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Ring-opening metathesis–cross-metathesis reactions (ROM–CM) of substituted norbornadienes and norbornenes

Peter Mayo and William Tam*

Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Guelph, Guelph, Ont., Canada N1G 2W1

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Abstract—Ring-opening metathesis–cross-metathesis reactions (ROM–CM) of substituted norbornadienes and norbornenes were investigated. The reactions with symmetrical 2,3-disubstituted norbornadienes were found to be highly chemoselective, with the ROM reactions occurring only on the less substituted or less sterically hindered double bonds regardless of the electronic nature of the substituents, giving highly substituted cyclopentenes in moderate to good yields. This study provides an efficient method for the stereoselective synthesis of highly substituted cyclopentenoids. Long-range electronic effect of a remote substituent on unsymmetrical norbornenes in the ROM–CM reactions was also investigated. Low levels of regioselectivities were observed (50:50 to 69:31) with various remote substituents on the norbornenes.

1. Introduction

Metal-catalyzed olefin metathesis represents a unique class of reactions in which the redistribution of unsaturated carbon–carbon bonds occurs in the presence of metal carbene complexes.[1] The development of well-defined metal alkylidene complexes by Schrock and Grubbs,[2,3] and recent advances in new catalysts design,[4] has significantly extended the scope of olefin metathesis reactions as valuable synthetic tools in organic synthesis. In recent years, olefin metathesis reactions have attracted widespread attention as a versatile carbon–carbon bond-forming method. There are five main types of olefin metathesis reactions: (a) ring-opening metathesis polymerization (ROMP),[5] (b) ring-closing metathesis (RCM),[6] (c) acyclic diene metathesis polymerization (ADMET),[7] (d) ring-opening metathesis (ROM),[8] and (e) cross-metathesis (CM).[9] In addition to these five main types of olefin metathesis reactions, tandem or domino process combining different metathesis types, e.g. tandem ROM–RCM,[10] tandem ROM–CM,[11] and tandem CM–RCM,[12] have also been reported.

In the past few years, we have been focusing on the study of metal-catalyzed and non-metal-catalyzed reactions of bicyclic alkenes.[13–19] In this paper, we would like to report our study on the ring opening metathesis–cross-metathesis reactions (ROM–CM) of substituted norbornadienes and substituted norbornenes (Fig. 1). There are two questions we would like to address in this paper: (a) the chemoselectivity of the ROM–CM reactions of symmetrical 2,3-disubstituted norbornadienes **1** (which carbon–carbon double bond, $C_5{=}C_6$ or $C_2{=}C_3$, will undergo ROM); and (b) the long-range electronic effect of a remote substitutent on the regioselectivity of the ROM–CM reactions of unsymmetrical 2-substituted 5-norbornenes **2** and **3**. Although some examples of tandem olefin metathesis reactions of bicyclic alkenes are known in the literature (Scheme 1),[20–24] to the best of our knowledge, the above questions have not been studied. Since most studies on tandem olefin metathesis reactions of bicyclic alkenes relies on substituted norbornenes which contain only one strained double bond in the system and therefore the question of chemoselectivity was not studied. Also, very few studies on the effect of a remote substitutent on the regioselectivity of the ROM–CM reactions of unsymmetrical norbornene systems have been reported.[25]

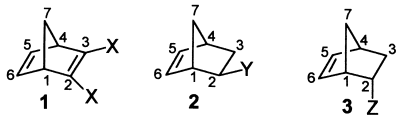

Figure 1. Substituted bicyclic alkenes.

2. Results and discussion

2.1. Ruthenium-catalyzed tandem ROM–CM of symmetrical 2,3-disubstituted norbornadienes (1a–1c)

In order to carry out the study of tandem Ru-catalyzed

Keywords: ring-opening metathesis; cross-metathesis; ruthenium catalyst; carbene; chemoselectivity; regioselectivity; remote substituent effect.

* Corresponding author. Tel.: +1-519-824-4120x2268; fax: +1-519-766-1499; e-mail: wtam@uoguelph.ca

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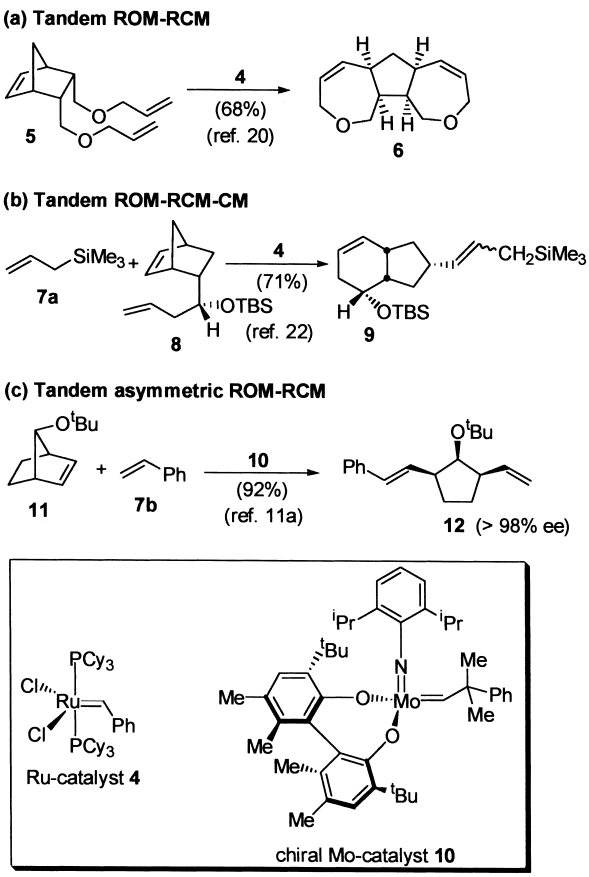
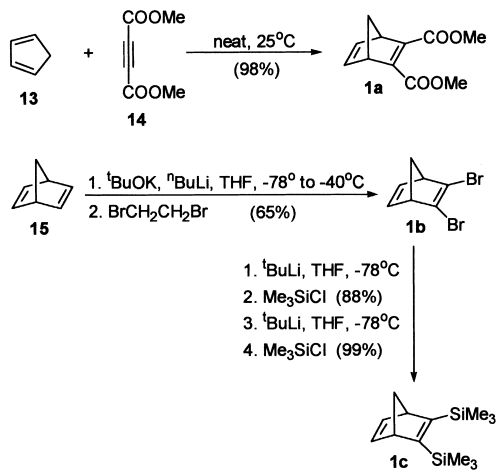
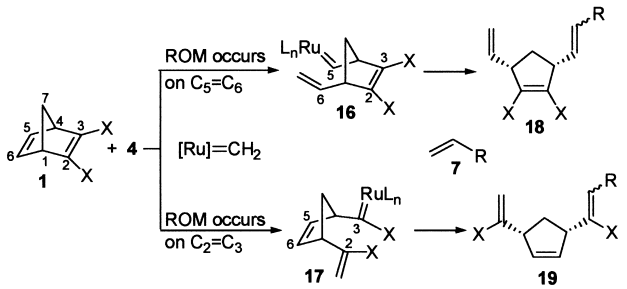


Scheme 1. Literature examples of tandem olefin metathesis reactions of bicyclic alkenes.

ROM–CM of symmetrical 2,3-disubstituted norbornadienes, **1a**–**1c** were prepared (Scheme 2). Diels–Alder cycloaddition of cyclopentadiene **13** with dimethyl acetylenedicarboxylate **14** provided 2,3-dicarbomethoxynorbornadiene **1a** in 98% yield.[26] Deprotonation of norbornadiene **15** using the Schlosser's base (^{t}BuOK/^{n}BuLi) followed by trapping with 1,2-dibromoethane afforded 2,3-dibromonorbornadiene **1b** in 65% yield.[16] Double lithium–halide exchange and trapping with trimethylsilyl chloride generated the required 2,3-bis(trimethylsilyl)norbornadiene **1c** in good yield.[16]



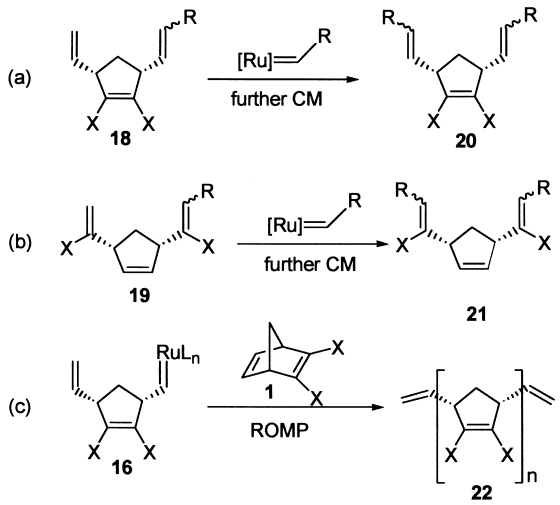
Scheme 2. Synthesis of symmetrical 2,3-disubstituted norbornadienes(**1a**–**1c**).



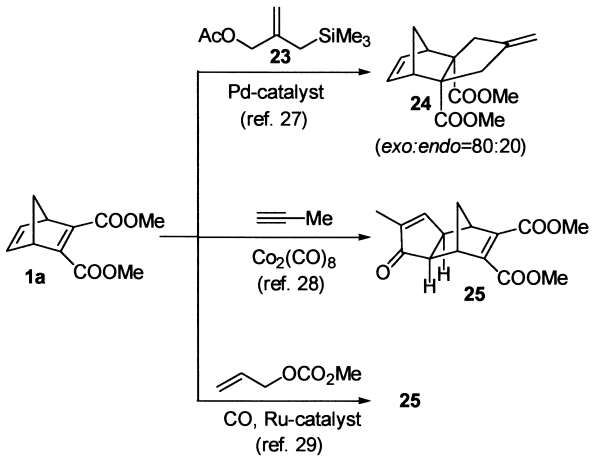
Scheme 3. Chemoselectivity in the tandem ROM–CM of 2,3-disubstituted norbornadienes **1**.

Two different regioisomers (**18** and **19**) could be formed from the ROM–CM reactions of symmetrical 2,3-disubstituted norbornadienes **1** (Scheme 3). ROM could occur on the less substituted double bond of the norbornadiene (C_5=C_6) or occur on the more substituted double bond (C_2=C_3). Apart from these two different regioisomers (**18** and **19**), other side products are also possible (Scheme 4). Further cross-metathesis of **18** or **19** could lead to the formation of **20** and **21**, and ROMP of **16** with the bicyclic alkene **1** could lead to polymer **22**.

Only very few examples of the study of chemoselectivity of

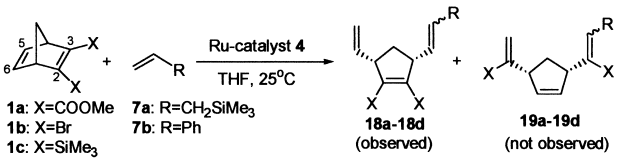


Scheme 4. Other possible side products.



Scheme 5. Literature examples of the study of chemoselectivity of the reactions of bicyclic alkenes.

Table 1. Ru-catalyzed tandem ROM–CM of 2,3-disubstituted norbornadienes **1a**–**1c**

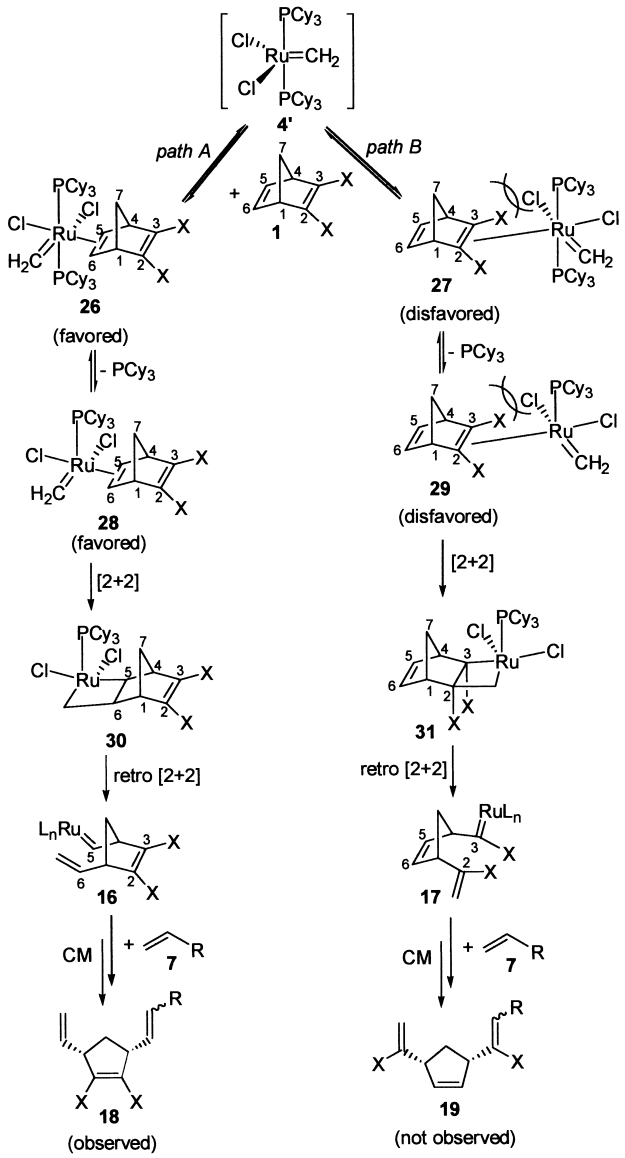


Entry	X	R	Chemo-selectivity (**18**/**19**)[a]	*cis*/*trans* of **18**[b]	Yield (%)[c]
1	COOMe	CH_2SiMe_3	100:0	(**18a**) 38:62	89
2	COOMe	Ph	100:0	(**18d**) 57:43	79
3	Br	CH_2SiMe_3	100:0	(**18b**) 43:57	80
4	$SiMe_3$	CH_2SiMe_3	100:0	(**18c**) 50:50	74

[a] No other isomers were detected by ^{1}H NMR (400 MHz) in the crude reaction mixture.
[b] Determined by ^{1}H (400 MHz) and ^{13}C NMR (100 MHz).
[c] Isolated yields after column chromatography.

transition metal-catalyzed reactions of substituted norbornadienes can be found in the literature (Scheme 5). For example, Pd-catalyzed [3+2] cycloaddition of palladium–trimethylenemethane (Pd–TMM) complex with **1a** occurs exclusively on the electron-deficient, more substituted double bond (with stereoselectivity *exo*/*endo*=80:20).[27] On the other hand, the opposite chemoselectivity was observed in the Co-catalyzed Pauson–Khand [2+2+1] cycloaddition of propyne and **1a**,[28] and in the Ru-catalyzed carbonylative cyclization of allylic carbonates,[29] in which the reactions occurred exclusively on the less substituted, less electron-deficient double bond.

The results of the ROM–CM reactions of symmetrical 2,3-disubstituted norbornadienes **1** is shown in Table 1. Although two regioisomers (**18** and **19**, Scheme 3) and other side products (**20**, **21** and **22**, Scheme 4) are possible, the tandem ROM–CM reactions of symmetrical 2,3-disubstituted norbornadienes **1a**–**1c** were found to be highly chemoselective, giving substituted cyclopentenes **18a**–**18d** as the only isolated products in good yields. In the presence of 5 mol% of Ru-catalyst **4** in THF (0.1 M) at 25°C, equimolar amount of 2,3-dicarbomethoxynorbornadiene **1a** (X=COOMe) and allyltrimethylsilane **7a** underwent ROM–CM to provide cyclopentene **18a** as the only regioisomer in 89% isolated yield (Table 1, entry 1). Similarly, ROM–CM of 2,3-dicarbomethoxynorbornadiene **1a** with styrene **7b** provided cyclopentene **18d** as the only regioisomer in 79% isolated yield (Table 1, entry 2). With other X substituents on the norbornadiene, both 2,3-dibromonorbornadiene **1b** and 2,3-bis(trimethylsilyl)norbornadiene **1c** underwent ROM–CM reactions with allyltrimethylsilane **7a** to afford cyclopentene **18b** and **18c** as the only regioisomers in 80 and 74% isolated yield, respectively (Table 1, entries 3 and 4). Thus, regardless of the electronic nature of the substituents X, the Ru-catalyzed tandem ROM–CM reactions of 2,3-disubstituted norbornadienes always occur faster on the less hindered, less substituted double bond of the norbornadiene. The regiochemistry of the products (**18** vs **19**) was easily distinguished by ^{1}H and ^{13}C (APT) NMR techniques as cyclopentenes **18** contain two quaternary olefinic carbons in the cyclopentene rings whereas cyclopentenes **19** contain two methine (C–H) olefinic carbons in the cyclopentene rings.



Scheme 6. Proposed mechanism.

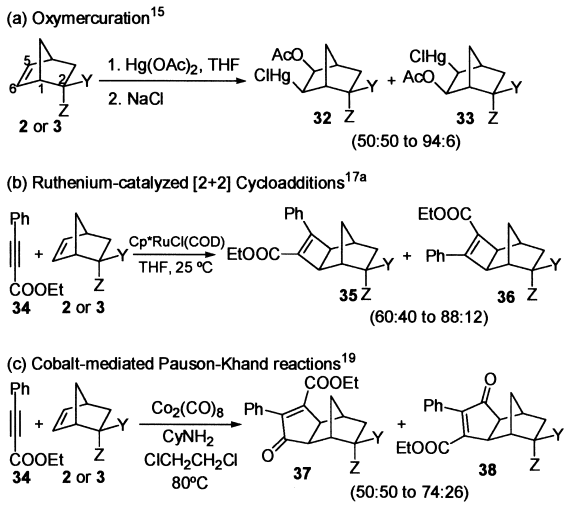
The excellent levels of chemoselectivities can be explained by the mechanism proposed in Scheme 6. Although the issue whether a ruthenium methylidene (Ru=CH_2) or a ruthenium alkylidene (Ru=CHPh) is the active species in the ring opening metathesis step is still controversial,[1a,8f,11c] mechanism proposed by Grubbs suggested that the ruthenium methylidene (Ru=CH_2) (**4**′) is likely to be the active species in the ring opening metathesis step. As proposed by Grubbs, the olefin will coordinate to the Ru center *trans* to one of the Cl ligands and *cis* to the alkylidene group.[1a] Thus, coordination of the less substituted double bond (C_5=C_6) of a 2,3-disubstituted norbornadiene to the Ru-complex **4**′ would lead to the formation of the olefin complex **26**, whereas coordination of the more substituted double bond (C_2=C_3) would provide of the olefin complex **27**. Due to the steric hindrance of the X substitutent on the norbornadiene with one of the Cl ligands, complex **27** is highly disfavored. Dissociation of one of the phosphine ligands (PCy_3) in complex **26** or **27** would provide the 16-electron intermediates **28** and **29**. The intermediate **29** is also unfavorable to form due to the steric hindrance of the X

substitutent on the norbornadiene with one of the Cl ligands. Since path B would lead to the formation of highly sterically hindered, unfavorable intermediates **27** and **29**, path A would be the preferred reaction pathway. A [2+2] cycloaddition followed by a retro [2+2] process of the intermediate **28** would provide the intermediate **16**. Cross-metathesis of the intermediate **16** with alkene **7** would lead to the formation of the observed product **18**.

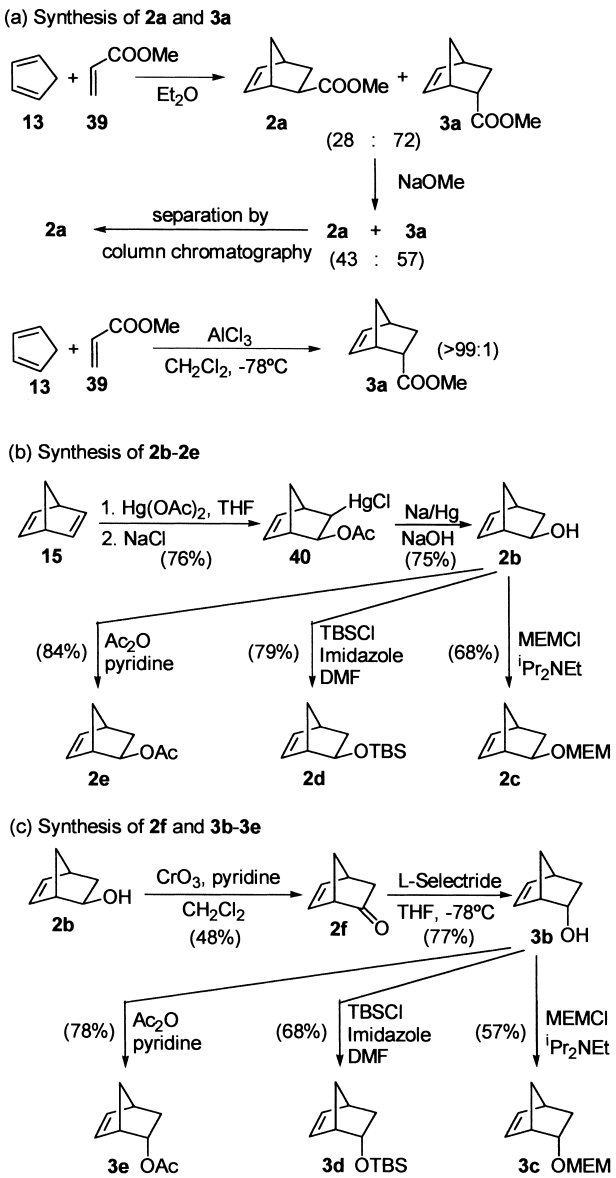
2.2. Ruthenium-catalyzed ROM–CM of unsymmetrical 2-disubstituted 5-norbornenes (2a–2f and 3a–3e)

The study of long-range stereoelectronic effect of a remote substituent in controlling regio- and stereoselectivities on nucleophilic and electrophilic additions to π-bonds has attracted considerable interest.[30] On the other hand, very few examples of the study of remote substituent effects on transition metal-catalyzed reactions can be found in the literature.[17a,19,25,31,32] We have recently reported the remote substituent effects on the regioselectivity in some metal-catalyzed and non-metal-catalyzed reactions of 2-substituted 5-norbornenes (Scheme 7).[15,17a,18,19] For example, the remote substituents showed strong long-range stereoelectronic effect on oxymercuration reactions (regioselectivity up to 94:6, Scheme 7(a)), whereas moderate levels of long-range stereoelectronic effect on Ru-catalyzed [2+2] cycloadditions (regioselectivity up to 88:12, Scheme 7(b)) and Co-mediated Pauson–Khand reactions (regioselectivity up to 74:26, Scheme 7(c)) were observed. To the best of our knowledge, there is no previous study on the effect of a remote substitutent on the regioselectivity of the tandem ROM–CM reactions of unsymmetrical norbornene systems.[25]

In order to study the remote substituent effects on regioselectivity in the tandem ROM–CM reactions of 2-substituted 5-norbornenes, *exo*-2-substituted 5-norbornenes **2a–2e**, *endo*-2-substituted 5-norbornenes **3a–3e** and 5-norbornen-2-one **2f** were prepared (Scheme 8). The *exo*-and *endo*-norbornenes **2a** and **3a** were prepared by Diels–Alder reactions (Scheme 8(a)). A thermal Diels–Alder reaction of cyclopentadiene (**13**) and methyl acrylate



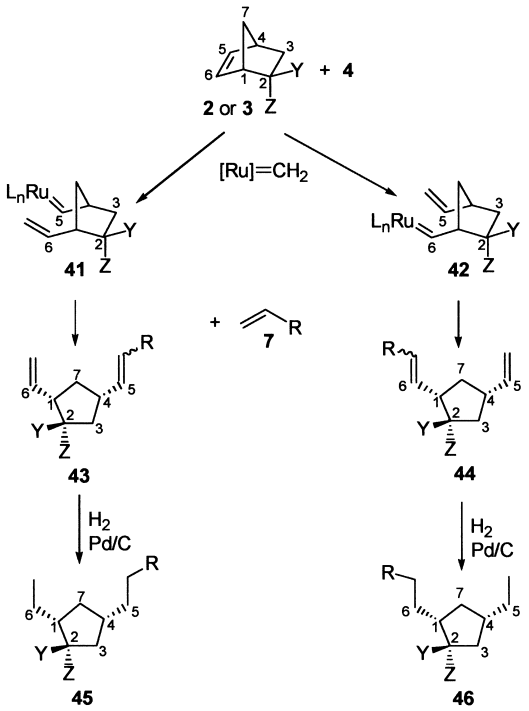
Scheme 7. Examples of some previous studies on the remote substituent effects of 2-substituted 5-norbornenes from our research group.



Scheme 8. Synthesis of 2-substituted 5-norbornenes.

(**39**), followed by epimerization of the *endo*/*exo* cycloadduct mixture with NaOMe, and separation of the *exo*- and *endo*-cycloadducts by column chromatography produced *exo*-norbornene **2a**.[33] The *endo*-norbornene **3a** was prepared from the Lewis acid-catalyzed Diels–Alder reaction of cyclopentadiene (**13**) and methyl acrylate (**39**).[34] *exo*-2-OH-norbornene **2b** was prepared by oxymercuration of norbornadiene **15** followed by demercuration and saponification (Scheme 8(b)).[15b] Collins oxidation of **2b** provided 5-norbornen-2-one **2f** in 48% yield. Reduction of **2f** with L-Selectride at −78°C provided the *endo*-2-OH-norbornene **3b** >99:1 *endo*/*exo* selectivity (Scheme 8(c)).[15b] Derivatization of **2b** and **3b** gave the *exo*-norbornenes **2c–2e** and *endo*-norbornenes **3c–3e**.

Two possible regioisomers (**43** and **44**) are possible in the ROM–CM reactions of 2-substituted 5-norbornenes (Scheme 9). The ROM could occur in such a way that the methylene group would end up on C_6 (**43**, closer to the remote substituent Y or Z) or end up on C_5 (**44**, further away



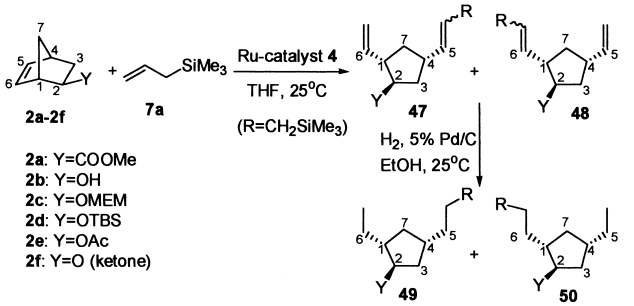
Scheme 9. Regioselectivity in the tandem ROM–CM of 2-substituted 5-norbornenes **2** and **3**.

from the remote substituent Y or Z). Since both regioisomers **43** and **44** could possess *cis*/*trans* isomers, and these regio- and geometrical isomers were not separable by column chromatography, it is difficulty to analyze the ratio of **43**/**44**. Thus, without detailed characterization of the mixture of the regio- and geometrical isomers (*cis*-**43**, *trans*-**43**, *cis*-**44** and *trans*-**44**), they were hydrogenated to **45** and **46** to avoid complication of the *cis*/*trans* isomers. The ratio of the inseparable mixture of **45** and **46** was then determined by the integration of the ^{1}H NMR (400 MHz).

The results of the study of the remote substituent effects on regioselectivity in the tandem ROM–CM reactions of 2-substituted 5-norbornenes are shown in Tables 2 and 3. Unlike most of our previous studies on the remote substituent effects of 2-substituted 5-norbornenes which showed strong long-range stereoelectronic effect, the remote substituents showed very little long-range stereoelectronic effect towards the tandem ROM–CM reactions and low levels of regioselectivities (50:50 to 69:31) were observed. The regiochemistry of the products (**49** vs **50**, and **53** vs **54**) was determined by comparing the ^{1}H NMR spectra with similar compounds in the literature.[25] In all the major products, the ^{1}H NMR of the CH_3 group (attached to C_6 in **49**/**53**, closer to the electron-withdrawing substituent Y or Z), which is a triplet, is always more downfield (greater chemical shift value, δ ppm) than the minor products (**50**/**54**, the CH_3 group attached to C_5 is further away from the electron-withdrawing substituent Y or Z).

Although the regioselectivities were low, we obtained some important information from this study. First of all, unlike in all of our previous studies of the remote substituent effects of 2-substituted 5-norbornenes, a remote ketone group (**2f**, Scheme 8) usually gave the highest regioselectivities,

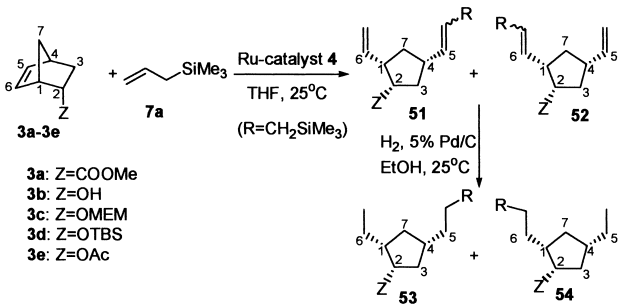
Table 2. Ru-catalyzed ROM–CM of *exo*-2-substituted norbornenes **2a**–**2f**



Entry	Y	Yield of ROM–CM (%)[a]	Yield of hydrogenation (%)[a]	**49**/**50**[b]
1	COOMe	60	92	68:32
2	OH	30	75	60:40
3	OMEM	45	57	60:40
4	OTBS	57	65	67:33
5	OAc	53	100	69:31
6	=O (ketone)	43	81	50:50

[a] Isolated yields after column chromatography. 1.4–1.8 equiv. of **7a** was used to avoid ROMP of the norbornene. Lower yields were observed when less than 1.2 equiv. of **7a** were used.
[b] The ratios were determined by ^{1}H NMR (400 MHz). Very little changes of the ratios were observed when changing the no. of equiv. of **7a**.

Table 3. Ru-catalyzed ROM–CM of *endo*-2-substituted norbornenes **3a**–**3e**

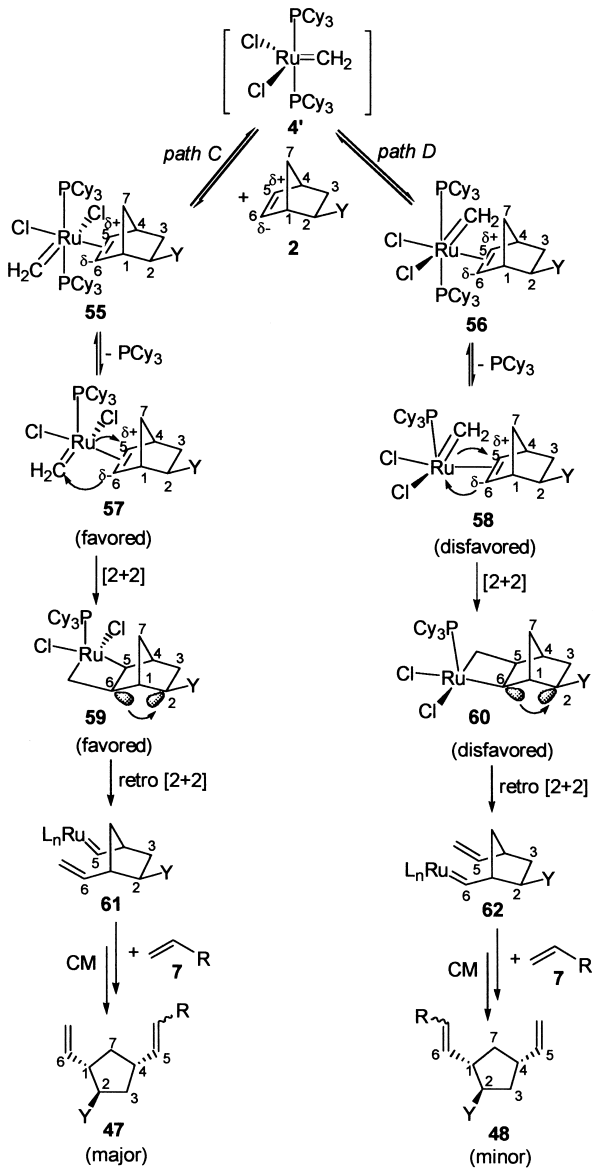


Entry	Z	Yield of ROM–CM (%)[a]	Yield of hydrogenation (%)[a]	**53**/**54**[b]
1	COOMe	58	93	60:40
2	OH	30	54	63:37
3	OMEM	33	86	60:40
4	OTBS	86	89	68:32
5	OAc	70	52	58:42

[a] Isolated yields after column chromatography. 1.4–1.8 equiv. of **7a** was used to avoid ROMP of the norbornene. Lower yields were observed when less than 1.2 equiv. of **7a** were used.
[b] The ratios were determined by ^{1}H NMR (400 MHz). Very little changes of the ratios were observed when changing the no. of equiv. of **7a**.

whereas it gave the lowest regioselectivity in the ROM–CM reaction. Secondly, there is still a slight preference for the formation of one major regioisomer and in all cases (Tables 2 and 3), the major regioisomers were found to be the ones with the methylene group on C_6 (**47** and **51**, closer to the remote substituent Y or Z). This result provides some important information of the mechanism of ROM reactions.

A proposed mechanism to account for the formation of the



Scheme 10. Proposed mechanism.

major product **47** is shown in Scheme 10. Coordination of the double bond (C_5=C_6) of 2-substituted 5-norbornene **2** to the Ru-complex **4′** would lead to the formation of the olefin complex **55** or **56**. Dissociation of one of the phosphine ligands (PCy_3) in complex **55** or **56** would provide the 16-electron intermediates **57** and **58**. According to our previous density function theory (DET) study of 2-substituted 5-norbornene systems, C_6 of 2-substituted 5-norbornenes (**2a**–**2f** and **3a**–**3e**) is always more 'negative' than C_5.[15b] The [2+2] cycloaddition could occur either with the more electron rich (δ-, more negative) carbon (C_6) attacking the methylene (=CH_2) group (in intermediate **57**) or attacking the Ru metal center group (in intermediate **58**). The [2+2] cycloaddition of intermediate **57** would provide the metallacyclobutane **59** and that of intermediate **58** would provide the metallacyclobutane **60**. Due to homo-conjugation of the σ* of the Ru–C_6 bond with the σ* of the C–Y in **60** (with Y=electron-withdrawing groups for **2a**–**2f**), the formation of intermediate **60** is unfavorable. Thus, the formation of intermediate **59** is more favorable and therefore path C is the major reaction pathway which leads to the formation of the major product **47**.

3. Conclusions

We have studied the ring-opening metathesis–cross-metathesis reactions (ROM–CM) of substituted norbornadienes and norbornenes. The reactions with symmetrical 2,3-disubstituted norbornadienes (**1a**–**1c**) were found to be highly chemoselective, with the ROM reactions occurring only on the less substituted or less sterically hindered double bonds regardless of the electronic nature of the substituents, giving highly substituted cyclopentenes in moderate to good yields. This study provides an efficient method for the stereoselective synthesis of highly substituted cyclopentenoids. We have also investigated the long-range electronic effect of a remote substituent on unsymmetrical norbornenes in the ROM–CM reactions. Although only low levels of regioselectivities were observed (50:50 to 69:31) with various remote substituents on the norbornenes, this study provided important information on the mechanism of Ru-catalyzed ROM reactions.

4. Experimental

4.1. General information

All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherwise stated. Standard column chromatography was performed on 230–400 mesh silica gel (obtained from Silicycle) by use of flash column chromatography techniques.[35] Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0). High-resolution mass spectra were done by McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. Elemental analyses were performed by Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey.

4.2. Materials

Unless stated otherwise, commercial reagents were used without purification. The ruthenium catalyst **4** was purchased from Strem Chemicals and was stored in an inert atmosphere dry box. THF was purified by distillation from potassium/benzophenone under dry nitrogen. CH_2Cl_2, DMF and pyridine were purified by distillation under dry nitrogen: from CaH_2. Norbornadienes **1a**[26] and **1b**,[16] and

norbornenes **2a**,[33] **2c**,[19] **3a**[34] and **3c**[19] were prepared according to literature procedure.

4.3. Synthesis of substituted norbornadienes and norbornenes

4.3.1. 2,3-Bis(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene (1c). To a flame-dried round-bottom flask containing 2-bromo-3-trimethylsilylnorbornadiene[16] (1.00 g, 4.13 mmol) and THF (12.0 mL) was added ^{t}BuLi (7.50 mL, 1.7 M, 12.8 mmol) dropwise at −78°C under nitrogen. The reaction mixture was stirred at −78°C for 1 h. The lithiated norbornadiene was trapped with TMSCl (2.6 mL, 20.5 mmol) at −78°C and stirred for 30 min. The reaction mixture was stirred at 0°C for 1 h and then quenched with saturated $NaHCO_3$ and H_2O. The aqueous layer was extracted with Et_2O, washed with water and saturated NaCl, and dried over $MgSO_4$. The crude product was purified by column chromatography (hexanes) to give **1c** (964 mg, 4.08 mmol, 99%) as a colorless liquid. R_f 0.66 (hexanes); IR (neat) 3065 (m), 2957 (s), 2898 (m), 2864 (m), 1523 (s), 1405 (m), 1301 (s), 1249 (s), 1193 (m), 1169 (s), 1052 (s), 1011 (s), 966 (s), 898 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.60 (t, 2H, J=1.9 Hz), 3.92 (m, 2H), 1.63 (m, 2H), 0.15 (s, 18H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 165.0, 141.9, 71.5, 58.0, 0.09. HRMS calcd for $C_{13}H_{24}Si_2$: m/z 236.1417, found m/z 236.1428.

4.3.2. *exo*-Bicyclo[2.2.1]hept-5-en-2-ol (2b). $Hg(OAc)_2$ (10.4 g, 32.6 mmol) was slowly added (over 45 min.) to a flame-dried flask containing norbornadiene **13** (5.39 mL, 50.0 mmol) in THF (25 mL). The mixture was stirred at room temperature for 12 h, quenched with NaCl (14.6 g, 25.0 mmol) and stirred for 30 min. After quenching with water, the aqueous layer was extracted into CH_2Cl_2, and the combined organic layers were washed with brine and dried ($MgSO_4$). Rotary evaporation and recrystallization from hot EtOAc yielded (2-acetoxy-*cis*-*exo*-bicyclo[2.2.1]hept-5-en-3-yl)mercuric chloride as white crystals (9.57 g, 24.7 mmol, 76%). Spectral data are identical to those reported in the literature.[36]

Sodium amalgam (6% w/w Na/Hg, 92.7 g) was added to a flame-dried flask containing the above (2-acetoxy-*cis*-*exo*-bicyclo[2.2.1]hept-5-en-3-yl)mercuric chloride (7.64 g, 19.7 mmol) in NaOH (2.5 M, 200 mL) and the reaction mixture was stirred for 18 h. The reaction was quenched with water (200 mL), extracted into diethyl ether (4×200 mL), and the combined organic layers were washed with water (200 mL), brine (200 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give **2b** (1.63 g, 14.8 mmol, 75%) as soft white crystals. Spectral data are identical to those reported in the literature.[37]

4.3.3. *exo*-(Bicyclo[2.2.1]hept-5-en-2-yl) *tert*-butyldimethylsilyl ether (2d). *tert*-Butyldimethylsilyl chloride (570 mg, 3.78 mmol) was added to a flame-dried flask containing alcohol **2b** (340 mg, 3.09 mmol) and imidazole (301 mg, 4.42 mmol) in DMF (4 mL) and the reaction mixture was stirred for 12 h. After quenching with water (10 mL), the reaction mixture was extracted into CH_2Cl_2/hexanes (1:9) (4×10 mL), and the combined extracts were washed with water (10 mL), brine (10 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give **2d** (550 mg, 2.45 mmol, 79%) as a colorless oil: R_f 65 (hexanes); IR (neat): 3064 (w), 2957 (s), 2931 (s), 2898 (m), 2857 (s), 1473 (m), 1463 (m), 1389 (w), 1362 (m), 1332 (m), 1256 (s), 1174 (m), 1156 (w), 1102 (s), 1080 (s), 1007 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.15 (dd, 1H, J=5.7, 2.9 Hz), 5.92 (dd, 1H, J=5.7, 3.2 Hz), 3.81 (d, 1H, J=5.5 Hz), 2.76 (br s, 1H), 2.61 (br s, 1H), 1.77 (d, 1H, J=8.1 Hz), 1.57–1.49 (m, 2H), 1.25 (ddd, 1H, J=11.5, 3.5, 1.9 Hz), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 133.4, 72.7, 50.4, 45.8, 40.6, 37.4, 25.9, 18.1, −4.6, −4.7. HRMS calcd for $C_{13}H_{24}SiO$: m/z 224.1596, found m/z 224.1600.

4.3.4. *exo*-Bicyclo[2.2.1]hept-5-en-2-yl acetate (2e). Acetic anhydride (0.91 mL, 9.64 mmol) was added to a flame-dried flask containing alcohol **2b** (667 mg, 6.05 mmol), pyridine (1.53 mL, 18.9 mmol) and dimethylaminopyridine (two crystals) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 24 h. After quenching with water (10 mL), the aqueous layer was extracted with CH_2Cl_2 (4×40 mL) and the combined organic layers were washed with saturated $CuSO_4$ (10 mL), water (10 mL), brine (10 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give **2e** (777 mg, 5.10 mmol, 84%) as a colorless oil. Spectral data are identical to those reported in the literature.[38]

4.3.5. Bicyclo[2.2.1]hept-5-en-2-one (2f). Alcohol **2b** (8.44 g, 76.6 mmol) in CH_2Cl_2 (250 mL) was added via a cannula to a flame-dried flask containing CrO_3 (47.2 g, 472 mmol) and pyridine (76 mL, 940 mmol) in CH_2Cl_2 (600 mL) and the reaction mixture was stirred for 48 h. The reaction mixture was filtered through a short plug of silica (eluted with CH_2Cl_2) and the organic layer was washed with 5% KOH, 5% HCl, saturated $NaHCO_3$, saturated NaCl, and dried (Na_2SO_4). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give ketone **2f** (3.95 g, 36.5 mmol, 48%) as a white solid. Spectral data are identical to those reported in the literature.[39]

4.3.6. *endo*-Bicyclo[2.2.1]hept-5-en-2-ol (3b). L-Selectride (1 M in THF, 40.0 mL, 40.0 mmol) was added to a flame-dried flask containing ketone **2f** (3.52 g, 32.5 mmol) in THF (35 mL) at −78°C. The reaction mixture was stirred at −78°C for 3 h and at −20°C for 1 h. After quenching with water (20 mL), the aqueous layer was extracted with diethyl ether (5×30 mL) and the combined organic layers were washed with water (100 mL), brine (100 mL), and dried (Na_2SO_4). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=3:7) to give **3b** (2.76 mg, 25.0 mmol, 77%) as a colorless oil. Spectral data are identical to those reported in the literature.[37b]

4.3.7. *endo*-(Bicyclo[2.2.1]hept-5-en-2-yl) *tert*-butyldimethylsilyl ether (3d). *tert*-Butyldimethylsilyl chloride

(933 mg, 6.19 mmol) was added to a flame-dried flask containing alcohol **3b** (287 mg, 2.61 mmol) and imidazole (269 mg, 3.95 mmol) in DMF (3.5 mL) and the reaction was stirred for 24 h. After quenching with water (5 mL), the reaction mixture was extracted into CH_2Cl_2/hexanes (1:9) (4×5 mL), and the combined organic layers were washed with water (10 mL), brine (10 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give **3d** (397 mg, 1.77 mmol, 68%) as a colorless oil: R_f 0.31 (hexanes); IR (neat): 3070 (m), 2957 (s), 2931 (s), 2886 (s), 2858 (s), 1472 (m), 1463 (m), 1368 (m), 1256 (s), 1161 (m), 1123 (s), 1103 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 6.29 (dd, 1H, J=5.6, 3.0 Hz), 5.96 (dd, 1H, J=5.6, 2.9 Hz), 4.45 (dt, 1H, J=7.9, 3.2 Hz), 2.85 (br s, 1H), 2.74 (m, 1H), 1.93 (ddd, 1H, J=15.6, 7.9, 3.8 Hz), 1.35 (m, 1H), 1.20 (d, 1H, J=8.2 Hz), 0.85 (s, 9H), 0.77 (dt, 1H, J=11.9, 3.2 Hz), 0.04 (s, 3H), 0.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.5, 132.0, 72.7, 48.5, 47.2, 42.6, 37.1, 25.9, 18.1, −4.6, −4.7. HRMS calcd for $C_{13}H_{24}SiO$: m/z 224.1596, found m/z 224.1598.

4.3.8. *endo*-Bicyclo[2.2.1]hept-5-en-2-yl acetate (3e). Acetic anhydride (0.40 mL, 4.2 mmol) was added to a flame-dried flask containing alcohol **3b** (323 mg, 2.93 mmol), pyridine (0.7 mL, 8.65 mmol) and dimethylaminopyridine (10 mg, 0.819 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 20 h. After quenching with water (5 mL), the aqueous layer was extracted with CH_2Cl_2 (4×5 mL) and the combined organic layers were washed with saturated $CuSO_4$ (5 mL), water (5 mL), brine (5 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give **3e** (348 mg, 2.29 mmol, 78%) as a colorless oil. Spectral data identical to those reported in the literature.[38]

4.4. Ru-catalyzed ROM–CM reactions

4.4.1. Cyclopentene (18a) (Table 1, entry 1). A solution of Ru-catalyst **4** (8.1 mg, 0.0098 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornadiene **1a** (43.6 mg, 0.209 mmol) and allyltrimethylsilane **7a** (30 μL, 0.189 mmol) via cannula and rinsed with THF (2×0.5 mL). The reaction was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of the *cis* and *trans* isomers (38:62, measured by ^1H NMR) of cyclopentene **18a** (59.9 mg, 0.186 mmol, 89%) as a clear, transparent liquid. R_f 0.55 (EtOAc/hexanes=1:4); IR (neat): 3082 (w), 3005 (m), 2954 (s), 2898 (m), 1605 (br, s), 1636 (br, s), 1436 (s), 1248 (br, s), 1197 (s), 1132 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.85 (ddd, 0.38H, J=10.2, 8.0, 2.3 Hz), 5.81 (ddd, 0.62H, J=10.2, 8.0, 2.4 Hz), 5.42–5.33 (m, 1H), 5.17–5.25 (m, 1H), 5.11 (m, 0.62H), 5.07 (m, 0.38H), 5.05 (m, 0.62H), 5.02 (m, 0.38H), 3.84–3.91 (m, 0.38H), 3.733 (s, 3H), 3.731 (s, 1.14H), 3.727 (s, 1.86H), 3.54–3.61 (m, 1.62H), 2.43–2.52 (m, 1H), 1.49–1.65 (1, 1.38H), 1.40–1.45 (m, 1.62H), 0.00 (s, 3.42H), −0.03 (s, 5.58H); ^{13}C NMR ($CDCl_3$, 100 MHz): major isomer (*trans*-**18a**) δ 166.0, 165.4, 144.53, 140.1, 139.3, 128.8, 128.6, 115.5, 51.8, 49.85, 49.82, 44.2, 37.8, 22.7, −2.1; minor isomer (*cis*-**18a**) δ 166.0, 165.3, 144.45, 140.3, 139.1, 127.7, 127.4, 115.6, 51.9, 50.0, 49.8, 44.2, 37.8, 18.6, −1.9; Anal. calcd for $C_{17}H_{26}O_4Si$: C, 63.32; H, 8.13. Found C, 63.05; H, 8.46.

4.4.2. Cyclopentene (18b) (Table 1, entry 3). A solution of Ru-catalyst **4** (7.1 mg, 0.0086 mmol) in THF (0.3 mL) was added to a flame-dried vial containing a solution of norbornadiene **1b** (44.0 mg, 0.177 mmol) and allyltrimethylsilane **7a** (28 μL, 0.176 mmol) in THF (1 mL) via cannula and rinsed with THF (2×0.2 mL). The reaction was stirred at room temperature for 3 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give an inseparable mixture the *cis* and *trans* isomers (43:57, measured by ^1H NMR) of cyclopentene **18b** (51.4 mg, 0.141 mmol, 80%) as a clear, transparent liquid. R_f 0.49 (hexanes); IR (neat): 3083 (w), 3009 (w), 2955 (s), 2894 (m), 1712 (w), 1648 (m), 1611 (m), 1443 (w), 1418 (m), 1248 (s), 1151 (m), 1096 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.50–5.73 (m, 2H), 5.03–5.17 (m, 3H), 3.62–3.69 (m, 0.43H), 3.23–3.36 (m, 1.57H), 2.57 (t, 0.43H, J=8.4 Hz), 2.54 (t, 0.57H, J=8.4 Hz), 1.56–1.68 (m, 1.43H), 1.42–1.51 (m, 1.57H), 0.03 (s, 3.9H), 0.02 (s, 5.1H); ^{13}C NMR ($CDCl_3$, 100 MHz): major isomer (*trans*-**18b**) δ 139.3, 130.0, 129.2, 128.6, 125.8, 116.8, 53.3, 52.3, 37.2, 22.8, −1.9; minor isomer (*cis*-**18b**) δ 139.3, 128.5, 128.3, 128.0, 125.9, 116.9, 53.3, 46.6, 37.3, 18.7, −1.7. Anal. calcd for $C_{13}H_{20}Br_2Si$: C, 42.87; H, 5.54. Found C, 42.55; H, 5.80.

4.4.3. Cyclopentene (18c) (Table 1, entry 4). A solution of Ru-catalyst **4** (4.4 mg, 0.0053 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornadiene **1c** (23.3 mg, 0.985 mmol) and allyltrimethylsilane **7a** (16 μL, 0.101 mmol) via cannula and rinsed with THF (2×0.5 mL). The reaction was stirred at room temperature for 27 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give an inseparable mixture of the *cis* and *trans* isomers (50:50, measured by ^1H NMR) of cyclopentene **18c** (25.6 mg, 0.0730 mmol, 74%) as a clear, transparent liquid. R_f 0.78 (hexanes); IR (neat): 2949 (m), 2891 (w), 1653 (s), 1559 (m), 1248 (s), 1145 (w), 1036 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.72–5.83 (m, 1H), 5.14–5.33 (m, 2H), 4.85–4.96 (m, 2H), 3.68 (t, 0.5H, J=9.0 Hz), 3.38–3.48 (m, 1.5H), 2.10–2.21 (m, 1H), 1.68 (dd, 0.5H, J=13.7, 9.3 Hz), 1.50 (dd, 0.5H, J=12.5, 0.7 Hz), 1.45 (dd, 0.5H, J=12.4, 0.8 Hz), 1.39 (s, 0.5H), 1.38 (br s, 0.5H), 1.34 (ddd, 0.5H, J=13.8, 6.2, 1.5 Hz), 0.172 (s, 4.5H), 0.170 (br s, 9H), 0.16 (s, 4.5H), 0.02 (s, 4.5H), −0.01 (s, 4.5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 158.3, 156.3, 156.1, 144.54, 144.50, 134.7, 134.2, 125.3, 123.8, 113.3, 113.2, 58.1, 57.9, 57.3, 51.8, 40.7, 40.6, 22.7, 18.8, 1.52, 1.48, 1.4, −1.5, −1.8. Anal. calcd for $C_{19}H_{38}Si_3$: C, 65.06; H, 10.92. Found C, 65.42; H, 10.67.

4.4.4. Cyclopentene (18d) (Table 1, entry 2). A solution of Ru-catalyst **4** (7.4 mg, 0.0090 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornadiene **1a** (37.3 mg, 0.179 mmol) and styrene **7b** (22 μL, 0.192 mmol) via cannula and rinsed with THF (2×0.5 mL). The reaction was stirred at room temperature for 21 h. The solvent was

removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of the *cis* and *trans* isomers (57:43, measured by ^{1}H NMR) of cyclopentene **18d** (44.0 mg, 0.141 mmol, 79%) as a clear, transparent liquid. R_f 0.39 (EtOAc/hexanes=1:4); IR (neat): 3081 (m), 3058 (m), 3025 (s), 2952 (s), 2845 (m), 1775 (br, s), 1633 (s), 1494 (s), 1440 (s), 1271 (br, s), 1250 (s), 1175 (s), 1102 (s), 1028 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22–7.36 (m, 5H), 6.53 (d, 0.57H, J=11.4 Hz), 6.48 (d, 0.43H, J=15.8 Hz), 6.17 (dd, 0.43H, J=15.8, 8.5 Hz), 5.80–5.92 (m, 1H), 5.61 (t, 0.57H, J=10.5 Hz), 5.06–5.17 (m, 2H), 4.19 (m, 0.57H), 3.81 (m, 0.43H), 3.77 (s, 1.29H), 3.76 (s, 1.71), 3.73 (s, 3H), 3.59–3.71 (m, 1H), 2.59 (dt, 0.43H, J=13.4, 8.6 Hz), 2.53 (dt, 0.57H, J=13.3, 8.5 Hz), 1.75 (dt, 0.43H, J=13.4, 6.2 Hz), 1.67 (dt, 0.57H, J=13.2, 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): major isomer (*cis*-**18d**) δ 165.5, 165.4, 142.6, 142.1, 138.5, 136.9, 132.3, 130.1, 128.5, 128.2, 126.9, 116.1, 52.0, 49.9, 44.7, 38.1; minor isomer (*trans*-**18d**) δ 165.6, 165.5, 142.3, 142.2, 138.6, 136.8, 131.2, 130.3, 128.5, 127.4, 126.3, 116.1, 52.04, 51.99, 50.2, 49.5, 37.3. Anal. calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found C, 73.28; H, 6.38.

4.4.5. Cyclopentanes (49a/50a) (Table 2, entry 1). A solution of Ru-catalyst **4** (8.0 mg, 0.0097 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **2a** (35.1 mg, 0.231 mmol), allyltrimethylsilane **7a** (60 μL, 0.38 mmol) and THF (2 mL) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 17 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an inseparable mixture of *cis*- and *trans*-**47a** and *cis*- and *trans*-**48a** (37.1 mg, 0.139 mmol, 60%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **47a** and **48a** was hydrogenated: 5 wt% Pd/C (4.1 mg, 0.0019 mmol) was added to a solution of the mixture of **47a** and **48a** (37.1 mg, 0.139 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 19 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an inseparable mixture of regioisomers **49a** and **50a** (34.7 mg, 0.128 mmol, 92%, **49a/50a**=68:32 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.28 (EtOAc/hexanes=1:49); IR (neat) 2954 (s), 2919 (s), 2875 (s), 2855 (s), 1737 (s), 1461 (m), 1435 (m), 1378 (w), 1248 (s), 1195 (s), 1163 (s), 1071 (s), 1028 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.66 (s, 3H), 2.36–2.40 (m, 1H), 1.98–2.06 (m, 4H), 1.44–1.57 (m, 2H), 1.24–1.31 (m, 5H), 0.88 (t, 2.04H, J=7.4 Hz), 0.87 (t, 0.96H, J=7.3 Hz), 0.74–0.77 (m, 1H), 0.44–0.48 (m, 2H), −0.041 (s, 6.12H), −0.043 (s, 2.88H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**49a**): δ177.5, 51.5, 49.0, 46.3, 40.2, 39.87, 38.8, 36.4, 28.2, 22.8, 16.9, 12.5, −1.7; minor isomer (**50a**): δ 177.5, 51.5, 49.4, 44.4, 40.9, 39.93, 39.6, 36.1, 28.9, 22.5, 16.8, 12.8, −1.7. HRMS calcd for $C_{15}H_{30}O_2Si$: m/z 270.2015, found m/z 270.2020.

4.4.6. Cyclopentanes (49b/50b) (Table 2, entry 2). A solution of Ru-catalyst **4** (4.1 mg, 0.0050 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **2b** (15.3 mg, 0.139 mmol) and allyltrimethylsilane **7a** (040 μL, 0.25 mmol) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 16 h at 25°C. The solvent was removed by rotary evaporation and the crude product was passed through a plug of silica gel (EtOAc/hexanes=1:4) to give an inseparable mixture of *cis*- and *trans*-**47b** and *cis*- and *trans*-**48b** (9.3 mg, 0.042 mmol, 30%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **47b** and **48b** was hydrogenated: 5 wt% Pd/C (8.7 mg, 0.0041 mmol) was added to a solution of the mixture of **47b** and **48b** (9.3 mg, 0.0416 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 48 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of regioisomers **49b** and **50b** (7.2 mg, 0.0315 mmol, 75%, **49b/50b**=60:40 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.23 (EtOAc/hexanes=1:9); IR (neat) 3348 (br s), 2955 (s), 2870 (s), 2840 (s), 1461 (m), 1409 (w), 1378 (w), 1259 (m), 1248 (s), 1176 (w), 1073 (br m), 1025 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.73–3.87 (m, 1H), 1.91–2.16 (m, 2H), 1.17–1.75 (m, 10H), 0.93 (t, 1.80H, J=7.4 Hz), 0.88 (t, 1.20H, J=7.4 Hz), 0.66–0.74 (m, 1H), 0.44–0.51 (m, 2H), −0.03 (s, 3.60H), −0.04 (s, 5.40H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**49b**): δ 78.6, 51.0, 41.7, 40.5, 37.9, 36.6, 27.2, 22.7, 16.8, 12.7, −1.6; minor isomer (**50b**): δ 78.9, 49.0, 41.3, 38.7, 38.6, 37.9, 29.2, 22.6, 16.9, 12.8, −1.6. HRMS calcd for $C_{13}H_{28}OSi$: m/z 228.1909, found m/z 228.1916.

4.4.7. Cyclopentanes (49c/50c) (Table 2, entry 3). A solution of Ru-catalyst **4** (3.9 mg, 0.0047 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **2c** (23.6 mg, 0.119 mmol) and allyltrimethylsilane **7a** (30 μL, 0.19 mmol) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 24 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of *cis*- and *trans*-**47c** and *cis*- and *trans*-**48c** (16.6 mg, 0.0531 mmol, 45%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **47c** and **48c** was hydrogenated: 5 wt% Pd/C (7.2 mg, 0.0034 mmol) was added to a solution of the mixture of **47c** and **48c** (16.6 mg, 0.0531 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 22 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give an inseparable mixture of regioisomers **49c** and **50c** (9.6 mg, 0.0303 mmol, 57%, **49c/50c**=60:40 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.23 (EtOAc/hexanes=1:19); IR (neat) 2954 (s), 2919 (s), 2871 (s), 1466 (m), 1247 (s), 1097 (br m), 1048 (br s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.72 (AB, 2H), 3.65–3.79 (m, 3H), 3.56 (t, 2H, J=4.7 Hz), 3.39 (br s, 3H), 1.18–2.04 (m, 11H), 0.84–0.93 (m, 3H), 0.64–0.70 (m, 1H), 0.43–0.50 (m, 2H), −0.04 (br s, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**49c**): δ 94.18, 83.0, 71.8, 66.70, 59.0, 48.3, 40.4, 38.6, 37.65, 37.1, 27.4, 22.7, 16.8, 12.6, −1.6; minor isomer (**50c**): δ 94.25, 83.4, 71.8, 66.72, 59.0,

46.3, 39.2, 38.8, 38.1, 37.60, 29.1, 22.5, 16.9, 12.8, −1.6. HRMS calcd for $C_{13}H_{28}OSi$: *m/z* 316.2434, found *m/z* 316.2446.

4.4.8. Cyclopentanes (49d/50d) (Table 2, entry 4). A solution of Ru-catalyst **4** (7.5 mg, 0.0091 mmol) in CH_2Cl_2 (1 mL) was added to a flame-dried vial containing norbornene **2d** (38.2 mg, 0.170 mmol) and allyltrimethylsilane **7a** (40 μL, 0.25 mmol) in CH_2Cl_2 (12 mL) via cannula and rinsed with CH_2Cl_2 (2×0.2 mL). The reaction mixture was stirred for 24 h at 25°C. The solvent was removed by rotary evaporation and the crude product was passed through a plug of silica gel (hexanes) to give an inseparable mixture of *cis*- and *trans*-**47d** and *cis*- and *trans*-**48d** (32.9 mg, 0.0971 mmol, 57%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **47d** and **48d** was hydrogenated: 5 wt% Pd/C (9.1 mg, 0.0043 mmol) was added to a solution the mixture of **47d** and **48d** (19.4 mg, 0.0573 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 18 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give an inseparable mixture of regioisomers **49d** and **50d** (12.8 mg, 0.0373 mmol, 65%, **49d/50d**=67:33 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.82 (hexanes); IR (neat) 2956 (s), 2900 (s), 2856 (s), 1472 (m), 1463 (m), 1408 (w), 1378 (m), 1361 (m), 1248 (s), 1176 (w), 1106 (m), 1058 (m), 1006 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71–3.75 (m, 1H), 1.04–2.04 (m, 11H), 0.86–0.91 (m, 12H), 0.58–0.66 (m, 1H), 0.41–0.57 (m, 2H), 0.04 (br s, 3H), 0.03 (br s, 3H), −0.03 (br s, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**49d**): δ 78.7, 50.6, 41.7, 41.1, 36.9, 36.1, 26.8, 25.9, 22.6, 18.1, 16.8, 12.7, −1.62, −4.4, −4.7; minor isomer (**50d**): δ 79.0, 48.6, 41.3, 38.24, 38.12, 37.0, 29.7, 25.9, 22.6, 18.1, 17.0, 12.7, −1.60, −4.4, −4.7. Anal. calcd for $C_{19}H_{42}OSi_2$: C, 66.59; H, 12.35. Found C, 66.93; H, 12.10.

4.4.9. Cyclopentanes (49e/50e) (Table 2, entry 5). A solution of Ru-catalyst **4** (7.8 mg, 0.0095 mmol) in CH_2Cl_2 (1 mL) was added to a flame-dried vial containing norbornene **2e** (34.1 mg, 0.224 mmol) and allyltrimethylsilane **7a** (50 μL, 0.31 mmol) in CH_2Cl_2 (12 mL) via cannula and rinsed with CH_2Cl_2 (2×0.2 mL). The reaction mixture was stirred for 24 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an inseparable mixture of *cis*- and *trans*-**47e** and *cis*- and *trans*-**48e** (31.4 mg, 0.118 mmol, 53%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **47e** and **48e** was hydrogenated: 5 wt% Pd/C (10.6 mg, 0.00498 mmol) was added to a solution the mixture of **47e** and **48e** (14.3 mg, 0.0537 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 72 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an inseparable mixture of regioisomers **49e** and **50e** (14.5 mg, 0.0537 mmol, 100%, **49e/50e**=69:31 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.25 (EtOAc/hexanes=1:49); IR (neat) 2956 (s), 2919 (s), 2876 (m), 2855 (m), 1736 (s), 1458 (m), 1411 (w), 1376 (m), 1248 (s), 1177 (w), 1023 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.70–4.78 (m, 1H), 2.02 (br s, 3H), 1.71–2.00 (m, 4H), 1.47–1.57 (m, 2H), 1.21–1.35 (m, 5H), 0.89 (t, 2.07H, *J*=7.4 Hz), 0.88 (t, 0.93H, *J*=7.3 Hz), 0.70–0.75 (m, 1H), 0.44–0.49 (m, 2H), −0.04 (br s, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**49e**): δ 171.0, 81.4, 47.5, 40.1, 39.1, 37.7, 37.5, 27.0, 22.7, 21.4, 16.9, 12.4, −1.65; minor isomer (**50e**): δ 171.0, 81.1, 45.5, 39.5, 38.7, 38.3, 37.7, 28.8, 22.3, 21.4, 16.7, 12.8, −1.65.

4.4.10. Cyclopentanones (49f/50f) (Table 2, entry 6). A solution of Ru-catalyst **4** (4.0 mg, 0.0049 mmol) in THF (0.5 mL) was added to a flame-dried vial containing norbornene **2f** (12.4 mg, 0.115 mmol), allyltrimethylsilane **7a** (30 μL, 0.189 mmol) and THF (1 mL) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 16 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give an inseparable mixture of *cis*- and *trans*-**47f** and *cis*- and *trans*-**48f** (10.9 mg, 0.0490 mmol, 43%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **47f** and **48f** was hydrogenated: 5 wt% Pd/C (5.2 mg, 0.0024 mmol) was added to a solution of the mixture of **47f** and **48f** (30.0 mg, 0.135 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 1 d at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an inseparable mixture of regioisomers **49f** and **50f** (24.3 mg, 0.107 mmol, 79%, **49f/50f**=50:50 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.30 (EtOAc/hexanes=1:49); IR (neat) 2957 (s), 2927 (s), 2879 (s), 1732 (s), 1461 (m), 1407 (m), 1380 (w), 1248 (s), 1160 (m), 1071 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65–2.50 (m, 6H), 0.24–1.50 (m, 5H), 1.03–1.15 (m, 1H), 0.95 (t, 1.50H, *J*=7.4 Hz), 0.92 (t, 1.50H, *J*=7.6 Hz), 0.48–0.52 (m, 2H), −0.02 (s, 4.50H), −0.03 (s, 4.50H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 220.8, 51.7, 50.2, 45.3, 44.9, 39.9, 36.7, 36.2, 35.8, 34.5, 33.5, 28.6, 22.5, 22.1, 21.9, 16.7, 16.5, 12.2, 11.7, −1.8. HRMS calcd for $C_{13}H_{26}OSi$: *m/z* 226.1753, found *m/z* 226.1740.

4.4.11. Cyclopentanes (53a/54a) (Table 3, entry 1). A solution of Ru-catalyst **4** (16.6 mg, 0.0202 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **3a** (71.9 mg, 0.472 mmol), allyltrimethylsilane **7a** (120 μL, 0.755 mmol) and THF (6 mL) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 17 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an inseparable mixture of *cis*- and *trans*-**51a** and *cis*- and *trans*-**52a** (72.8 mg, 0.273 mmol, 58%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **51a** and **52a** was hydrogenated: 5 wt% Pd/C (9.4 mg, 0.0044 mmol) was added to a solution of the mixture of **51a** and **52a** (72.8 mg, 0.273 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 19 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:49) to give an

inseparable mixture of regioisomers **53a** and **54a** (68.4 mg, 0.253 mmol, 93%, **53a/54a**=60:40 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.30 (EtOAc/hexanes=1:49); IR (neat) 2953 (s), 2919 (s), 2875 (s), 1736 (s), 1642 (w), 1460 (m), 1434 (s), 1411 (w), 1371 (m), 1248 (s), 1228 (m), 1194 (s), 1159 (s), 1071 (m), 1027 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.63 (s, 1.80H), 3.62 (s, 1.20H), 2.81–2.88 (m, 1H), 0.94–2.02 (m, 12H), 0.88 (t, 1.20H, J=7.3 Hz), 0.86 (t, 1.80H, J=7.2 Hz), 0.41–0.48 (m, 2H), −0.049 (s, 5.4H), −0.053 (s, 3.6H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**53a**): δ 176.2, 51.0, 46.96, 44.8, 39.9, 39.1, 38.2, 35.3, 24.7, 23.0, 16.9, 12.9, −1.7; minor isomer (**54a**): δ 176.3, 51.0, 47.00, 42.7, 41.3, 38.2, 35.8, 35.1, 28.6, 22.7, 16.9, 13.0, −1.7. HRMS calcd for $C_{15}H_{30}O_2Si$: m/z 270.2015, found m/z 270.2028.

4.4.12. Cyclopentanes (53b/54b) (Table 3, entry 2). A solution of Ru-catalyst **4** (4.6 mg, 0.0056 mmol) in THF (0.5 mL) was added to a flame-dried vial containing norbornene **3b** (13.9 mg, 0.126 mmol), allyltrimethylsilane **7a** (30 μL, 0.189 mmol) and THF (1 mL) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 24 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give an inseparable mixture of *cis*- and *trans*-**51b** and *cis*- and *trans*-**52b** (8.6 mg, 0.0383 mmol, 30%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **51b** and **52b** was hydrogenated: 5 wt% Pd/C (4.3 mg, 0.0020 mmol) was added to a solution of the mixture of **51b** and **52b** (23.0 mg, 0.102 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 24 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give an inseparable mixture of regioisomers **53b** and **54b** (12.7 mg, 0.0556 mmol, 54%, **53b/54b**=63:37 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.31 (EtOAc/hexanes=1:19); IR (neat) 3428 (br m), 2954 (s), 2919 (s), 2857 (s), 2826 (s), 1461 (w), 1259 (m), 1247 (s), 1176 (w), 1062 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.13–4.14 (m, 1H), 2.13–2.19 (m, 1H), 1.00–1.89 (m, 12H), 0.95 (t, 1.89H, J=7.4 Hz), 0.88 (t, 1.11H, J=7.4 Hz), 0.44–0.53 (m, 2H), −0.02 (s, 3.33H), −0.03 (s, 5.67H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**53b**): δ 74.3, 47.9, 41.8, 37.1, 36.4, 30.4, 22.9, 21.9, 16.8, 12.9, −1.6; minor isomer (**54b**): δ 74.6, 45.8, 41.5, 39.3, 36.3, 33.0, 22.8, 21.9, 17.1, 13.0, −1.6. Anal. calcd for: C, 68.35; H, 12.35. Found C, 68.74; H, 12.09.

4.4.13. Cyclopentanes (53c/54c) (Table 3, entry 3). A solution of Ru-catalyst **4** (16.8 mg, 0.0204 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **3c** (92.7 mg, 0.467 mmol), allyltrimethylsilane **7a** (0.120 mL, 0.755 mmol) and THF (6 mL) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 15 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give an inseparable mixture of *cis*- and *trans*-**51c** and *cis*- and *trans*-**52c** (48.1 mg, 0.154 mmol, 33%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **51c** and **52c** was hydrogenated: 5 wt% Pd/C (9.3 mg, 0.0044 mmol) was added to a solution of the mixture of **51c** and **52c** (48.1 mg, 0.154 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 18 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give an inseparable mixture of regioisomers **53c** and **54c** (41.8 mg, 0.132 mmol, 86%, **53c/54c**=60:40 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.34 (EtOAc/hexanes=1:19); IR (neat) 2954 (s), 2923 (s), 2875 (s), 1455 (m), 1408 (w), 1361 (w), 1247 (s), 1193 (m), 1158 (m), 1133 (s), 1106 (s), 1071 (s), 1048 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.38–4.50 (m_{AB}, 2H), 3.73–3.78 (m, 1H), 3.37–3.49 (ABX_2, 2H), 3.29 (t, 2H, J=4.8 Hz), 3.13 (br s, 3H), 1.71–1.79 (m, 1H), 0.95–1.63 (m, 10H), 0.70–0.78 (m, 1H), 0.64 (t, 1.80H, J=7.4 Hz), 0.60 (t, 1.20H, J=7.4 Hz), 0.17–0.24 (m, 2H), −0.30 (s, 3.60H), −0.31 (s, 5.40H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**53c**): δ 94.04, 79.1, 71.8, 66.75, 59.0, 47.0, 41.7, 38.6, 36.9, 36.76, 33.2, 22.8, 16.8, 13.0, −1.7; minor isomer (**54c**): δ 93.97, 79.3, 71.8, 66.74, 59.0, 44.8, 41.7, 39.0, 38.2, 36.8, 30.2, 22.1, 17.0, 13.0, −1.7. Anal. calcd for: C, 64.50; H, 11.46. Found C, 64.29; H, 11.62.

4.4.14. Cyclopentanes (53d/54d) (Table 3, entry 4). A solution of Ru-catalyst **4** (4.2 mg, 0.0051 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **3d** (26.5 mg, 0.118 mmol), allyltrimethylsilane **7a** (30 μL, 0.19 mmol) via cannula and rinsed with THF (2×0.5 mL). The reaction mixture was stirred for 16 h at 25°C. The solvent was removed by rotary evaporation and the crude product was passed through a plug of silica gel (EtOAc/hexanes=1:19) to give an inseparable mixture of *cis*- and *trans*-**51d** and *cis*- and *trans*-**52d** (34.4 mg, 0.102 mmol, 86%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **51d** and **52d** was hydrogenated: 5 wt% Pd/C (10.0 mg, 0.0047 mmol) was added to a solution of the mixture of **51d** and **52d** (34.4 mg, 0.102 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 19 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give an inseparable mixture of regioisomers **53d** and **54d** (31.2 mg, 0.0910 mmol, 89%, **53d/54d**=68:32 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.96 (hexanes); IR (neat) 2955 (s), 2928 (s), 2857 (s), 1472 (s), 1462 (s), 1415 (w), 1361 (m), 1249 (s), 1214 (w), 1112 (w), 1051 (br s), 1006 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.02–4.06 (m, 1H), 1.19–2.05 (m, 11H), 0.87–0.89 (m, 12H), 0.44–0.50 (m, 2H), 0.01–0.02 (m, 6H), −0.03 (br s, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**53d**): δ 74.5, 48.4, 41.94 41.90, 36.6, 36.4, 33.5, 25.8, 22.7, 22.2, 17.1, 12.9, −1.7, −4.4, −5.1; minor isomer (**54d**): δ 74.7, 46.2, 41.94, 41.6, 38.9, 36.4, 30.5, 25.8, 18.0, 17.1, 16.7, 12.9, −1.7, −4.4, −5.1. HRMS calcd for $C_{19}H_{42}OSi$: m/z 342.2774, found m/z 342.2788.

4.4.15. Cyclopentanes (53e/54e) (Table 3, entry 5). A solution of Ru-catalyst **4** (3.9 mg, 0.0047 mmol) in THF (1 mL) was added to a flame-dried vial containing norbornene **3e** (18.0 mg, 0.118 mmol), allyltrimethylsilane **7a** (30 μL, 0.19 mmol) via cannula and rinsed with THF

(2×0.5 mL). The reaction mixture was stirred for 16 h at 25°C. The solvent was removed by rotary evaporation and the crude product was passed through a plug of silica gel (EtOAc/hexanes=1:19) to give an inseparable mixture of *cis*- and *trans*-**51e** and *cis*- and *trans*-**52e** (22.0 mg, 0.0826 mmol, 70%) as a colorless, transparent liquid. Without detailed characterization, the mixture of **51e** and **52e** was hydrogenated: 5 wt% Pd/C (8.2 mg, 0.0039 mmol) was added to a solution of the mixture of **51e** and **52e** (22.0 mg, 0.0826 mmol) in EtOH (5 mL) and a balloon of H_2 was attached to the flask. The reaction mixture was stirred for 19 h at 25°C. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give an inseparable mixture of regioisomers **53e** and **54e** (11.7 mg, 0.0433 mmol, 52%, **53e/54e**=58:42 measured by ^{1}H NMR) as a colorless, transparent liquid. R_f 0.29 (EtOAc/hexanes=1:49); IR (neat) 2955 (s), 2920 (s), 2857 (s), 2888 (s), 1738 (s), 1460 (m), 1440 (m), 1410 (w), 1374 (s), 1247 (s), 1175 (m), 1021 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.09–5.14 (m, 1H), 2.17–2.25 (m, 1H), 2.020 (s, 1.74H), 2.016 (s, 1.26H), 1.69–1.95 (m, 3H), 1.21–1.57 (m, 7H), 0.98–1.06 (m, 1H), 0.88 (t, 1.74H, J=7.4 Hz), 0.87 (t, 1.26H, J=7.4 Hz), 0.44–0.48 (m, 2H), −0.038 to −0.036 (m, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer (**53e**): δ 170.92, 77.2, 46.4, 39.4, 37.2, 36.9, 33.1, 22.8, 22.1, 21.3, 16.8, 12.8, −1.6; minor isomer (**54e**): δ 170.89, 77.5, 44.2, 39.12, 39.08, 37.0, 29.9, 22.6, 22.1, 21.3, 17.0, 12.8, −1.6. HRMS calcd for $C_{15}H_{30}O_2Si$: *m/z* 270.2015, found *m/z* 270.2012.

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