HETEROCYCLES, Vol. 97, No. 2, 2018, pp. 806 - 822. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 14th February, 2018, Accepted, 16th March, 2018, Published online, 28th March, 2018
DOI: 10.3987/COM-18-S(T)56

ACTIVATION OF GRUBBS–HOVEYDA SECOND-GENERATION CATALYSTS EMPLOYING AROMATIC LIGANDS BEARING A WIDESPREAD ARYL SUBSTITUENT

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We would like to dedicate this article to Prof. Kiyoshi Tomioka on his 70th birthday.

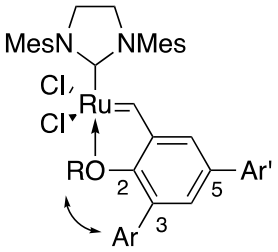
Abstract – In this study, an activation strategy for Grubbs–Hoveyda second-generation-type catalysts by utilizing the intramolecular steric strain on the ligands is described. The variant, which is expected to exhibit intramolecular steric strain, containing extensively spread aromatic and alkoxy groups in the ligand structure was prepared and examined. The combination of tricyclic anthracenyl and isopropoxy groups are observed to exhibit the highest catalytic activity among these synthetic catalysts. The activated catalyst was successfully used in a ring-closing metathesis reaction depicting a catalyst loading of the order of 20 mol ppm in dry benzene. The X-ray crystallographic analysis suggests the existence of an intramolecular CH/π interaction between the sp^2 carbon of the anthracenyl group and the methyne hydrogen of the isopropoxy group.

INTRODUCTION

Olefin metathesis has become a very useful and popular method for carbon–carbon bond formation, and the Grubbs–Hoveyda second-generation (GH 2nd) catalyst **1a** is one of the most extensively used catalysts in the field of organic synthetic chemistry (Figure 1).[1] To date, considerable effort has been devoted toward improving the catalytic activity, selectivity, and operability of such catalysts.[2] With respect to the modifications related to activity and selectivity, the ligand structure of *N*-heterocyclic carbene (NHC) has been modified. Further, more activated catalysts have been reported by pioneers in organic chemistry.[3] Additionally, since it is known that the catalytic activity can also be controlled by the

electron withdrawing groups[4] and/or steric hindrance[5] of the ligand, a variety of attractive catalysts have been discovered by modifying the aromatic bidentate ligand moiety (2-isopropoxystyrene).[6] Recently, we have also reported a novel activation method for **1a** by immobilization of the molecular conformation *via* the intramolecular steric strain in the ligand moiety.[7] In the study, we have clarified that catalysts bearing an aryl substituent in the ligand structure depicts high activity for ring-closing metathesis (RCM). Namely, **1e** (Figure 1) bearing both the 9-anthracenyl group on the 3-position and an isopropoxy group on the 2-position can be successfully used in an RCM reaction to generate a 4-substituted product, which is generally difficult to produce using RCM.

Here, we report a detailed study of the activation of GH 2nd-type catalysts using aromatic ligands containing both an aryl substituent and various alkoxy groups in the ligand structure; several novel catalysts (**1h**–**1m**) have also been reported. We additionally examined the amount of catalyst that can be reduced in the RCM reaction using the catalyst, which depicted the highest catalytic activity.



1a[2]: R = ^{i}Pr, Ar = H, Ar' = H (GH 2nd)
1b[6]: R = ^{i}Pr, Ar = Ph, Ar' = H
1c[7]: R = ^{i}Pr, Ar = 1-naphthyl, Ar' = H
1d[7]: R = ^{i}Pr, Ar = 2-methoxy-1-naphthyl, Ar' = H
1e[7]: R = ^{i}Pr, Ar = 9-anthracenyl, Ar' = H
1f[7]: R = ^{i}Pr, Ar = 9-phenanthrenyl, Ar' = H
1g[7]: R = ^{i}Pr, Ar = H, Ar' = 9-anthracenyl
1h: R = ^{i}Bu, Ar = 9-anthracenyl Ar' = H
1i: R = Me, Ar = 9-anthracenyl Ar' = H
1j: R = Et, Ar = 9-anthracenyl Ar' = H
1k: R = ^{n}Pr, Ar = 9-anthracenyl Ar' = H
1l: R = ^{i}Pr, Ar = 1-pyrenyl Ar' = H
1m: R = ^{i}Pr, Ar = 9-anthracenyl, Ar' = C_8F_{17}

Figure 1. GH 2nd catalyst **1a**, known catalysts (**1b**–**1g**), and novel analogs (**1h**–**1m**) bearing aromatic ligands

RESULTS AND DISCUSSION

Initially, we illustrate a new observation regarding the three-dimensional structure of catalyst **1e**. As described in the introduction, the catalyst **1e** that bears an anthracenyl functional group on the 3-position of the ligand is one of the most active GH 2nd-type catalyst among the analogs (**1b**–**1g**).[7] In our previous study, we assumed that an intramolecular CH/π interaction[8] may exist between the isopropoxy group and the aromatic moiety on the ligand based on their comparison with UV–Vis absorption spectra.[7] In this study, we were able to obtain single crystals of **1e**, and X-ray crystallographic analysis was conducted. Using X-ray crystallographic analysis,[9] we observed that the CH-moiety of the methine hydrogen of isopropyl function, and not the CH-moiety of the methyl group, was located close to the π-face of the anthracenyl group (Figure 2). Since the quality of the crystal was good and the resolution was high, the

position of the hydrogen atom could be determined.

The closest interatomic distance (2.358 Å) between the CH-moiety (methyne group) and the sp^2 carbon of the aromatic π plane was observed to be shorter than the sum of the individual radii of van der Waals. The C-Ru-O bond angle was observed to be 78.8°, which is much narrower than the corresponding value (79.3°)[2] of the original GH 2nd catalyst **1a**. Further, the Ru-O bond length was 2.271 Å, which is longer than the corresponding length (2.261 Å)[2] of the original **1a**. This longer bond length indicates that the bidentate ligand site is likely to be more dissociated. We infer that the intramolecular steric strain that was caused by the intramolecular CH/π interaction resulted in the remarkably high catalytic activity of **1e**. The steric strain would further influence the bond length between the lone electron pair on the isopropoxy oxygen and the ruthenium, thereby accelerating the dissociation of the ligand that is observed to be involved in the rate-determining step.[10]

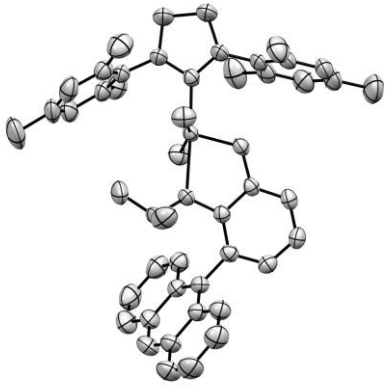
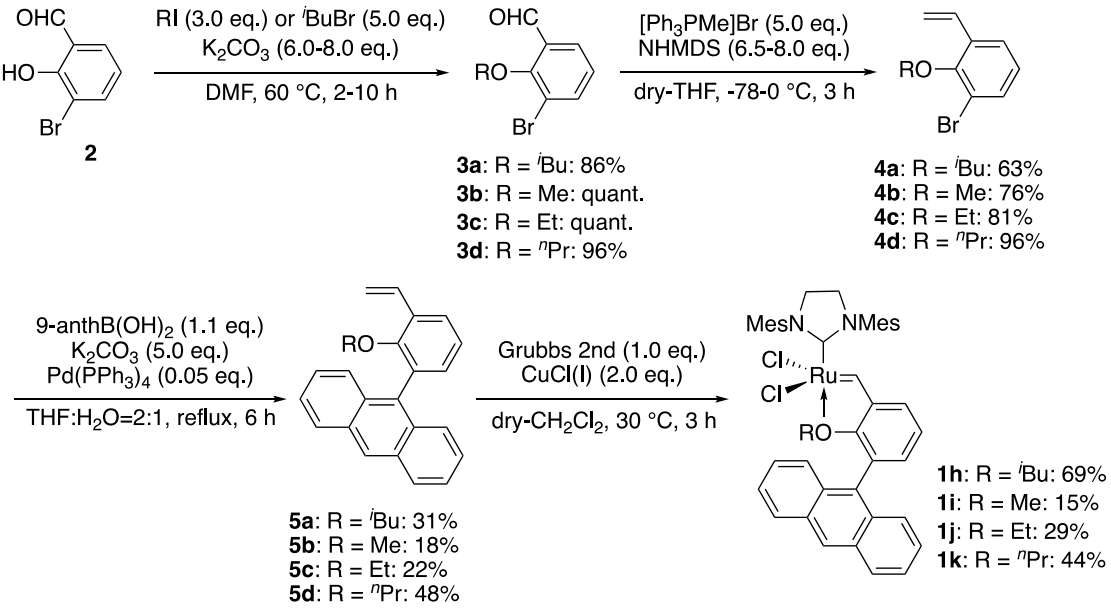


Figure 2. ORTEP drawing of catalyst **1e** (hydrogen atoms are omitted for clarity)

To investigate the influence of the intramolecular CH/π interaction on the catalytic activity, several catalysts (**1h**–**1k**) bearing a 9-anthracenyl group in the ligand were prepared from 3-bromo-2-hydroxybenzaldehyde **2** in moderate yields *via O*-alkylation, Wittig reaction, Suzuki–Miyaura coupling, and successive ligand exchange with a second-generation Grubbs catalyst (Scheme 1).

The relative turnover rates of the catalysts were determined by comparing the RCM reaction rates of these catalysts during the conversion of diethyl 2-allyl-2-(2-methylallyl)malonate (**6**)[11] to diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (**7**).[11] This substrate depicts suitable reactivity with regard to the catalyst activities, which is observed to be not too fast or slow at room temperature (23 °C). Therefore, the catalytic activities can be compared at room temperature. The reactions were conducted using $CDCl_3$ as the solvent to allow the nuclear magnetic resonance (^{1}H NMR)-monitoring of reaction aliquots. Separate reactions using catalysts **1h**–**1k** were conducted under identical conditions with identical catalyst loadings (0.03 M). At the given time points, the percentage conversion of the reaction was determined by

recording the ^{1}H NMR spectra of the reaction mixtures and by calculating the relative integrals of the corresponding methylene protons of product **7**. The plots of the percentage conversion versus time for various catalysts are depicted in Figure 3. Catalyst **1e** exhibited much higher activity than that depicted by the remaining prepared catalysts (**1h**–**1k**), and the order of the catalytic activity was as follows: **1e** >> **1j** > **1k** > **1h** > **1i**. These results indicate that the structure comprising an aryl group *ortho* to the isopropoxy group on the ligand is critical for the catalyst to achieve high activity and that the catalyst is not activated by the steric hindrance of the alkoxy group on the ligand.



Scheme 1. Synthesis of GH 2nd-type catalysts (**1h**–**1k**) bearing a 9-anthracenyl group in the ligand

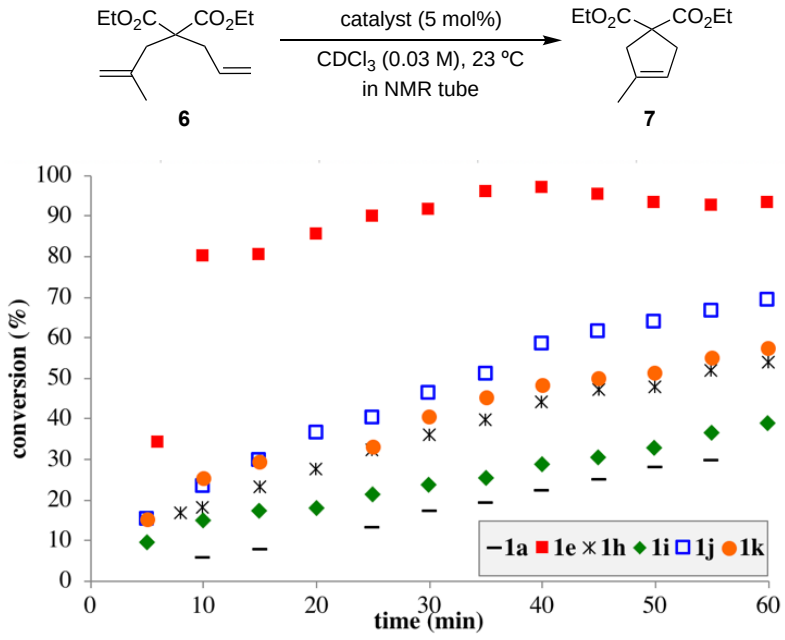
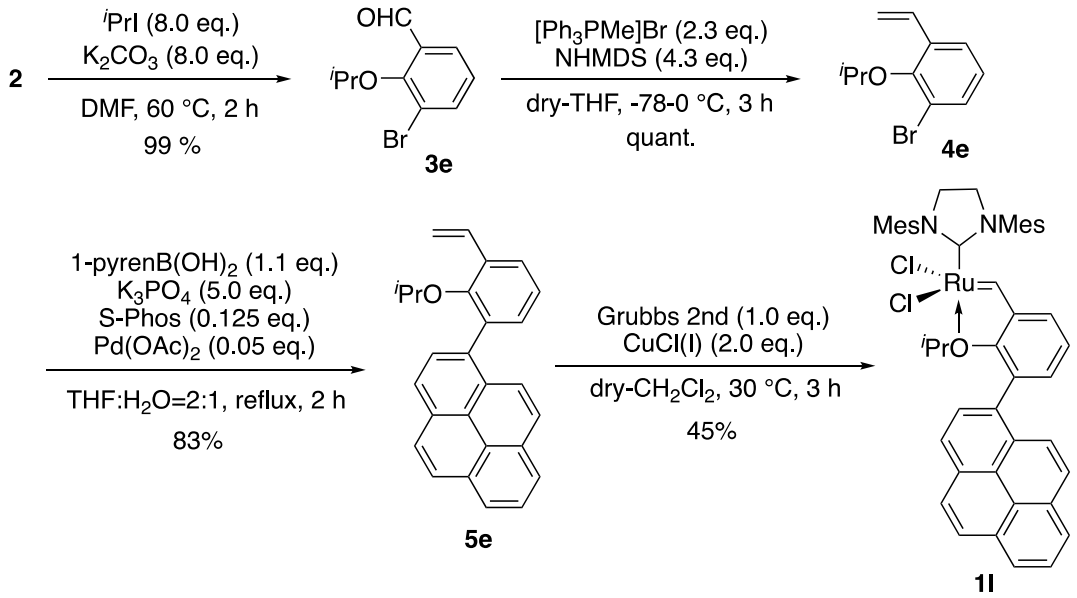


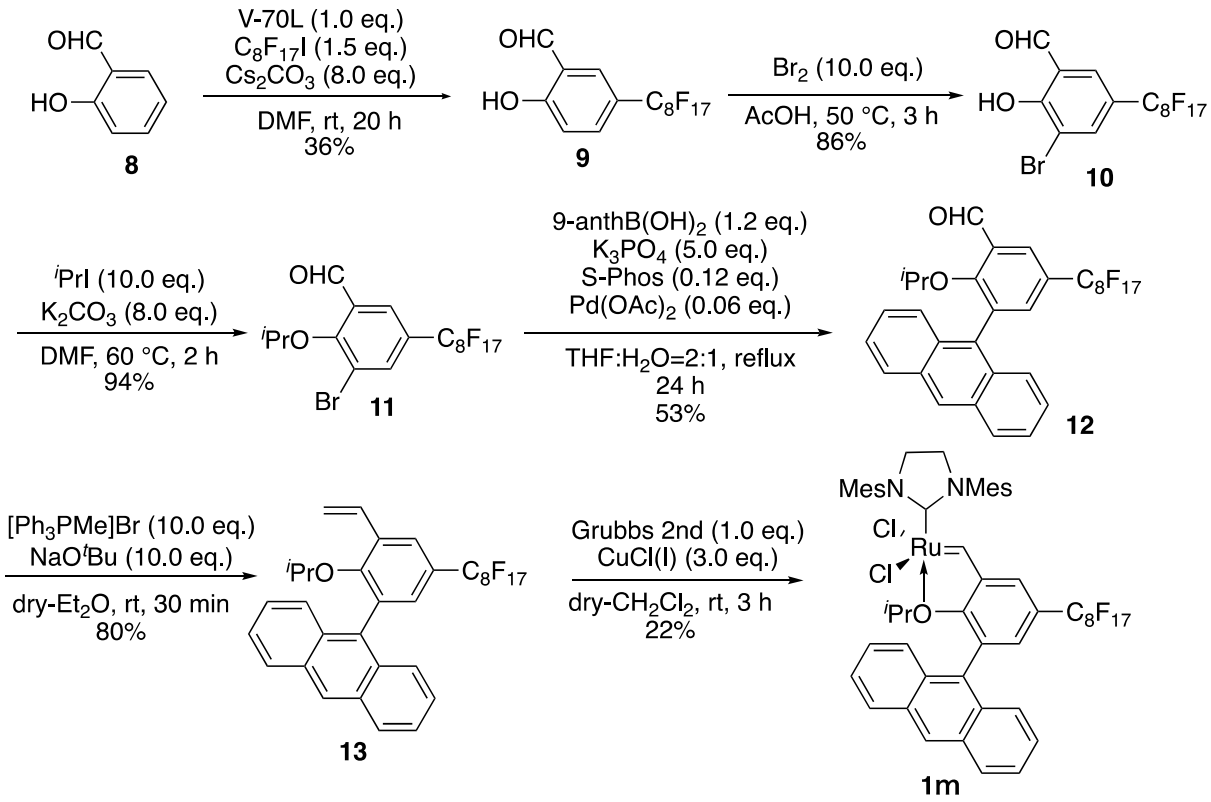
Figure 3. Comparison of the catalytic activity among the catalysts bearing different alkoxy groups

Catalyst **1l**, which depicts a more extensively spread aromatic plane on *ortho* to the isopropoxy group on the ligand, was prepared using **2** (Scheme 2). Additionally, catalyst **1m**, in which a light C_8F_{17} tag was introduced at the 5-position of the ligand of **1e**, was prepared using the synthetic method that is depicted in Scheme 3. Based on our previous experience with a fluorous metathesis catalyst, it was expected that the catalytic activity would increase if a fluorous tag was introduced into the aromatic ligand.[11]

Figure 4 depicts a comparison of the catalytic activities during the RCM reaction of **6**. The relative catalytic activities were **1e** > **1l** > **1m**. **1l** exhibited lower catalytic activity than **1e**, which suggests that the direction of the aromatic plane is more important than that of the extended π-conjugated system. However, the catalytic activity of **1m** was lower than that of the non-fluorous catalyst **1e**. We assume that the electron-withdrawing effect of the fluorous tag may disturb the effective intramolecular CH/π interaction based on the charge-transfer character.[8] Therefore, we conclude that **1e** is the most active catalyst among the catalysts that we have produced so far bearing the π-conjugated systems on the ligands.



Scheme 2. Synthesis of catalyst **1l**



Scheme 3. Synthesis of a light fluorous GH 2nd catalyst **1m**

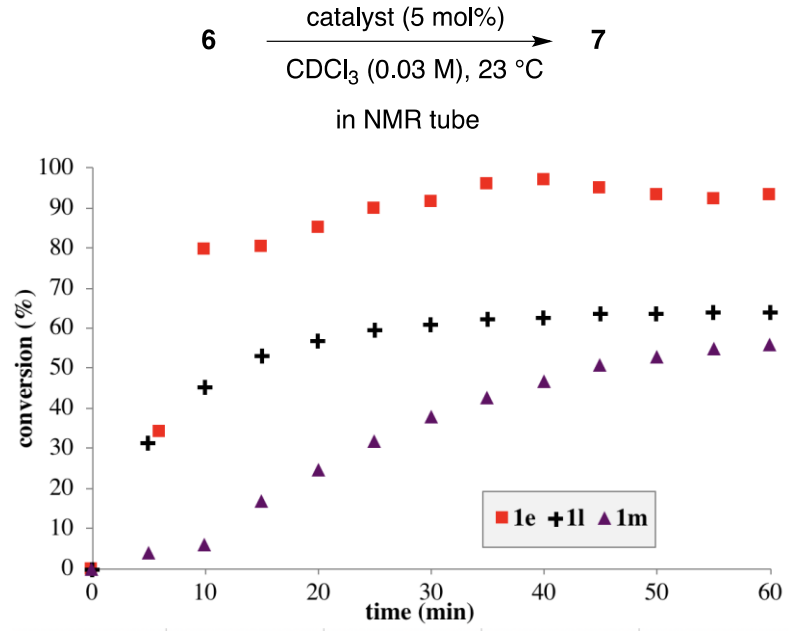
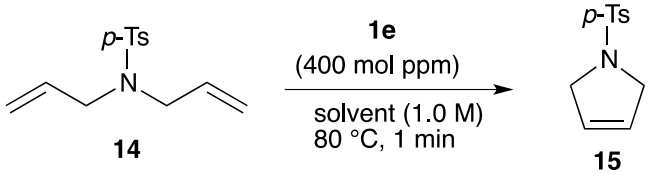


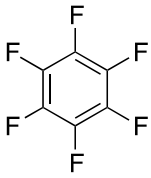
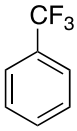
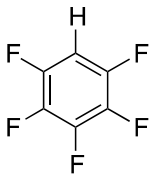
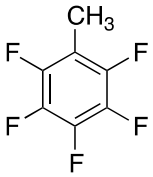
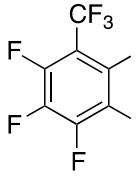
Figure 4. Comparison of the catalytic activity of the catalysts **1l**, **1m**, and **1e**

Further, we attempted to investigate the amount of catalyst that can be reduced using **1e** in the RCM reaction of *N,N*-diallyl-*p*-toluenesulfonamide (**14**)[12] to yield 1-tosyl-2,5-dihydro-1*H*-pyrrole (**15**).[12] To

date, several studies involving modifications of the NHC ligand of **1a** have been conducted to improve its catalytic loading, and several pioneering catalysts have been reported.[13] After some optimization of the catalytic loading, we observed that catalyst **1e** functioned effectively in various aromatic solvents at 80 °C within one minute (Table 1). Although it has been reported that the use of pentafluorotoluene as a solvent was effective to activate GH 2nd-type catalysts,[14] the use of non-fluorous aromatic solvents was also observed to be effective. Interestingly, the RCM reaction achieved almost no progress while hexafluorobenzene was used, and this result was reproducible. Although we used three kinds of commercially available hexafluorobenzene (99.8%, 99.9%, and 100.0% purities),[15] the RCM reaction was observed to almost stop proceeding in all situations. We assume that trace amounts of impurities that could not be detected using gas chromatography during the quality management process may exist in the solvent, which may poison the catalyst.

Table 1. Low catalyst-loading RCM reaction using **1e** (400 mol ppm) in various aromatic solvents

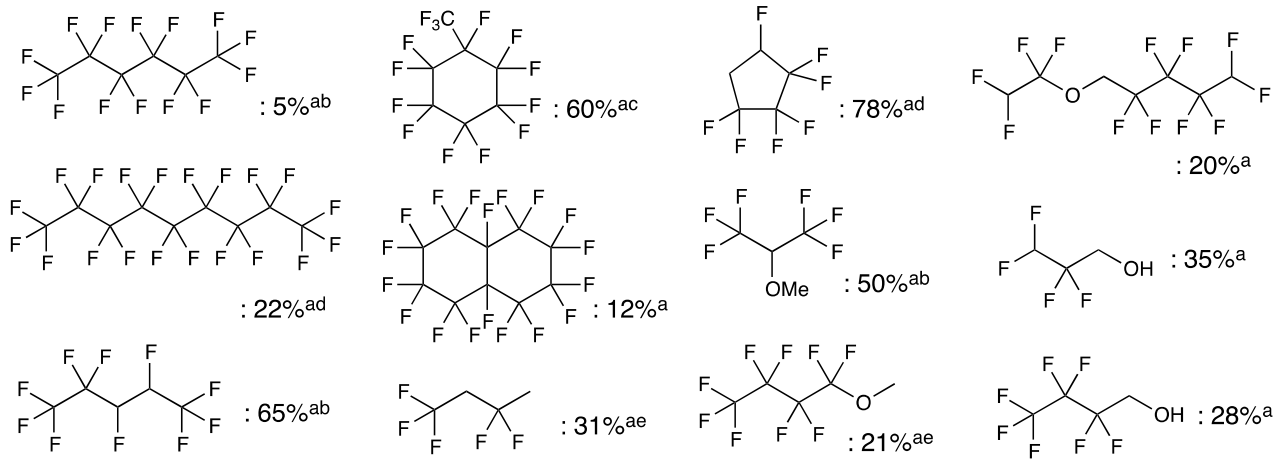


benzene (75 °C) : 97%[a]	 : trace[ab]
toluene : 98%[a]	
xylenes : 94%[a]	
mesitylene : 90%[a]	
 : 86%[a]	 : 97%[a]
 : 99%[a]	 : 90%[a]

[a]Conversion yield determined by ^{1}H NMR
[b]Confirmed three times with different manufacturer's solvent

Several other fluorous solvents were also examined, and their results are depicted in Table 2. The RCM reactions using 400 mol ppm of **1e** in acyclic and cyclic fluorous hydrocarbons were observed to be not as effective as compared with those that were using fluorous aromatic solvents. No advantageous effect of the solvent was observed when fluorous ethers or alcohols were used as the solvent.

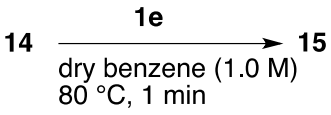
Table 2. Low catalyst-loading RCM reaction with **1e** (400 mol ppm) in non-aromatic fluorous solvents



[a]Conversion yield determined by ^{1}H NMR; [b]40 °C; [c]60 °C; [d]70 °C; [e]rt

Subsequently, we examined the amount of catalyst that can be reduced using dry benzene as a solvent. It was observed that the use of 50 mol ppm of the catalyst yielded the same conversion rate as that yielded using 400 mol ppm catalyst (Table 3, entry 1). However, we observed that the reaction proceeded smoothly and that it depicted a yield of 87% even though only 20 mol ppm of the catalyst was used (entry 5).

Table 3. Low catalyst-loading RCM reaction with **1e** in dry benzene



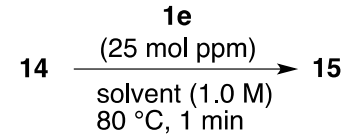
entry	cat. (mol ppm)	conv. (%)[a]
1	50	97
2	40	96
3	30	89
4	25	85
5	20	87
6	10	40
7	5	20

[a]Determined by ^{1}H NMR

A comparison of the catalytic activity of **1e** in various aromatic and fluorous aromatic solvents was conducted using 25 mol ppm of the catalyst. Although we observed that there was almost no difference in the catalytic activities of aromatic solvents and fluorous aromatic solvents (except for

pentafluorobenzene) with a 400 mol ppm of catalyst loading, as illustrated in Table 1 and described previously, the use of dry benzene produced a higher yield than that produced using other aromatic solvents (Table 4). For now, we conclude that refluxing in dry benzene for one minute is the most appropriate condition for reducing the catalyst amount.

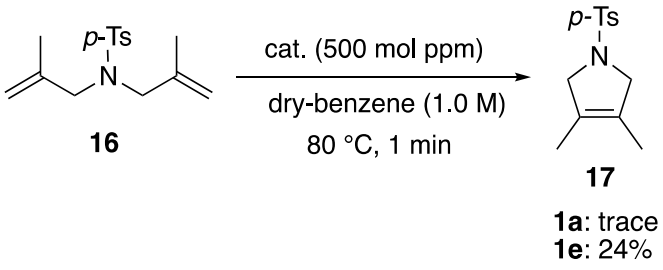
Table 4. RCM reaction using 25 mol ppm of **1e** in aromatic solvents



entry	solvent	conv. (%)[a]
1	dry-benzene	85
2	dry-benzene (15 h)	34[b]
3	dry-toluene	59
4	perfluorotoluene	44
5	2,3,4,5,6-pentafluorotoluene	48
6	pentafluorobenzene	47

[a]Determined by ^{1}H NMR; [b]Decomposed products were observed in ^{1}H NMR

It was reported that an RCM reaction of **14** could be performed to produce a yield of 70% using 25 mol ppm of the GH 2nd catalyst **1a** in toluene at 50 °C for 15 min.[16] Our experiments that employ the activated GH 2nd catalyst **1e** in dry benzene also produced comparable yields using a lower catalytic amount of 20 mol ppm. In particular, the use of **1e** was advantageous in the RCM reaction, which generated a tetrasubstituted olefin.[17] A considerable difference in the catalytic activities of the original GH 2nd catalysts **1a** and **1e** was observed when a more sterically bulky substrate was used. The RCM reaction of 4-methyl-*N,N*-bis(2-methylallyl)benzenesulfonamide **16**[7] using 500 mol ppm of catalyst **1e** generated the corresponding RCM product **17** in a yield of 24%, whereas catalyst **1a** generated almost no product under same conditions (Scheme 4).



Scheme 4. RCM reaction of **16** to produce tetrasubstituted olefin **17** using 500 mol ppm of catalyst

To summarize, we have prepared modified GH 2nd catalysts activated using the intramolecular steric strain. Catalyst **1e** exhibited the highest activity among the prepared catalysts, which contain a 9-anthracenyl group *ortho* to the isopropoxy group on the bidentate ligand. We have depicted that the catalyst **1e** can be successfully used in an RCM reaction even with a low catalyst amount of 20 mol ppm and that dry benzene is a suitable solvent for RCM reactions under such catalyst-loading conditions. Furthermore, it is recommended that catalyst **1e** should be used instead of the GH 2nd catalyst **1a** when sterically bulky substrates are used under low catalyst-loading conditions.

EXPERIMENTAL

All the laboratory chemicals were purchased from Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd., Sigma-Aldrich Co. LLC, and Kanto Chemical Co., Inc. used without further purification unless otherwise stated. Solvents were removed by rotary evaporation under reduced pressure using a 40 °C water bath. Non-volatile compounds were dried *in vacuo* at 0.01 mbar. All reactions were magnetically stirred and monitored by thin layer chromatography using silica gel plates. Purification by column chromatography was performed on silica gel 60 N (spherical, neutral, 63–210 μm, Kanto Chemical Co., Inc.). Melting points were determined in open-ended capillaries using a Bibby Scientific Ltd. Stuart® SMP-30 instrument and are uncorrected. All nuclear magnetic resonance (NMR) spectra were recorded with JEOL JNM-EX270 (^{1}H: 270 MHz, ^{13}C: 67.8 MHz) and JEOL ECA-500 (^{19}F: 466 MHz, ^{13}C: 124.5 MHz) spectrometers. Chemical shifts (δ) are given in units of ppm, and coupling constants (*J*) are given in Hz. Abbreviations for multiplicity are as follows: *s* (singlet), *d* (doublet), *dd* (double doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *bs* (broad singlet). High-resolution mass spectra (HRMS) were performed by FAB and EI using a magnetic sector analyzer. High resolution mass spectra were calibrated with Ultramark 1621® and PFK prior to data acquisition.

X-Ray Structural Analysis; A single crystal of **1e** was mounted to the end of the glass capillary using a minimal amount of adhesive. Data collections were carried out on a CCD-type diffractometer (Bruker SMART APEX II) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods (SIR2004[18]) and refined by a full-matrix least-squares method on F2 using SHELXL.[19]

General Procedures for Ring-closing Metathesis Reaction of 6 in $CDCl_3$ in Figure 3 and Figure 4; Diethyl 2-allyl-2-(2-methylallyl)malonate **6** and catalyst (5.0 mol%) were in dissolved $CDCl_3$ (0.03 M) in NMR tube at 23 °C. The reaction mixture was analyzed by ^{1}H NMR. Conversion was evaluated from the ^{1}H NMR spectra by integration of **6** and RCM product **7** signals.

Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (7)[7]: colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ:

5.12 (s, 1H), 4.12 (q, *J* = 14.3, 7.0 Hz, 4H), 2.83-2.90 (m, 4H), 1.64 (s, 3H), 1.18 (t, *J* = 7.3 Hz, 6H).

Preparation of 1e Stock Solution; **1e** (0.39 mg, $0.485*10^{-3}$ mmol) was weighed into a glass vessel (4 mL), and then dry benzene (390 μL) was added to the vessel.

General Procedures for Low Catalyst-Loading Ring-closing Metathesis Reactions of 14 or 16 using 1e in Table 1, Table 2, Table 3, Table 4, and Scheme 4; 4-Methyl-*N,N*-bis(2-methylallyl)-benzenesulfonamide **16** (46.8 mg, 0.168 mmol) in dry benzene (101 μL) was stirred for 5 min at 80 °C. **1e** (500 mol ppm) from stock solution in dry benzene (67 μL) was added to the solution with syringe, and then the reaction mixture was stirred at this temperature for 1 min. After the addition of Et_2O to the reaction mixture, the resulting mixture was concentrated and analyzed by ^{1}H NMR. Conversion was evaluated from the ^{1}H NMR spectra by integration of **16** and RCM product **17** signals.

3,4-Dimethyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (17)[7]: ash color solid; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.54 (s, 6H), 2.43 (s, 3H), 3.97 (s, 4H), 7.32 (d, *J* = 7.83 Hz, 2H), 7.72 (d, *J* = 7.83 Hz, 2H).

1-Tosyl-2,5-dihydro-1*H*-pyrrole (15)[14]: white crystals; mp 124.5-125.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 5.65 (s, 2H), 4.12 (s, 4H), 2.43 (s, 3H).

catalyst (1b)[6]: green crystal; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.86 (d, *J* = 6.2 Hz, 6H), 2.43 (bs, 18 H), 4.20 (s, 4 H), 4.34-4.44 (m, 1 H), 6.86-6.96 (m, 2 H), 7.06 (bs, 4 H), 7.26-7.35 (m, 6 H), 16.67 (s, 1 H).

catalyst (1c)[7]: green crystal; mp 169.0-171.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.75 (dd, *J* = 52.1, 6.2 Hz, 6H), 2.50 (bs, 18H), 4.06-4.18 (m, 5H), 5.30 (s, 1H), 6.96-7.06 (m, 6H), 7.34-7.44 (m, 5H), 7.76-7.82 (m, 3H), 16,72 (s, 1H).

catalyst (1d)[7]: green crystal; mp 172.5-173.2 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.67 (d, *J* = 6.21 Hz, 3H), 0.90-0.93 (m, 3H), 2.50 (bs, 18H), 3.79 (s, 3H), 4.15 (s, 4H), 4.20-4.24 (m, 1H), 6.93-7.04 (m, 4H), 7.24-7.35 (m, 5H), 7.48-7.54 (m, 2H), 7.69-7.75 (m, 1H), 7.82 (d, *J* = 9.18 Hz, 1H), 16.64 (s, 1H).

catalyst (1e)[7]: green crystal; mp 172.3-173.7 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.57 (d, *J* = 6.2 Hz, 6H), 2.52 (bs 18H), 3.82-3.91 (m, 1H), 4.18 (s, 4H), 6.95-7.15 (m, 6H), 7.33-7.45 (m, 6H), 7.80 (d, *J* = 8.64 Hz, 2H), 7.97 (d, *J* = 7.56 Hz, 2H), 8,44 (s, 1H), 16.76 (s, 1H).

catalyst (1f)[7]: green crystal; mp 163.7-165.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.77 (dd, *J* = 56.7, 5.9 Hz, 6H), 2.52 (bs, 18H), 4.17-4.28 (m, 5H), 6.95-7.03 (m, 6H), 7.39-7.42 (m, 1H), 7.50-7.87 (m, 8H), 8.67 (d, *J* = 8.1 Hz, 2H), 16.74 (s, 1H).

catalyst (1g)[7]: green crystal; mp dec. 300 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.33 (d, *J* = 5.7 Hz, 6H), 2.11-2.42 (bs, 18H), 4.10 (s, 4H), 4.92-5.01 (m, 1H), 6.93-6.97 (m, 6H), 7.28-7.50 (m, 6H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.43 (s, 1H), 16.64 (s, 1H).

2-Hydroxy-5-(perfluorooctyl)benzaldehyde (9)[13]: To a stirred solution of salicylaldehyde **8** (300 mg, 2.46 mmol), perfluorooctyl iodide (2.0 g, 3.68 mmol), and V-70L (758.5 mg, 2.46 mmol) in DMF was added cesium carbonate (6.41 g, 19.7 mmol) at room temperature. The reaction mixture was stirred at this

temperature for 20 h. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 2-hydroxy-5-(perfluorooctyl)-benzaldehyde **9** (476.4 mg, 36%). pale yellow crystals; mp 57-58 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 7.13 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 9.97 (s, 1H), 11.33 (s, 1H).

2-Isopropoxy-3-bromo-5-(perfluorooctyl)benzaldehyde (10)[13]: To a solution of 2-hydroxy-5-(perfluorooctyl)benzaldehyde **9** (1.8 g, 3.33 mmol) in acetic acid was added a solution of bromine (5.0 g, 31.29 mmol) in acetic acid at 50 °C and stirred for 16 h. After the addition of sodium thiosulfate aq. and EtOAc, the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 2-isopropoxy-3-bromo-5-(perfluorooctyl)benzaldehyde **10** (1.8 g, 86%). pale yellow crystals; mp 45-46 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 1.9 Hz, 1H), 9.94 (s, 1H), 11.95 (s, 1H).

Typical Procedure for the Preparation of Products 3a-3e, and 11.

3-Bromo-2-isobutoxybenzaldehyde (3a): To a solution of 3-bromo-2-hydroxybenzaldehyde **2** (300 mg, 1.5 mmol) and isobutyl bromide (0.8 ml, 7.4 mmol) in DMF was added K_2CO_3 (1.7 g, 12.0 mmol). The mixture was heated to 60 ºC under N_2 in oil bath and stirred for 10 h. 1 M aq. HCl and EtOAc were added to the resulting mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 5) to afford 3-bromo-2-isobutoxybenzaldehyde **3a** (329.4 mg, 86%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.12 (d, *J* = 7.3 Hz, 6H), 2.19-2.29 (m, 1H) 3.84 (d, *J* = 6.5 Hz, 2H), 7.12 (t, *J* = 15.1 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 10.37 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 19.2, 29.3, 83.1, 118.4, 125.6, 127.7, 131.1, 139.5, 159.5, 189.3; HRMS (EI+) *m/z* calcd for $C_{11}H_{13}BrO_2$ 256.0099, found 256.0113.

Typical Procedure for the Preparation of Products 4a-4e.

1-Bromo-2-isobutoxy-3-vinylbenzene (4a): Under N_2 atmosphere, methyltriphenylphosphonium bromide (3.7 g, 10.4 mmol) was dissolved in dry THF. NHMDS (1.9 M THF solution of 8.8 mL, 16.7 mmol) was slowly added to this solution at -78 ºC. The reaction mixture was stirred at 0 ºC for 2 h and then was cooled to -78 ºC. A solution of 3-bromo-2-isobutoxybenzaldehyde **3a** (449.4 mg, 2.1 mmol) in dry THF was syringed into the reaction mixture. The resulting mixture was warmed to 0 ºC and stirred for 3 h. The mixture was quenched with 1 M aq. HCl. After the addition of EtOAc, the organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column

chromatography on silica gel (EtOAc : hexane = 1 : 10) to afford 1-bromo-2-isobutoxy-3-vinylbenzene **4a** (334.6 mg, 75%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 1.09 (d, *J* = 6.75 Hz, 6H), 2.05-2.27 (m, 1H), 3.65 (d, *J* = 6.5 Hz, 2H), 5.31 (dd, *J* = 5.35, 10.8 Hz, 1H), 5.78 (dd, *J* = 5.72, 16.2 Hz, 1H), 6.92-7.05 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 17.5, 27.4, 78.3, 114.2, 116.2, 123.3, 123.6, 129.4, 130.9, 131.5, 151.8; HRMS (FAB+) *m/z* calcd for $C_{12}H_{16}BrO$ 255.0385, found 255.0409.

2-Isopropoxy-3-(9-anthracenyl)-5-(perfluorooctyl)-1-vinylbenzene (13): A supension of sodium *tert*-butoxide (63.4 mg, 0.660 mmol) and methyltriphenylphosphonium bromide (238 mg, 0.664 mmol) in dry Et_2O was stirred for 30 min at ambient temperature under N_2. A solution of 2-isopropoxy-3-(9-anthracenyl)-5-(perfluorooctyl)benzaldehyde **12** (50.0 mg, 0.0659 mmol) in dry Et_2O was added to the suspension with a syringe, and then the reaction mixture was stirred at ambiemt temperature for 3 h. The mixture was quenched with 1 M aq. HCl. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 20) to afford 2-isopropoxy-3-(9-anthracenyl)-5-(perfluorooctyl)-1-vinylbenzene **13** (40.0 mg, 80%). white solid; mp 88-89 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.54 (d, *J* = 6.4 Hz, 6H), 3.33-3.42 (m, 1H), 5.44 (d, *J* = 11.1 Hz, 1H), 5.90 (d, *J* = 17.8 Hz, 1H), 7.38-7.50 (m, 6H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 1.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 8.54 (s, 1H); ^{19}F NMR (466 MHz, $CDCl_3$) δ: -80.6 (4F), -110.1 (2F), -121.1 (2F), -121.5 (1F), -121.7 (4F), -122.6 (2F), -126.0 (2F); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 22.2, 29.8, 76.5, 104.0-124.5 (m, C_8F_{17}), 124.9, 125.3, 126.18, 126.22, 127.7, 128.6, 129.9, 130.5, 130.6, 131.4, 131.9, 132.1, 132.6, 132.7, 133.3, 152.8; HRMS (FAB+) *m/z* calcd for $C_{33}H_{22}F_{17}O$ 757.1399, found 757.1427.

Typical Procedure for the Preparation of Products 5a-5d.

9-(2-Isobutoxy-3-vinylphenyl)anthracene (5a): To a stirred solution of 1-bromo-2-isobutoxy-3-vinylbenzene **4a** (262.8 mg, 1.0 mmol) and 9-anthraceneboronic acid (251.9 mg, 1.1 mmol) in mixed solvent (THF : H_2O = 2 : 1) were added K_2CO_3 (724.2 mg, 5.2 mmol) and $Pd(PPh_3)_4$ (59.9 mg, 0.05 mmol). The mixture was heated to reflux in oil bath for 6 h. After cooling the reaction mixture to room temperature, 1M aq. HCl was added to quench unreacted K_2CO_3, and then the mixture was filtered through a plug of Celite® using pipette with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1 : 3) to afford 9-(2-isobutoxy-3-vinylphenyl)anthracene **5a** (112.3 mg, 31%). pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ: -0.04 (d, *J* = 5.9 Hz, 6H), 1.07-1.21 (m, 1H), 2.94 (d, *J* = 5.94 Hz, 2H), 5.31 (d, *J* = 10.5 Hz, 1H), 5.87 (dd, *J* = 5.8, 18.9 Hz, 1H), 7.05-7.16 (m, 1H), 7.25-7.41 (m, 6H), 7.62-7.71 (m, 3H), 7.81

(d, *J* = 8.6 Hz, 2H), 8.44 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 18.2, 28.3, 79.8, 114.8, 123.8, 125.0, 125.4, 125.9, 126.6, 126.8, 128.3, 130.4, 131.3, 131.8, 131.8, 132.4, 132.7, 133.4, 155.5; HRMS (EI+) *m/z* calcd for $C_{26}H_{25}O$ 353.1905, found 353.1872.

Typical Procedure for the Preparation of Products 5e and 12.

1-(2-Isopropoxy-3-vinylphenyl)pyrene (5e): To a stirred solution of 1-bromo-2-isopropoxy-3-vinylbenzene **4e** (50 mg, 0.21 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (10.9 mg, 0.0265 mmol), and 1-pyreneboronic acid (56.5 mg, 0.2296 mmol) in mixed solvent (THF : H_2O = 2 : 1) were added K_3PO_4 (222.7 mg, 1.049 mmol) and $Pd(OAc)_2$ (2.44 mg, 0.0108 mmol). The mixture was heated to reflux under N_2 in oil bath for 2 h. After cooling the reaction mixture to room temperature, 1M aq. HCl was added, and then the mixture was filtered through a plug of Celite® and washed with EtOAc. The filtrate was extracted with EtOAc. The combined organic phase was washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1 : 5) to afford 1-(2-isopropoxy-3-vinylphenyl)pyrene **5e** (62.4 mg, 83%). white solid; mp 114-116 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.66 (dd, *J* = 32.0, 5.9 Hz, 6H), 3.45-3.57 (m, 1H), 5.34 (dd, *J* = 10.8, 1.4 Hz, 1H), 5.83 (dd, *J* = 17.8, 1.4 Hz, 1H), 7.21-7.38 (m, 3H), 7.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.92-8.22 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 22.1, 22.2, 75.9, 114.5, 123.5, 124.6, 124.90, 124.92, 125.0, 125.2, 125.5, 126.0, 126.1, 127.4, 127.5, 127.6, 128.4, 128.8, 130.7, 131.1, 131.5, 132.75, 132.79, 134.8, 153.78; HRMS (FAB+) *m/z* calcd for $C_{27}H_{23}O$ 363.1749, found 363.1755.

Typical Procedure for the Preparation of Products 1h-1m.

catalyst (1h): To a suspension of 9-(2-isobutoxy-3-vinylphenyl)anthracene **5a** (11.3 mg, 0.03 mmol) and CuCl (6.65 mg, 0.07 mmol) in dry CH_2Cl_2 was added Grubbs 2nd (27.2 mg, 0.04 mmol). The reaction mixture was heated at 30 ºC under N_2 and stirred for 3 h. The mixture was concentrated. The residue was purified by column chromatography on the silica gel (EtOAc : hexane = 1 : 6) to obtain catalyst **1h** (7.0 mg, 27%). green crystal; mp 164.0-175.0 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: -0.30 (d, *J* = 6.5 Hz, 5H), 0.68-0.78 (m, 1H), 2.49 (bs, 18H), 3.12 (d, *J* = 7.0 Hz, 2H), 4.17 (s, 1H), 7.08-7.12 (m, 5H), 7.36-7.44 (m, 6H), 7.66 (d, *J* = 8.6, Hz, 2H), 7.97 (d, *J* = 8.4, 2H), 8.46 (s, 1H), 16.81 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 19.4, 19.6, 21.1, 28.0, 51.5, 78.1, 111.7, 113.7, 116.9, 121.0, 121.3, 122.4, 123.3, 129.4, 129.6, 135.9, 138.8, 139.0, 139.1, 145.5, 154.5, 215.2, 297.0; HRMS (FAB+) *m/z* calcd for $C_{46}H_{50}Cl_2N_2ORu$ 818.2344, found 818.2349.

catalyst (1i): green crystal; mp 176.0-177.0 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 2.37 (s, 6H), 2.48 (s, 12H), 2.93 (s, 3H), 4.14 (s, 4H), 7.07 (t, J = 13.2, 5H), 7.30-7.44 (m, 6H), 7.76-7.82 (d, *J* = 8.64 Hz, 3H), 16.72 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 19.3, 21.2, 51.7, 62.7, 122.2, 124.2, 125.4, 126.4, 126.8, 127.6, 128.3, 129.6, 130.6, 131.2, 138.6, 138.8, 146.4, 152.9, 159.8, 293.5; HRMS (FAB+) *m/z* calcd for

$C_{43}H_{44}Cl_2N_2ORu$ 776.1874, found 776.1893.

catalyst (1j): green crystal; mp 180.0-181.0 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.29 (t, *J* = 13.8 Hz, 3H), 2.34 (bs, 5H), 2.49 (s, 13H), 3.41 (dd, *J* = 3.4, 13.5 Hz, 2H), 4.18 (s, 4H), 7.06 (t, *J* = 7.0 Hz, 5H), 7.29-7.44 (m, 6H), 7.62 (d, *J*= 8.6 Hz, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 8.44 (s, 1H), 16.77 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 13.7, 21.1, 22.8, 51.4, 69.0, 76.5, 77.0, 77.2, 77.5, 122.7, 123.8, 125.4, 126.3, 126.4, 127.0, 127.4, 128.2, 129.4, 130.4, 131.1, 132.8, 135.1, 138.8, 147.2, 152.4, 211.3, 297.9; HRMS (FAB+) *m/z* calcd for $C_{44}H_{46}Cl_2N_2ORu$ 790.2031, found 790.2005.

catalyst (1k): green crystal; mp 164.0-166.5 ºC; ^{1}H NMR (270 MHz, $CDCl_3$) δ: -0.31 (t, *J* = 14.9 Hz, 3H), 0.61 (dd, *J* = 0.6, 13.5 Hz, 2H), 2.35 (bs, 5H), 2.49 (s, 13H), 3.29 (t, *J* = 13.2 Hz, 2H), 4.17 (s, 4H), 7.03-7.10 (m, 5H), 7.30-7.44 (m, 6H), 7.65 (d, *J*= 8.6 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.45 (s, 1H), 16.79 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ: 8.8, 21.1, 21.5, 51.4, 74.3, 122.6, 124.2, 125.4, 126.3, 127.1, 127.4, 128.1, 129.4, 130.1, 131.2, 132.4, 134.9, 138.8, 147.7, 152.6, 211.0, 298.0; HRMS (FAB+) *m/z* calcd for $C_{45}H_{48}Cl_2N_2ORu$ 804.2187, found 804.2202.

catalyst (1l): green crystal; mp 208 ºC (dec.); ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.71 (dd, *J* = 45.4, 6.5 Hz, 6H), 2.53 (bs, 18H), 3.99-4.08 (m, 1H), 4.20 (s, 4H), 6.99-7.04 (m, 6H), 7.44-7.48 (m, 1H), 7.95-8.20 (m, 10H), 16.78 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 18.5, 20.7, 20.9, 78.0, 51.0, 122.9, 123.3, 124.4, 124.6, 124.7, 125.3, 125.4, 125.5, 126.2, 127.4, 127.9, 128.0, 128.5, 129.1, 129.4, 131.06, 131.11, 131.4, 134.3, 135.3, 138.9, 140.0, 147.9, 150.0, 211.3, 299.7; HRMS (FAB+) *m/z* calcd for $C_{47}H_{48}Cl_2N_2ORu$ 828.2187, found 828.2161.

catalyst (1m): green crystal; mp 145 °C (dec.); ^{1}H NMR (270 MHz, $CDCl_3$) δ: 0.57 (d, *J* = 6.2 Hz, 6H), 2.50 (bs, 18H), 3.90-3.99 (m, 1H), 4.22 (s, 4H), 6.95-7.16 (m, 4H), 7.37-7.47 (m, 5H), 7.59-7.71 (m, 4H), 7.99 (d, *J* = 7.6 Hz, 2H), 8,48 (s, 1H), 16.56 (s, 1H); ^{19}F NMR (466 MHz, $CDCl_3$) δ: 125.9 (2F), -122.6 (2F), -121.8 (6F), -121.0 (2F), -109.8 (2F), -80.6 (3F); HRMS (FAB+) *m/z* calcd for $C_{53}H_{47}Cl_2F_{17}N_2ORu$ 1222.1837, found 1222.1832.

ACKNWLEDGEMENTS

This work was supported by JSPS KAKENHI Grant Number 26450145 and Prof. Y. Uozumi's JST-ACCEL program (JPMJAC1401). We also thank Nissan Chemical Industries, Ltd. for the funding that has been provided.

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