41 min, 52 sec







Archive directory:  
Sample directory:

Pulse Sequence: s2pul

Solvent: c6d6  
Temp. 25.0 C / 298.1 K  
User: 1-14-87  
File: KKII-246-C  
INOVA-500 "nmr"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 30165.9 Hz  
6856 repetitions  
OBSERVE C13, 125.6870224 MHz  
DECOUPLE H1, 499.8514260 MHz  
Power 30 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 6414 hr, 56 min, 34 sec

