Poly(fluoroalkyl acrylate)-Bound Ruthenium Carbene Complex: A Fluorous and Recyclable Catalyst for Ring-Closing Olefin Metathesis

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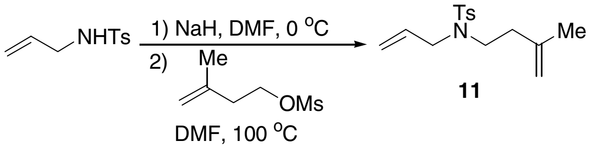
Supporting Information

General. Unless otherwise noted, all reactions were performed under an atmosphere of dry Ar with oven-dried glassware and anhydrous solvents. THF and diether ether were distilled from sodium/benzophenone under a nitrogen atmosphere. CH_2Cl_2 and $PhCF_3$ (purchased from Aldrich, 99+%) were dried over CaH_2, and distilled prior to use. FC-72 were purchased from Acros Organics (Fluoro-compound FC-72$^{®}$, b.p. 51-59 °C) and 3M Company (3M^{TM} Fluorinert^{TM} Electronic Liquid FC-72, b.p. 50-60 °C), and were used as received for the fluorous extraction experiments and distilled under Ar over molecular sieves for use as a solvent for the fluorous biphasic reaction. NMR spectra were acquired in $CDCl_3$ at 500 MHz for ^1H and 125 MHz for ^{13}C. Acryloyl chloride was purchased from Aldrich and distilled prior to use. Heptadecafluorodecyl acrylate was purchased from Aldrich and used as received. All other chemicals or reagents were obtained from commercial sources or prepared according to literature procedures.

Preparation and Characterization of New Diene Substrates

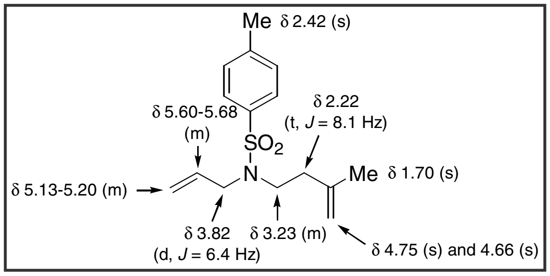
N-Allyl-*N*-(3-methyl-3-butenyl)-*p*-toluenesulfonamide (11)



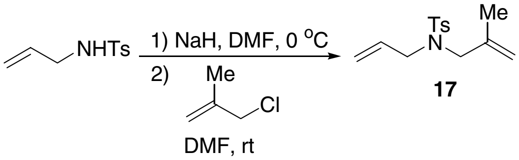
11

To a solution of *N*-allyl-*p*-toluenesulfonamide (4.23 g, 20 mmol) in DMF (50 mL) was added NaH (1.04 g, 60%, 26 mmol) in one portion at 0 °C. After H_2 evolution ceased, a solution of 3-methyl-3-butenyl methanesulfonate (3.94 g, 24 mmol) in DMF (20 mL) was added via syringe. The reaction mixture was heated to 100 °C for 6 h before being cooled to rt. Standard aqueous workup followed by silica gel chromatography (hexanes:EtOAc, 8:1 v/v) gave pure **11** (5.30 g, 95%) as a colorless oil.

11: ^1H NMR ($CDCl_3$, 500 MHz): δ 7.70 (d, 2 H, *J* = 8.3 Hz), 7.29 (d, 2 H, *J* = 8.1 Hz), 5.60-5.68 (m, 1 H), 5.13-5.20 (m, 2 H), 4.75 (s, 1 H), 4.66 (s, 1 H), 3.82 (d, 2 H, *J* = 6.4 Hz), 3.23 (m, 2 H), 2.42 (s, 3 H), 2.22 (t, 2 H, *J* = 8.1 Hz), 1.70 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.2, 142.4, 137.2, 133.2, 129.7, 127.1, 118.8, 112.0, 50.6, 45.8, 36.5, 22.4, 21.5. Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.16; H, 7.65; N, 4.98.



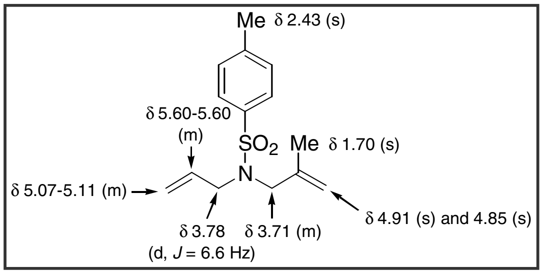
N-Allyl-*N*-methallyl-*p*-toluenesulfonamide (17)



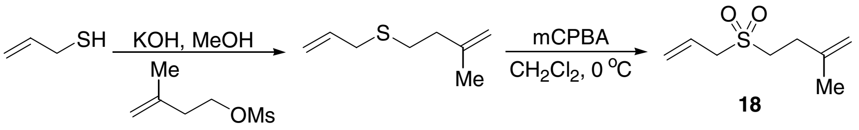
17

To a solution of *N*-allyl *p*-toluenesulfonamide (4.23 g, 20 mmol) in DMF (50 mL) was added NaH (1.04 g, 60%, 26 mmol) at 0 °C in one portion. After H_2 evolution ceased, methallyl chloride (2.40 mL, 2.17 g, 24 mmol) was added via syringe. The reaction mixture was stirred at rt for 12 h. Standard aqueous workup followed by silica gel chromatography (hexanes:EtOAc, 8:1 v/v) gave pure **17** (5.24 g, 99%) as a colorless oil.

17: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, 2 H, *J* = 8.3 Hz), 7.30 (d, 2 H, *J* = 8.2 Hz), 5.50-5.60 (m, 1 H), 5.07-5.11 (m, 2 H), 4.91 (s, 1 H), 4.85 (s, 1 H), 3.78 (d, 2 H, *J* = 6.6 Hz), 3.71 (s, 2 H), 2.43 (s, 3 H), 1.70 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1, 140.1, 137.6, 132.4, 129.5, 127.2, 119.0, 114.4, 52.8, 49.4, 21.4, 19.7. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.23; H, 7.39; N, 5.22.

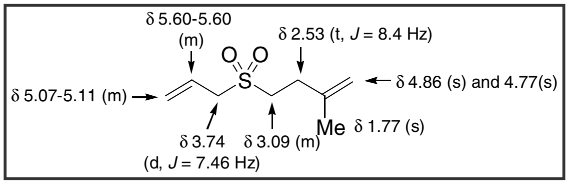


Allyl 3-methyl-3-butenyl sulfone (18)

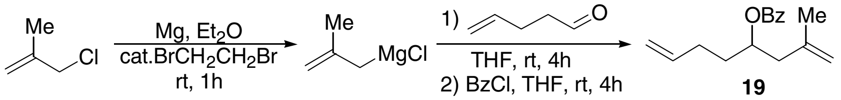


To a solution of allyl mercaptan (800 μL, 742 mg, 80%, 8.0 mmol) and KOH (3.37 g, 60 mmol) in MeOH (10 mL) was added dropwise a solution of 3-methyl-3-butenyl methanesulfonate (1.97 g, 12 mmol) in MeOH (10 mL). After stirring at rt for 60 min, the reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated to give the crude sulfide. The sulfide was then taken up with CH_2Cl_2 (30 mL) and treated with mCPBA (3.47 g, ~ 70%, 14 mmol) at 0 °C. After stirring at 0 °C for 60 min, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (30 mL). The organic extracts were washed with 10% $Na_2S_2O_5$ and brine, and dried (Na_2SO_4). Purification by silica gel chromatography (hexanes:CH_2Cl_2, 1:2 v/v) gave **18** (700 mg, 50 % based on allyl mercaptan) as a colorless oil.

18: ^{1}H NMR: δ 5.94-5.99 (m, 1 H), 5.45-5.53 (m, 2 H), 4.86 (s, 1 H), 4.77 (s, 1 H), 3.74 (d, 2 H, *J* = 7.4 Hz), 3.09 (m, 2 H), 2.53 (t, 2 H, *J* = 8.4 Hz), 1.77 (s, 3 H). ^{13}C NMR: δ 141.4, 125.2, 124.6, 112.3, 57.8, 49.7, 29.5, 22.3. Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10. Found: C, 54.80; H, 8.41.

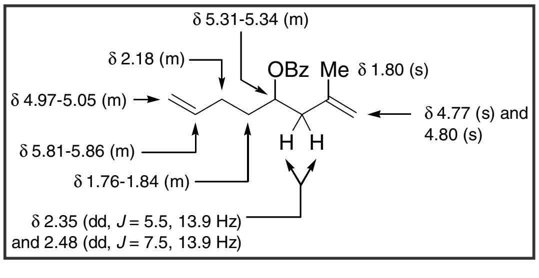


2-Methyl-1,7-octadien-4-yl benzoate (19)



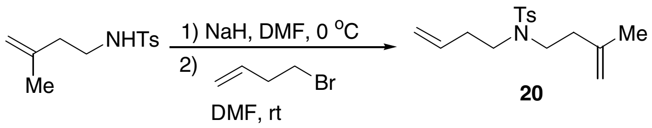
A flame-dried flask equipped with a reflux condenser was charged with magnesium powder (972 mg, 40 mmol). The flask was then dried on vacuum line with occasional and moderate heating with a heating gun for 3 h and charged with diethyl ether (15 mL) followed by 1, 2-dibromoethane (86 μL, 188 mg, 1 mmol). After gas evolution ceased, 3-chloro-2-methylpropene (988 μL, 906 mg 10 mmol) was added via syringe and the reaction mixture stirred at rt for 1 h. The Grignard reagent was then transferred dropwide at 0 °C to a 50 mL flask containing 4-pentenal (421 mg, 5 mmol) in THF (20 mL) and the reaction mixture stirred at rt for 4 h. Benzoyl chloride (672 μL, 843 mg, 6 mmol) was then added via syringe. After stirring at rt for 4 h, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with brine and dried with anhydrous Na_2SO_4. Purification by silica gel chromatography (hexanes/EtOAc, 95:5 v/v) gave **19** (540 mg, 44%) as a colorless oil.

19: ^{1}H NMR: δ 8.05 (d, 2 H, *J* = 8.1 Hz), 7.56 (t, 1 H, *J* = 7.5 Hz), 7.45 (t, 2 H, *J* = 7.7 Hz), 5.81-5.86 (m, 1 H), 5.31-5.34 (m, 1 H), 4.97-5.05 (m, 2 H), 4.80 (s, 1 H), 4.77 (s, 1 H), 2.48 (dd, 1 H, *J* = 7.5, 13.9 Hz), 2.35 (dd, 1 H, *J* = 5.5, 13.9 Hz), 2.18 (m, 2 H), 1.76-1.84 (m, 2 H), 1.80 (s, 3 H). ^{13}C NMR: δ 166.1, 141.6, 137.8, 132.8, 130.6, 129.6, 128.3, 115.0, 113.6, 72.3, 42.9, 33.3,



29.7, 22.6. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.55; H, 8.35.

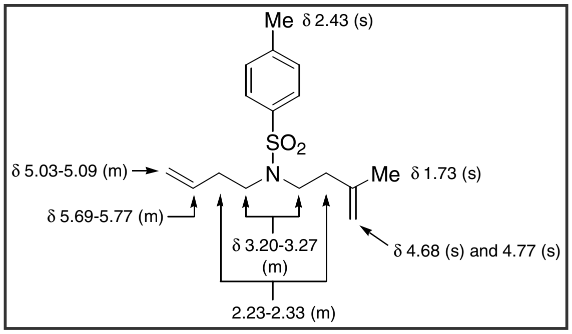
N-(3-Butenyl)-*N*-(3-methyl-3-butenyl)-*p*-toluenesulfonamide (20)



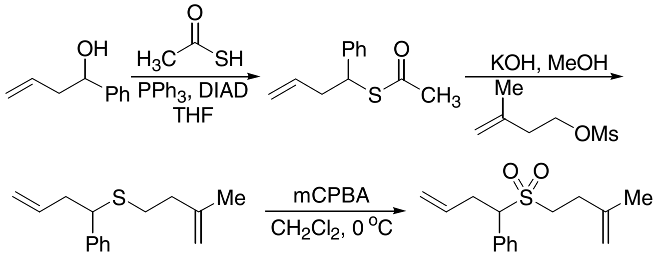
20

To a solution of *N*-(3-methyl-3-butenyl)-*p*-toluenesulfonamide (1.51 g, 6.3 mmol) in DMF (40 mL) was added NaH (380 mg, 60%, 9.5 mmol) in one portion at 0 °C. After H_2 evolution ceased, 4-bromobutene (706 µL, 939 mg, 7.0 mmol) was added via syringe. The reaction mixture was stirred at rt for 18 h. Standard aqueous workup followed by flash column chromatography on silica (hexanes:EtOAc, 8:1 v/v) gave pure **20** (509 mg, 28%) as a colorless oil.

20: ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.71 (d, 2 H, *J* = 8.2 Hz), 7.30 (d, 2 H, *J* = 8.1 Hz), 5.69-5.77 (m, 1 H), 5.03-5.09 (m, 2 H), 4.77 (s, 1 H), 4.68 (s, 1 H), 3.20-3.27 (m, 4 H), 2.43 (s, 3 H), 2.23-2.33 (m, 4 H), 1.73 (s, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 143.1, 142.4, 137.1, 134.7, 129.6, 127.1, 117.1, 112.0, 47.6, 46.8, 36.8, 33.2, 22.5, 21.5. Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.21; H, 7.77; N, 4.86.



3-Methyl-3-butenyl 1-phenyl-3-butenyl sulfone (21)



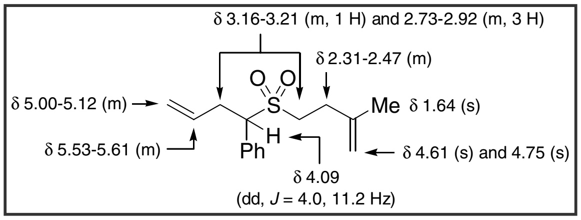
21

To a stirred solution of 1-phenyl-3-propen-1-ol (1.48 g, 10.0 mmol) and Ph_3P (3.93 g, 15 mmol) in dry THF (30 mL) was added dropwise by syringe diisopropyl azodicarboxylate (2.50 mL, 15 mmol) at 0 °C. After stirring for 10 min at 0 °C, thiolacetic acid (1.07 mL, 15 mmol) was added dropwise and the resulting reaction mixture stirred at rt for 16 h. The solvent and volatiles were then removed under vacuum. The crude reaction mixture was triturated with hexanes (50 mL) and the precipitate filtered off. The crude product was purified by flash chromatography on silica gel (hexanes/CH_2Cl_2, 3:1 then 2:1 v/v) to give the corresponding thiolester (1.38 g, 67%) as a thick oil. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.23-7.34 (m, 5 H), 5.66-5.74 (m, 1 H), 5.02-5.10 (m, 2 H), 4.66 (t, 1 H, *J* = 7.7 Hz), 2.66-2.75 (m, 2 H), 2.31 (s, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 194.46, 141.18, 134.61, 128.49, 127.65, 127.28, 117.60, 47.53, 40,31, 30.40. $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.77; H, 6.49.

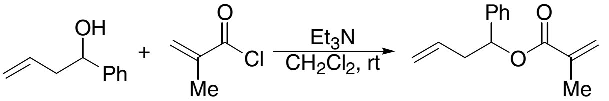
A solution of the thiolester (825 mg, 4 mmol) in MeOH (10 mL) was then treated with KOH (1.35 g, 24 mmol) followed by 3-methyl-3-butenyl methanesufonate (788 mg, 4.8mmol) in MeOH (5 mL). After stirring at rt for 90 min, the reaction was quenched by saturated aqueous NH_4Cl and extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated. Purification by flash column chromatography on silica (hexanes/CH_2Cl_2, 2:1v/v) gave corresponding sulfide (768 mg, 83%) as a pale yellow oil. ^{1}H NMR: δ 7.23-7.37 (m, 5 H), 5.69-5.75 (m, 1 H), 5.00-5.06 (m, 2 H), 4.72 (s, 1 H), 4.64 (s, 1 H), 3.86 (t, 1 H, *J* = 7.5 Hz), 2.62-2.64 (m, 2 H), 2.36-2.44 (m, 2 H), 2.15-2.21 (m, 2 H), 1.64 (s, 3 H). ^{13}C NMR: δ 144.1, 142.2, 135.4, 128.4, 127.9, 127.1, 116.9, 111.1, 49.7, 40.9, 37.5, 29.3, 22.1.

To a stirred solution of the sulfide (768 mg, 3.3 mmol) in CH_2Cl_2 (20 mL) was added 0 °C 3-chloroperbenzoic acid (1.63 g, ~ 70%, 6.6 mmol,) in one portion and the reaction mixture was stirred at 0 °C for 90 min. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (30 mL). The combined organic extracts were washed with 10 % aqueous $Na_2S_2O_5$ and brine, and dried (Na_2SO_4). After concentration to dryness, the crude product was purified by flash column chromatography on silica (hexanes: CH_2Cl_2 1:4) to give **21** (470 mg, 54%) as a slightly yellow oil.

21: ^{1}H NMR: δ 7.38-7.46 (m, 5 H), 5.53-5.61 (m, 1 H), 5.00-5.12 (m, 2 H), 4.75 (s, 1 H), 4.61(s, 1 H), 4.09 (dd, 1 H, J = 4, 11.2 Hz), 3.16-3.21 (m, 1 H), 2.73-2.92 (m, 3 H), 2.31-2.47 (m, 2 H), 1.64 (s, 3 H). ^{13}C NMR: δ 141.5, 132.8, 132.5, 129.5, 129.2, 129.1, 118.7, 112.1, 68.4, 49.3, 31.6, 29.3, 22.2. Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62. Found: C, 68.12; H, 7.65.



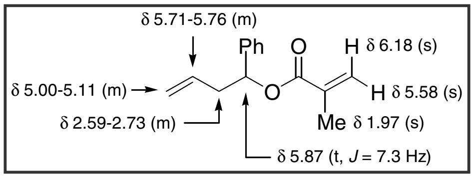
1-Phenyl-3-butenyl methacrylate (28)



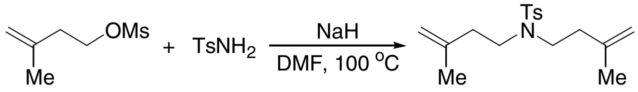
28

To a stirred solution of 1-phenyl-3-buten-1-ol (742 mg, 5 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (1.4 mL, 10 mmol) and methacryloyl chloride (580 μL, 627 mg, 6 mmol) via syringe. The reaction mixture was then stirred at rt for 3 h. Standard aqueous workup followed by flash chromatography on silica (hexanes:CH_2Cl_2, 2:1 v/v) gave pure **28** (397 mg, 37%).

28: ^{1}H NMR ($CDCl_3$, 500MHz): δ 7.27-7.40 (m, 5 H), 6.18 (s, 1 H), 5.87 (t, 1 H, J = 7.3 Hz), 5.71-5.76 (m, 1 H), 5.58 (s, 1 H), 5.05-5.11 (m, 2 H), 2.59-2.73 (m, 2 H), 1.97 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.5, 140.2, 136.5, 133.3, 128.4, 127.9, 126.4, 125.5, 118.1, 75.4, 40.9, 18.3. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.61; H, 7.54.



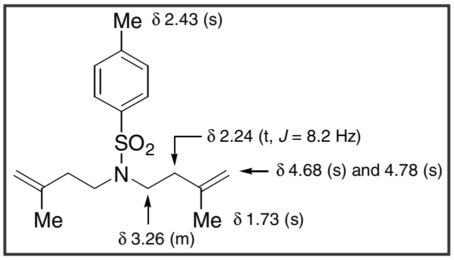
N, N-Bis(3-methyl-3-butenyl))-*p*-toluenesulfonamide (30)



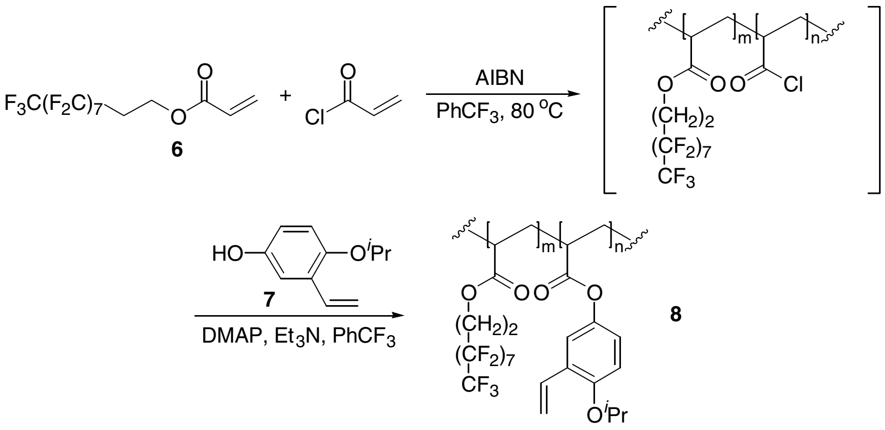
30

To a solution of $TsNH_2$ (7.70 g, 45 mmol) in DMF (100 mL) was added at 0 °C NaH (2.00 g, 60%, 50 mmol) in one portion. After H_2 evolution ceased, a solution of 3-methyl-3-butenyl methanesulfonate (6.85 g, 40 mmol) in DMF (40mL) was added via syringe. he reaction mixture was heated to 100 °C for 12 h before cooled to rt. Standard aqueous work followed by flash column chromatography on silica (hexanes:EtOAc, 8:1 v/v) gave **30** (2.25 g, 17%) and *N*-(3-methyl-3-butenyl) *p*-toluenesulfonamide (5.56 g, 58%).

30: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, 2 H, J = 8.1 Hz), 7.30 (d, 2 H, J = 8.1 Hz), 4.78 (s, 2 H), 4.68 (s, 2 H), 3.26 (m, 4 H), 2.43 (s, 3 H), 2.24 (t, 4 H, J = 8.2 Hz), 1.73 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1, 142.4, 137.1, 129.6, 127.1, 112.0, 46.7, 36.8, 22.5, 21.5. Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.41; H, 8.20; N, 4.56. Found: C, 66.14; H, 7.89; N, 4.48.

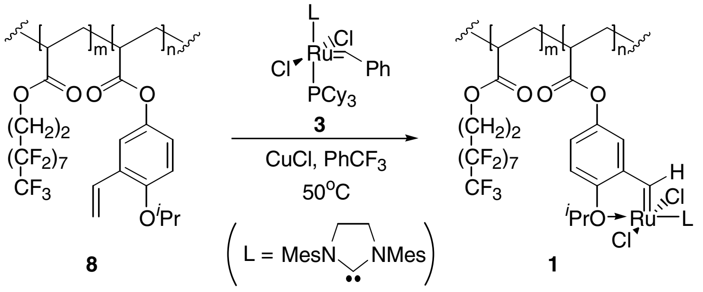


Synthesis of Polymer-Bound Styrene Ligand 8.



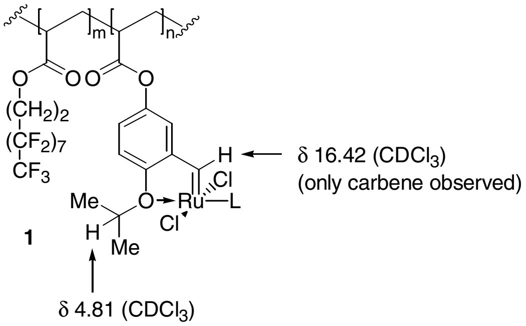
A 10 mL flame-dried Schlenk flask was charged with heptadecafluorodecyl acrylate **6** (950 µL, 1.55 g, 3.0 mmol) and $PhCF_3$ (3 mL). Acryoyl chloride (41 µL, 45.3 mg, 0.5 mmol,) was then added via syringe followed by AIBN (99 mg, 0.6 mmol, 20 mol %) under an Ar atmosphere. The flask was sealed and immersed in an oil bath preheated to 80 °C. After stirring for 20 h at this temperature, the reaction was cooled to rt. DMAP (12 mg, 0.1 mmol) and Et_3N (111 µL, 81 mg, 0.8 mmol) were added followed by a solution of 5-hydroxy-2-isopropoxylstyrene **7**[1](89 mg, 0.5 mmol) in $PhCF_3$ (1 mL). The reaction mixture was stirred at rt under Ar for 18 h and concentrated to dryness in vacuo. The crude reaction mixture was partitioned in FC-72 (20 mL) and CH_2Cl_2 (20 mL). The FC-72 layer was separated and washed with CH_2Cl_2 (2 x 20 mL). After concentration and drying on vacuum line, polymer **8** was obtained as a glassy white powder (1.57 g, 97%). Analysis by 500 MHz ^1H NMR ($CDCl_3$, 50 °C) revealed a ratio of about 10:1 between the fluoroalkyl unit and the styrene ligand, pointing a loading of 0.19 mmol/g.

Polymer-Bound Ru Carbene Complex 1: Synthesis and Structural Characterization.

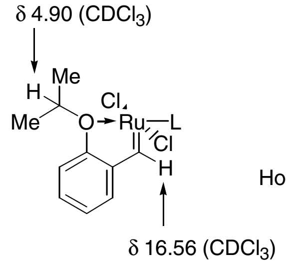


[The procedure for the preparation of **1** described below is representative of all other experiments of Tables 1 and 2 of the text, with the quantities of the appropriate reactants and solvents adjusted in accordance with the scales and conditions specified for each reaction.]

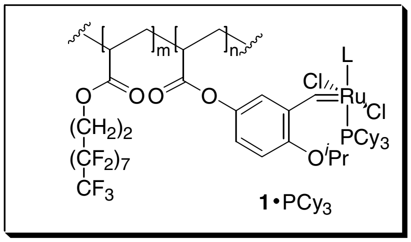
A 5 mL flame-dried Schlenk flask was charged with **8** (56 mg, 0.0106 mmol) and degassed three times by evacuation and then filling with Ar. Ruthenium carbene complex **3** (10 mg, 0.015 mmol), CuCl (1.0 mg, 0.01 mmol) were added under argon. $PhCF_3$ (1 mL) was added via syringe and the flask was sealed and heated to 50 °C (bath temperature) for 1.5 h. After cooling to rt, the reaction mixture was concentrated to dryness under vacuum and partitioned in FC-72 (5 mL) and EtOAc (5 mL). The FC-72 layer was separated and the EtOAc layer extracted with FC-72 (2 x 3 mL). The FC-72 extracts were combined and washed with EtOAc (5 mL). After removal of the solvent and drying on vacuum line, **1** (62 mg) was obtained as a dark green powder. ^1H NMR ($CDCl_3$, 50 °C) analysis revealed a conversion of greater than 90% of the styrene ligand. Partial ^1HNMR ($CDCl_3$, 500 MHz, with presaturation of the polymer backbone signals): δ 16.42 (br, 1H, Ru=C**H**Ar), 4.81 (br, 1 H, OC**H**Me_2), 4.16-4.34 (br, ~ 20 H, OC**H**$_2$CH_2). The structure of **1** was characterized by its characteristic carbene signal at δ 16.42, which is the only carbene peak observed, as well as the methine proton peak at δ 4.81 of the Ru-bound isopropoxy ligand. The structural assignment was further secured by comparison with those of the original Hoveyda-Grubbs' catalyst **5**[3] (δ 16.56 of Ru=C**H**Ar and 4.90 of OC**H**Me_2). NMR peaks attributable to structure **1**•PCy_3 (cf. the known carbene **5**•PCy_3[4]) were not detected.



1

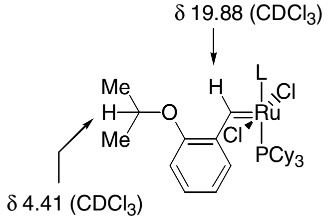


5
Hoveyda *et al.*[3]



1•PCy$_3$

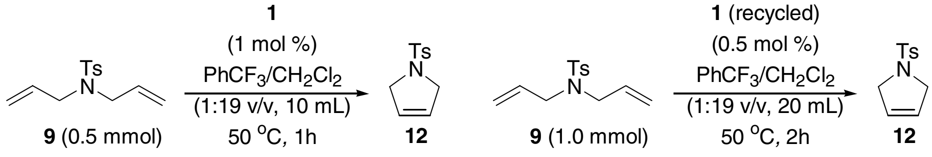
not formed



5•PCy$_3$
Blechert *et al.*[4]

General Procedure for the Recycling and Reuse of Catalyst 1 in Ring-closing Metathesis (RCM)

RCM of Diene 9.



cycle	1 to 15
% conv	>98%

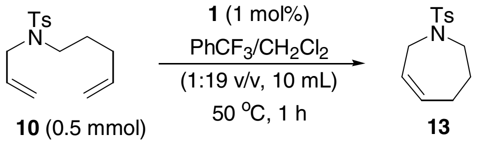
cycle	16	17	18	19	20
% conv	>98	97	97	95	94

Catalyst **1**, prepared according to the general procedure from 28 mg (0.0053 mmol) of **8**, 5.0 mg (0.0075 mmol) of **3** and 0.5 mg (0.005 mmol) of CuCl, was placed in a 50 mL flask equipped with a reflux condenser. After the flask was degassed three times by evacuation and then filling with Ar, PhCF$_3$ (0.5 mL) and CH$_2$Cl$_2$ (4.5 mL) were was added to dissolve the catalyst followed by *N*-tosyldiallylamine **9** (126 mg, 0.50 mmol) dissolved in CH$_2$Cl$_2$ (5 mL). After heating to reflux (bath temperature 45-50°C) for 1 h, the reaction mixture was cooled to rt and concentrated to dryness under vacuum.

General procedure for product isolation and catalyst recycling by fluorous extraction. The crude reaction mixture was partitioned in FC-72 (5 mL) and EtOAc (5 mL). The FC-72 layer was separated and the EtOAc layer extracted with FC-72 (3 mL). The FC-72 extracts were combined and washed with EtOAc (3 mL). After concentration of the combined EtOAc extracts, the crude reaction product was analyzed by 500 MHz ^{1}H NMR which indicated complete conversion of diene **9** and clean, essentially quantitative formation of the known cyclized product **12**.[5] **12**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.73 (d, 2 H, *J* = 8.3 Hz), 7.33 (d, 2 H, *J* = 8.1 Hz), 5.66 (s, 2 H), 4.13 (s, 4 H), 2.44 (s, 3 H). The FC-72 extracts were concentrated under reduced pressure. After drying on vacuum line, the recycled catalyst was used directly in a subsequent RCM reaction.

A second run of the RCM of **9** was performed in exactly the same way as described for the first run using the recycled catalyst. After fluorous extraction of the reaction mixture as described above, ^{1}H-NMR analysis of the crude reaction product revealed a complete conversion of the diene **9** and quantitative formation of **12**. This reaction was repeated 13 more times, each using the catalyst recycled from the previous run. This was continued for another 5 cycles (cycles 16 to 20) using 1.0 mmol of diene **9** in PhCF$_3$ (1:19 v/v, 20 mL) with the reaction time being 2h for each cycle. The results were listed in Table 1 of the text.

RCM of Diene 10.

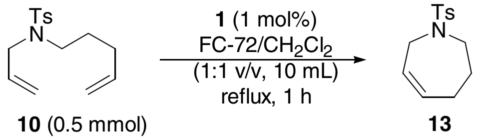


cycle	1 to 9	10	11	12
% conv	> 98	97	96	95

Catalyst **1**, prepared according to the general procedure from 28 mg (0.0050 mmol) of **8**, 5.0 mg (0.0075 mmol) of **3** and 0.5 mg (0.005 mmol) of CuCl, was placed in a 50mL flask equipped with a reflux condenser. After the flask was degassed three times by evacuation and then filling with Ar, $PhCF_3$ (0.5 mL) was added to dissolve the catalyst followed by diene **10** (140 mg, 0.50 mmol) dissolved in CH_2Cl_2 (9.5 mL). After heating to reflux (bath temperature 45-50°C) for 1 h, the reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture following the general procedure, the crude reaction product was analyzed by 500 M Hz ^{1}H NMR which indicated complete conversion of the diene **10** and clean and quantitative formation of the known cyclized product **13**.[6] **13**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.69 (d, 2 H, *J* = 8.2 Hz), 7.29 (d, 2 H, *J* = 8.1 Hz), 5.76-5.80 (m, 1 H), 5.64-5.68 (m, 1 H), 3.84 (dd, 2 H, *J* = 0.9, 4.8 Hz), 3.40 (t, 2 H, *J* = 6.1 Hz), 2.43 (s, 3 H), 2.17-2.21 (m, 2 H), 1.81 (quint, 2 H, *J* = 6.0 Hz). The FC-72 extracts were concentrated under reduced pressure. After drying on vacuum line, the recycled catalyst was used directly in a subsequent RCM reaction.

A second run of the RCM of **10** was performed in exactly the same way as described for the first run using the recycled catalyst. After fluorous extraction of the reaction mixture following the general procedure, ^{1}H-NMR analysis of the crude reaction product revealed a complete conversion of the diene **10** and quantitative formation of **13**. This reaction was repeated 10 more times, each using the catalyst recycled from the previous run. The results were listed in Table 1 of the text.

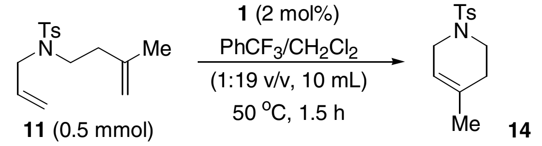
RCM of Diene 10 under Fluorous Biphasic Conditions



cycle	1	2	3	4	5	6
% conv	> 98	93	92	90	72	52

Catalyst **1**, prepared according to the general procedure from 28 mg (0.0050 mmol) of **8**, 5.0 mg (0.0075 mmol) of **3** and 0.5 mg (0.005 mmol) of CuCl, was placed in a 50mL flask equipped with a reflux condenser. After the flask was degassed three times by evacuation and then filling with Ar, FC-72 (5 mL, dried over 4 Å molecular sieves and freshly distilled under an Ar atmosphere before use) was added to dissolve the catalyst followed by diene **10** (140 mg, 0.50 mmol) dissolved in CH_2Cl_2 (5 mL). The reaction mixture was then heated to reflux (bath temperature 45-50°C), resulting in the formation of a greenish creamy emulsion. After being refluxed for 1h, the reaction mixture was cooled to rt and evaporated to dryness under vacuum. After fluorous extraction of the reaction mixture following the general procedure, the crude reaction product was analyzed by 500 MHz ^{1}H NMR which indicated complete conversion of diene **10** and quantitative formation of **13**. This reaction was repeated for 5 more cycles, each using the catalyst recycled from a previous run. Conversions for cycles 2–6 were 93%, 92%, 90%, 72% and 52%, respectively. The gradual and significant diminishment in the conversion of **10** may be attributed to the biphasic nature of the reaction. Phase separation of the rebounding ligand of **8** in the FC-phase and the catalytic species in the CH_2Cl_2 phase may be the reasons for the gradual decomposition of the catalyst.

RCM of Diene 11



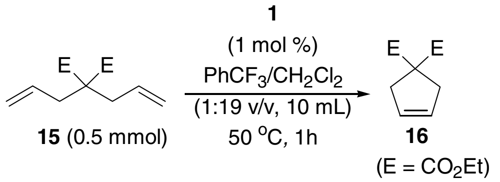
cycle	1	2	3	4	5	6
% conv	> 98	> 98	> 98	> 98	> 98	96

Catalyst **1**, prepared according to the general procedure from 56 mg (0.010 mmol) of **8**, 10 mg (0.015 mmol) of **3** and 1.0 mg (0.010 mmol) of CuCl, was placed in a 50 mL flask equipped with a reflux condenser and the flask was degassed three times by evacuation and then filling with Ar. $PhCF_3$ (0.5 mL) was then added to dissolve the catalyst followed by diene **11** (140 mg, 0.50 mmol) in CH_2Cl_2 (9.5 mL). After heating to reflux (bath temperature 45-50 ^oC) for 1.5 h, the reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture following the general procedure, the crude reaction product was analyzed by 500 M Hz ^1H NMR which indicated complete conversion of the diene **11** and clean and quantitative formation of the known cyclized product **14**.[7] **14**: ^1H NMR ($CDCl_3$, 500 MHz): δ 7.68 (d, 2 H, *J* = 8.2 Hz), 7.32 (d, 2 H, *J* = 8.1 Hz), 5.31 (m, 1 H), 3.53(m, 2 H), 3.17 (t, 2 H, *J* = 5.8 Hz), 2.43 (s, 3 H), 2.11 (bs, 2 H), 1.66 (s, 3 H).

This reaction was repeated 5 more times, each using the catalyst recycled from the previous run. The results were listed in Table 1 of the text.

To further test the limit of the recyclability of **1**, the catalyst recycled from run 6 was reused for two more runs of the RCM of **11** in exactly the same way as in the previous runs. The conversion of **11** dropped to 94 % and 90 % for run 7 and run 8, respectively. The recycled catalyst was then treated with another portion of **3** in the presence of CuCl in the same way as described for its initial preparation. The recharged catalyst obtained (60 mg) was used in another run of the RCM of **11** under otherwise identical condition. After fluorous extraction of the reaction mixture, the crude reaction product was analyzed 500 MHz ^1H NMR which indicated complete conversion of the diene **11** and clean and quantitative formation of the cyclized product **14**.

RCM of Diene 15 (Table 2, catalyst batch A)



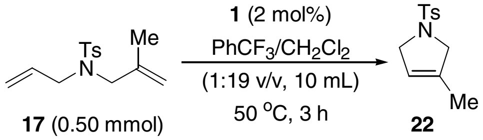
cycle	1	2	3	4	5	6	7
% conv	> 98	> 98	98	98	95	93	92

Catalyst **1**, prepared according to the general procedure from 28 mg (0.0050 mmol) of **8**, 5.0 mg (0.0075 mmol) of **3** and 0.5 mg (0.005 mmol) of CuCl, was placed in a 50mL flask equipped with a reflux condenser. After the flask was degassed three times by evacuation and then filling with Ar, $PhCF_3$ (0.5 mL) was added to dissolve the catalyst followed by diethyl diallylmalonate **15** (120 mg, 0.50 mmol) dissolved in CH_2Cl_2 (9.5 mL). After heating to reflux (bath temperature 45-50^oC) for 1 h, the reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture following the general procedure, the crude reaction product was analyzed by 500 M Hz ^1H NMR which indicated complete conversion of **15** and clean and quantitative formation of the known cyclized product **16**.[8] **16**: ^1H NMR ($CDCl_3$, 500 MHz): δ 5.62(s, 2H), 4.21 (q, 4H, *J* = 7.2 Hz), 3.02 (s, 4H), 1.26 (t, 6 H, *J* = 7.1 Hz).

This reaction was repeated 6 more times, each using the catalyst recycled from the previous run. The results were listed in Table 2 of the text.

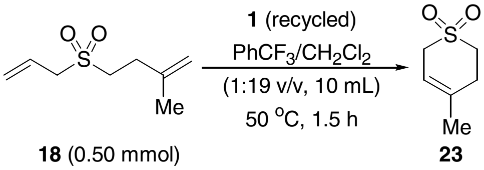
RCM of Dienes 17–21 (Table 2, catalyst batch B)

Cycle 1:



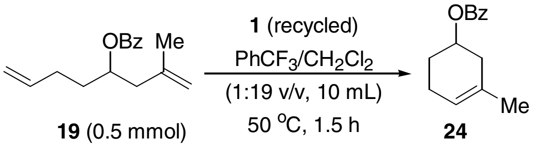
Catalyst **1**, prepared according to the general procedure from 56 mg (0.010 mmol) of **8**, 10 mg (0.015 mmol) of **3** and 1.0 mg (0.010 mmol) of CuCl, was placed in a 50 mL flask equipped with a reflux condenser and the flask was degassed three times by evacuation and then filling with Ar. $PhCF_3$ (0.5mL) was then added to dissolve the catalyst followed by diene **17** (133 mg, 0.50 mmol) in CH_2Cl_2 (9.5 mL). After heating to reflux (bath temperature 45-50°C) for 3 h, the reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture, the crude reaction product was analyzed by 500 MHz ^{1}H NMR which indicated complete conversion of the diene **17** and the clean formation of cyclized product **22.** Purification by flash column chromatography (hexanes/EtOAc, 8:1 v/v) gave the known compound **22**[9] (111 mg, 94 %) as a white solid. **22**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, 2 H, *J* = 8.2 Hz), 7.32 (d, 2 H, *J* = 8.1 Hz), 5.25 (m, 1 H), 4.06-4.08 (m, 2 H), 3.97 (bs, 2 H), 2.43 (s, 3 H), 1.66 (s, 3 H).

Cycle 2:



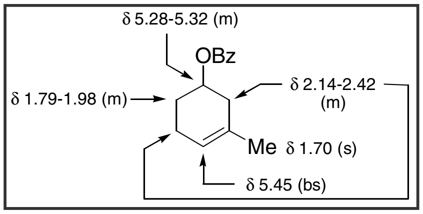
The catalyst recycled from the RCM of **17** (cycle 1) was used in the RCM of **18** (86 mg, 0.50 mmol) under identical conditions to these of **17** except that the reaction mixture was heated to reflux (bath temperature 45-50°C) for 1.5 h. The reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture, 500 MHz ^{1}H NMR analysis of the crude reaction product indicated complete conversion of the diene **18** and clean formation of **23**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 1:3 v/v) gave the known cyclic sulfone **23**[10] (66 mg, 90%) as a white solid. **23**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.33-5.34 (m, 1 H), 3.55 (bs, 2 H), 3.05 (t, 2 H, *J* = 6.5 Hz), 2.65 (t, 2 H, *J* = 5.5 Hz), 1.77 (s, 3 H).

Cycle 3:

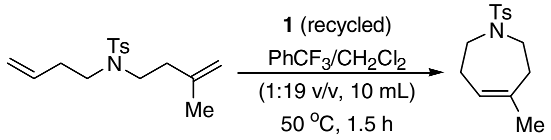


The catalyst recycled from the RCM of **18** (cycle 2) was used in the RCM of **19** (124 mg, 0.50 mmol) under identical conditions to these of **18**. The reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture, 500 MHz ^{1}H NMR analysis of the crude reaction product indicated complete conversion of the diene **19** and clean formation of **24**. Purification by flash column chromatography (hexanes/EtOAc, 95:5 v/v) gave **24** (102 mg, 94%) as colorless oil.

24: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (d, 2 H, *J* = 7.4 Hz), 7.56 (t, 1 H, *J* = 7.4 Hz), 7.44 (t, 2 H, *J* = 7.8 Hz), 5.45 (bs, 1 H), 5.28-5.32 (m, 1 H), 2.14-2.42 (m, 4 H), 1.79-1.98 (m, 2 H), 1.70 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.2, 132.7, 131.0, 130.9, 129.6, 128.3, 120.6, 70.8, 35.5, 27.1, 23.4, 22.9. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.79; H, 7.62.



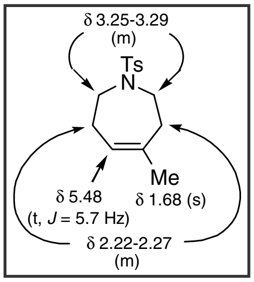
Cycle 4:



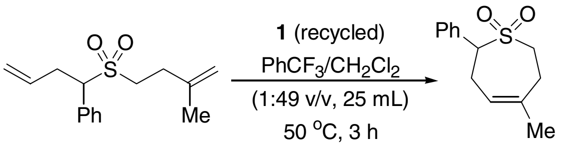
20 (0.5 mmol) **25**

The catalyst recycled from the RCM of **19** (cycle 3) was used in the RCM of **20** (147 mg, 0.50 mmol) under identical conditions to these of **19**. The reaction mixture was cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture, 500 MHz ^{1}H NMR analysis of the crude reaction product indicated complete conversion of the diene **20** and clean formation of **25**. Purification by flash column chromatography (hexanes/EtOAc, 6:1 v/v) gave **25** (128 mg, 96 %) as a slightly yellow oil.

25: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, 2 H, *J* = 8.0 Hz), 7.30 (d, 2 H, *J* = 8.0 Hz), 5.48 (t, 1 H, *J* = 5.7 Hz), 3.25-3.29 (m, 4 H), 2.43 (s, 3 H), 2.22-2.27 (m, 4 H), 1.68 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1, 138.8, 135.5, 129.6, 127.1, 123.9, 48.2, 46.8, 34.7, 28.3, 26.0, 21.5. Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.36; H, 7.22; N, 5.28. Found: C, 63.19; H, 7.54; N, 5.26.



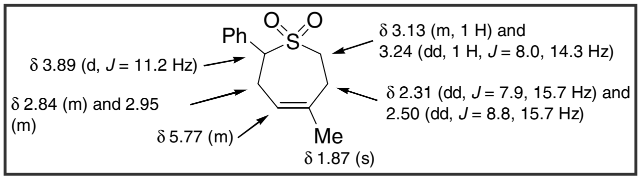
Cycle 5:



21 (0.5 mmol) **26**

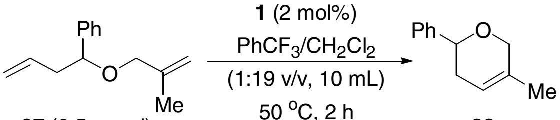
The catalyst recycled from the RCM of **20** (cycle 4) was used in the RCM of **21** (132 mg, 0.50 mmol) in the mixed solvent system $PhCF_3/CH_2Cl_2$ (25 mL, 1:49 v/v). The reaction mixture was heated to reflux (bath temperature 45-50°C) for 3 h and then cooled to rt and concentrated to dryness under vacuum. After fluorous extraction of the reaction mixture, 500 MHz ^{1}H NMR analysis of the crude reaction product indicated complete conversion of the diene **21** and clean formation of **26**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 1:2 v/v) gave **26** (107 mg, 91%) as a white solid.

26: ^{1}HNMR ($CDCl_3$, 500 MHz): δ 7.38 (m, 5 H), 5.77 (m, 1 H), 3.89 (d, 1 H, *J* = 11.2 Hz), 3.24 (dd, 1 H, *J* = 8.0, 14.3 Hz), 3.13 (m, 1 H), 2.95 (m, 1 Hz), 2.84 (m, 1 H), 2.50 (dd, 1 H, *J* = 8.8, 15.7 Hz), 2.31 (dd, 1 H, *J* = 7.9, 15.7 Hz), 1.87 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.7, 131.9, 130.2, 129.1, 128.9, 124.2, 68.9, 53.4, 29.2, 26.9, 25.5. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.87; H, 6.72.



RCM of Diene 27, Cross Metathesis of 28 and RCM of the Enyne 29 (Table 2, catalyst batch C)

Cycle 1:

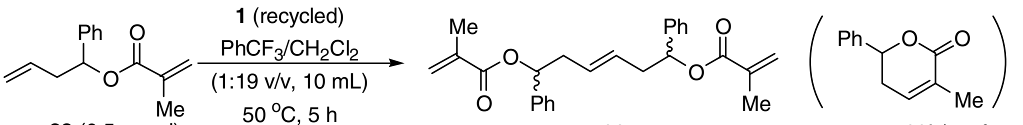


27 (0.5 mmol) **32**

Catalyst **1**, prepared according the general procedure from 56 mg (0.010 mmol) of **8**, 10 mg (0.015 mmol) of **3** and 1.0 mg (0.010 mmol) of CuCl, was placed in a 50mL flask equipped with a reflux condenser and the flask was degassed three times by evacuation and then filling with Ar. $PhCF_3$ (0.5 mL) was then added to dissolve the catalyst followed by diene **27** (101 mg, 0.5 mmol) in CH_2Cl_2 (9.5mL). After heating to reflux (bath temperature 45-50°C) for 2 h, the reaction mixture was cooled to rt and concentrated under vacuum. After fluorous extraction of the reaction mixture, 500 MHz ^{1}H NMR analysis of the crude reaction product indicated complete conversion of diene **27** and clean formation of the cyclized product **32**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 4:1 v/v) gave the known cyclic ether **32**[11] (83 mg, 95%) as a colorless oil. **32**:

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27-7.40 (m, 5 H), 5.61 (m, 1 H), 4.51 (dd, 1 H, *J* = 3.6, 10.2 Hz), 4.27 (d, 2 H, *J* = 16.1 Hz), 4.18 (d, 1 H, *J* = 16.1 Hz), 2.22-2.36 (m, 2 H), 1.68 (s, 3 H).

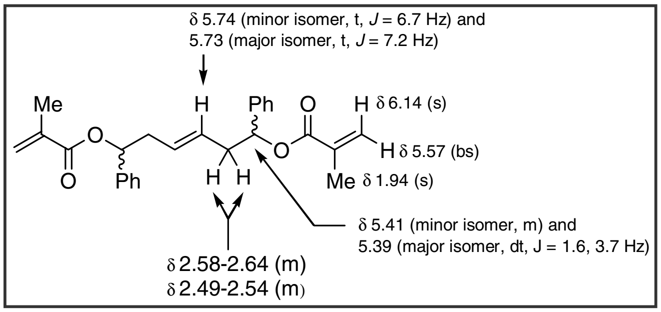
Cycle 2:



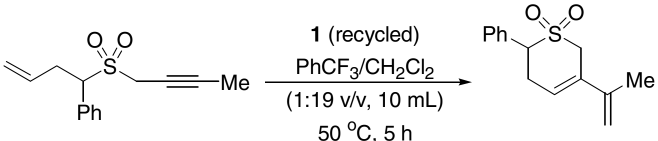
28 (0.5 mmol) **33** **33'** (not formed)

The catalyst recycled from the RCM of **27** (cycle 1) was used in the metathesis reaction of **28** (109 mg, 0.50 mmol) under identical conditions to these of **27** except that the reaction mixture was heated to reflux (bath temperature 45-50°C) for 5 h. After fluorous extraction of the reaction mixture, 500 MHz ^{1}H NMR analysis of the reaction crude revealed a ratio of 89:11 between the cross metathesis product **33** and diene **28** with no indication for the formation of the cyclized product **33´**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 2:1 v/v then hexanes/EtOAc, 8:1 v/v) gave the *trans*-olefin **33** (80 mg, 85%) as a mixture of inseparable diastereomers.

33: ^{1}H NMR ($CDCl_3$, 500 MHz): δ7.27-7.35 (m, 5 H), 6.14(s, 1 H), 5.74 (minor isomer, t, *J* = 6.7 Hz) and 5.73 (major isomer, t, *J* = 7.2 Hz) (total 1 H), 5.57 (bs, 1 H), 5.41 (minor isomer, m) and 5.39 (major isomer, dt, *J* = 1.6, 3.7 Hz) (total 1 H), 2.58-2.64 (m, 1 H), 2.49-2.54 (m, 1 H), 1.94 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.5, 140.2, 136.5, 128.4, 127.9, 127.0, 126.4, 125.5, 75.7 (major isomer) and 75.5 (minor isomer), 39.7 (major isomer) and 34.5 (minor isomer), 18.2. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.03; H, 7.31.



Cycle 3**:**

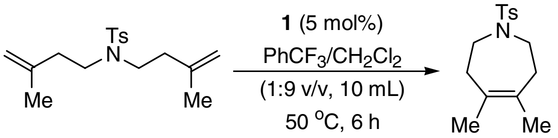


29 (0.5 mmol) **34**

The catalyst recycled from the reaction of **28** (cycle 2) was used the RCM of the enyne **29**^{12} (124 mg, 0.50 mmol) under identical conditions to these of **28**. After fluorous extraction of the reaction mixture, ^{1}H NMR analysis of the reaction crude revealed a ratio of 80:20 between the cyclized product **34** and enyne **29**. Purification by flash column chromatography (hexanes/CH_2Cl_2, 1:1 v/v then CH_2Cl_2) gave the known cyclic sulfone **34**^{12} (92 mg, 74%) as a white solid. **34**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ7.48-7.50 (m, 2 H), 7.41-7.43 (m, 3 H), 6.11 (bs, 1 H), 5.04 (s, 1 H), 4.91 (s, 1 H), 4.21(dd, 1 H, *J* = 4.9, 10.6Hz), 3.97 (d, 1 H, *J* = 17.1 Hz), 3.88 (d, 1 H, *J* = 17.0 Hz), 3.34 (dd, 1 H, *J* = 10.7, 18.7 Hz), 3.05 (dt, 1 H, *J* = 18.9, 5.3 Hz), 1.99 (s, 3 H).

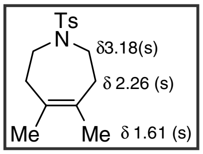
RCM of Diene 30 (Table 2, catalyst batch D)

Cycle 1:



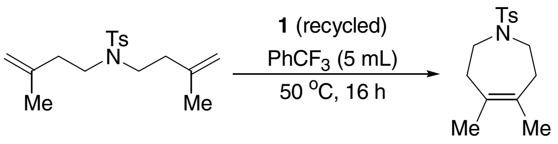
30 (0.25 mmol) **35**

The catalyst **1**, prepared according to the general procedure from 70 mg (0.013 mmol) of **8**, 16 mg (0.019 mmol) of **3** and 1.3 mg (0.013 mmol) of CuCl, was placed in a 50 mL flask equipped with a reflux condenser and the flask was degassed three times by evacuation and then filling with Ar. $PhCF_3$ (0.5 mL) was then added to dissolve the catalyst followed by diene **30** (77 mg, 0.25 mmol) in CH_2Cl_2 (4.5 mL). After heating to reflux (bath temperature 45-50°C) for 6 h, the reaction mixture was cooled to rt and concentrated under vacuum. After fluorous extraction of the reaction mixture, ^1H NMR analysis of the reaction crude revealed a ratio of 43:57 between the cyclized product **35** and diene **30**. Purification by flash column chromatography (hexanes/EtOAc, 12:1 v/v) gave **35** (27 mg, 39 %) as a colorless oil.



35: ^1H NMR ($CDCl_3$, 500 MHz): δ 7.64 (d, 2 H, J = 8.2 Hz), 7.29 (d, 2 H, J = 8.1 Hz), 3.18 (t, 4 H, J = 5.2 Hz), 2.42 (s, 3 H), 2.26 (t, 4 H, J = 5.2 Hz), 1.61 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1, 135.3, 130.2, 129.6, 127.3, 46.8, 35.4, 21.5, 21.3. Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.37; H, 7.68; N, 4.89.

Cycle 2:

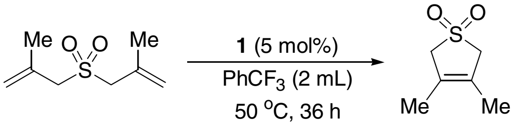


30 (0.25 mmol) **35**

A second run of the RCM of **30** (77 mg, 0.25 mmol) in $PhCF_3$ (5 mL) was performed using the catalyst recycled from the first run. After heating to reflux (bath temperature 45-50°C) for 16 h, the reaction mixture was cooled to rt and concentrated to dryness. After fluorous extraction of the reaction mixture, ^1H NMR analysis of the reaction crude revealed a ratio of 94:6 between the cyclized product **35** and the diene **30**. Purification by flash column chromatography (hexanes/EtOAc, 12:1 v/v) gave **35** (65 mg, 93%) as a colorless oil.

RCM of Dienes 31 and 20 (Table 2, catalyst batch E)

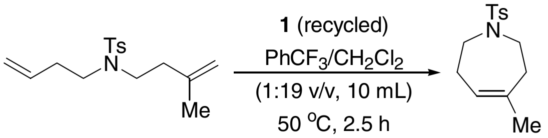
Cycle 1:



31 (0.1 mmol) **36**

Catalyst **1**, prepared according to the general procedure from 28 mg (0.0050 mmol) of **8**, 5.0 mg (0.0075 mmol) of **3** and 0.5 mg (0.005 mmol) of CuCl in $PhCF_3$ (0.5 mL), was placed in a 50 mL flask equipped with a reflux condenser and the flask was degassed three times by evacuation and then filling with Ar. A solution of diene **31** (18 mg, 0.10 mmol) in $PhCF_3$ (2 mL) was added. After heating to 45-50 °C (bath temperature) for 36 h, the reaction mixture was cooled to rt and concentrated under vacuum. After fluorous extraction of the reaction mixture, ^1H NMR analysis of the reaction crude revealed a ratio of 51:49 between the cyclized product **36** and diene **31**. Purification by flash column chromatography (hexanes:CH_2Cl_2, 1:2 v/v) gave the known cyclic sulfone **36**[12] (7 mg, 50%) as a white foam. **36**: ^1H NMR ($CDCl_3$, 500 MHz): δ 3.74 (s, 4 H), 1.79 (s, 6 H).

Cycle 2:



20 (0.5 mmol) **25**

The catalyst recycled from the RCM of **31**was used for the RCM of diene **20** (74 mg, 0.25 mmol) in $PhCF_3/CH_2Cl_2$ (1:9 v/v, 5 mL). After heating to reflux (bath temperature 45-50°C) for 2.5 h, the reaction mixture was cooled to rt and concentrated to dryness. After fluorous extraction of the reaction mixture, 500 MHz ^1H NMR analysis of the crude reaction product revealed a ratio of 96:4 between the cyclized product **25** and diene **20**. Purification by flash column chromatography (hexanes/EtOAc, 6:1 v/v) gave pure **25** (64 mg, 96%).

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