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Synthesis and Evaluation of Sterically Demanding Ruthenium Dithiolate Catalysts for Stereoretentive Olefin Metathesis

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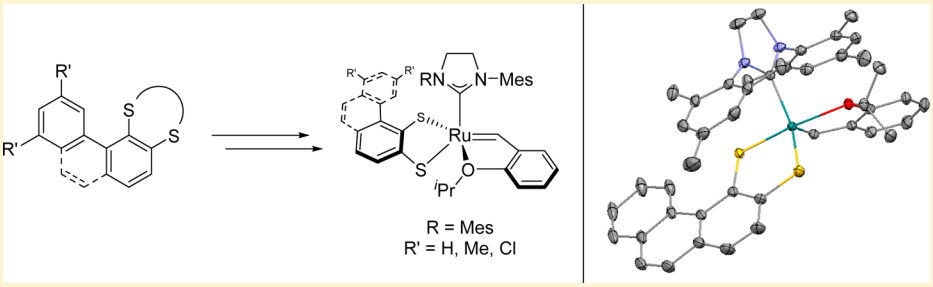
Supporting Information



ABSTRACT: Dithiolate ligands have recently been used in ruthenium-catalyzed olefin metathesis and have provided access to a kinetically *E* selective pathway through stereoretentive olefin metathesis. The typical dithiolate used is relatively simple with low steric demands imparted on the catalyst. We have developed a synthetic route that allows access to sterically demanding dithiolate ligands. The catalysts generated provided a pathway to study the intricate structure–activity relationships in olefin metathesis. It was found that DFT calculations can predict the ligand arrangement around the ruthenium center with remarkable accuracy. These dithiolate catalysts proved resistant to ligand isomerization and were stable even under forcing conditions. Additionally, catalyst initiation and olefin metathesis studies delivered a better understanding to the interplay between dithiolate ligand structure and catalyst activity and selectivity.

INTRODUCTION

The employment of olefin metathesis as a method to form carbon–carbon double bonds is pervasive in chemical synthesis.[1−7] Development of well-defined transition-metal alkylidenes has provided a scaffold to modify both the steric and electronic properties of the catalysts, delivering access to a wide range of olefin metathesis catalysts.[8−11] Recent advancements in catalytic architecture have focused on the construction of stereoselective catalysts.[12,13] A longstanding challenge in olefin metathesis was the development of kinetically *Z* selective olefin metathesis catalysts. Schrock, Hoveyda, and co-workers identified both molybdenum and tungsten systems that performed *Z*-selective olefin metathesis,[14−23] while Grubbs and co-workers developed cyclometalated ruthenium-based catalysts that performed *Z*-selective olefin metathesis.[24−31] Jensen and co-workers reported ruthenium monothiolate catalysts which show kinetic *Z* selectivity.[32−34] All of these catalysts function through the employment of some large ligand which can sterically shield one side of the forming metallacycle, favoring the formation of a *syn*-ruthenacyclobutane, producing (*Z*)-olefins.[12,13,25,35−37]

Traditional olefin metathesis catalysts provide olefinic products in thermodynamic ratios, which typically favor the *E* isomer.[38−41] In some cases the energy differences between *E* and *Z* isomers are quite small or can favor the *Z* isomer.[42] Until recently, methods for kinetically *E* selective olefin metathesis remained elusive. Procedures to form olefins in high *E* selectivity rely on traditional approaches such as Wittig,[43] Julia,[44] and Peterson[45] olefinations. Alkyne metathesis followed by semireduction[46] or *E*-selective hydrosilylation/protodesilylation[47] is also operative. More recent strategies have included *Z*-selective ethenolysis using *Z*-selective olefin metathesis catalysts.[48−50] Unfortunately, many methods to form (*E*)-olefins selectively are plagued by the requirement of additional synthetic manipulations and/or harsh reaction conditions. Thus, a kinetically *E* selective olefin metathesis catalyst would be valuable.

Recent studies in olefin metathesis have focused on the development of kinetically *E* selective olefin metathesis catalysts which function through stereoretention of the starting olefin. Initial efforts utilized ruthenium dithiolate catalyst **I**, which had previously been shown to catalyze *Z*-selective olefin metathesis through stereoretention.[51−54] The large *N*-aryl groups on the N-heterocyclic carbene (NHC) function to force the substituents at the α-positions of the ruthencycle down (Figure 1). Upon cycloreversion, a (*Z*)-olefin is generated. Grubbs and co-workers found that exposure of **I** to (*E*)-olefins led to cross-

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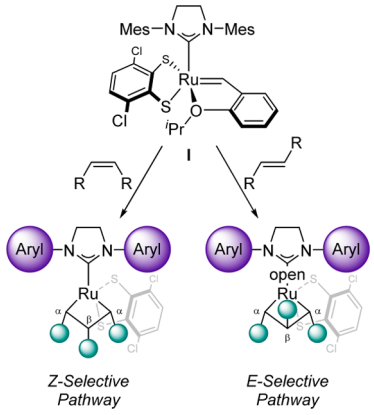

Figure 1. Model for stereoretention using **I** in olefin metathesis.

metathesis products formed in high *E* content (>99:1).[55] It is believed that the NHC has a space between the *N*-aryl groups, allowing the substituent at the *β*-position to point up, generating an *anti*-ruthenacycle and furnishing (*E*)-olefins upon cycloreversion (Figure 1). This model was supported by increasing the size of the space between the *N*-aryl groups. Decreasing the size of the substituents on the *N*-aryl rings (which increases the space) led to higher rates of metathesis for (*E*)-olefins in comparison to larger substituents on the *N*-aryl rings. Additional manipulations to the isopropoxy-chelating group have enhanced the initiation rate of these catalysts, rendering them more effective stereoretentive catalysts for the formation of (*E*)-olefins.[56] Progress has also been made using molybdenum-based catalysts, which deliver (*E*)-alkenyl halides[57] and (*E*)-macrocycles.[58]

Although manipulations to the catalytic scaffold have enhanced the reactivity of ruthenium catalysts in kinetically *E* selective olefin metatheses through stereoretention,[56] no kinetic *E* selectivity directly imparted by the catalyst has been detected. It was proposed that increasing the steric demands of the dithiolate ligand could favor the formation of the *anti*-ruthenacycle over the *syn*-ruthenacycle due to steric interactions of the substituent at the *β*-position with the large dithiolate ligand (Figure 2). We now report a new class of unsymmetrical

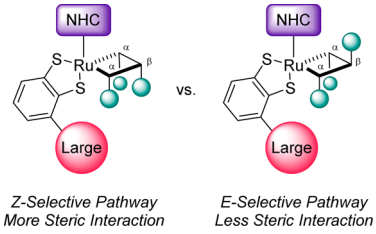

Figure 2. Design of dithiolate ligands to provide a pathway for kinetic *E* selectivity.

dithiolate ligands and their employment in olefin metathesis. Additionally, computational predictions for the formation of isomeric ruthenium dithiolate species are discussed as a tool for catalyst design.

RESULTS AND DISCUSSION

Catalyst Design and Synthesis. When considering the interaction between the dithiolate ligand and the *β*-position of the ruthenacycle in Figure 2, it was thought that a dithiolate ligand containing a sterically demanding group must be employed to obtain the necessary steric clash to disfavor the *syn*-ruthenacycle. Dithiolates with the necessary structure have not been reported in the literature; therefore, we set out to design a new class of dithiolate ligands that met the requirements (Figure 3). We believed ruthenium dithiolate species **II**–**VI** would provide some indication to the effect sterically demanding dithiolates would have on stereoretentive olefin metathesis.

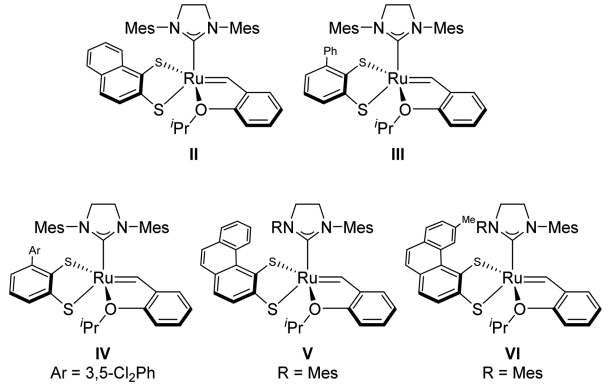

Figure 3. Ruthenium dithiolate species synthesized to evaluate dithiolate effects on olefin metathesis.

Initial studies in the synthesis of these novel dithiolates focused on the formation of thiol **6a** (Figure 4). A Wittig olefination was performed with aldehyde **2** to generate aryl alcohol **3a**. Early efforts at annulation to generate phenanthrol **4a** focused on photochemical methods[59] using the debrominated variant of **3a** but were not successful. Employment of an annulation developed by Daugulis and Bajracharya for the arylation of phenols was more effective.[60] Using KO^{t}Bu, **4a** was isolated in 32% yield. Competing cyclization at the para position of the aryl alcohols was also observed (29% yield), but the products were easily separable via flash column chromatography. With the carbon-framework set, attention was turned to installation of the 1,2-thiol motif. Palladium-catalyzed sulfurylations of aryl triflates are known methods for exchanging alcohols for thiols.[61] **4a** was treated with trifluoromethylsulfonic anhydride to form triflate **5a** in 75% yield. Thiol **6a** was generated in good yield from **5a** through palladium-catalyzed sulfurylation followed by deprotection with concentrated HCl. Thiols **6b**–**d** were produced using the developed synthetic sequence (Figure 4) from commercially available material.

With thiols **6a**–**e** in hand (**6e** is commercially available), installation of the second thiol was attempted. Ortho-metalation techniques using *n*BuLi and quenching with elemental sulfur[62] failed to deliver the desired dithiol using thiol **6a**, returning starting material (80%) and a mixture of dithiol products. A two-step procedure to generate benzodithiolylidenes, precursors to zinc dithiolate species, was developed by Klein and Yeung[63] and further utilized by Hoveyda and co-workers to generate a variety of dithiolylidenes.[54] Dithioesters **8a**–**e** were formed by treatment of thiols **6a**–**e** with sodium hydride and dithietane **7** (Figure 5). Using H_2SO_4, dithioesters **8c**–**e** were oxidized to form **9c**–**e** (Figure 5), but dithioesters **8a**,**b** were completely degraded to an unidentifiable material. A trend was observed in that the more electron rich the aromatic system (**8d** < **8c** < **8e** < **8a** < **8b**), the lower the yield of product detected. It is believed that increased

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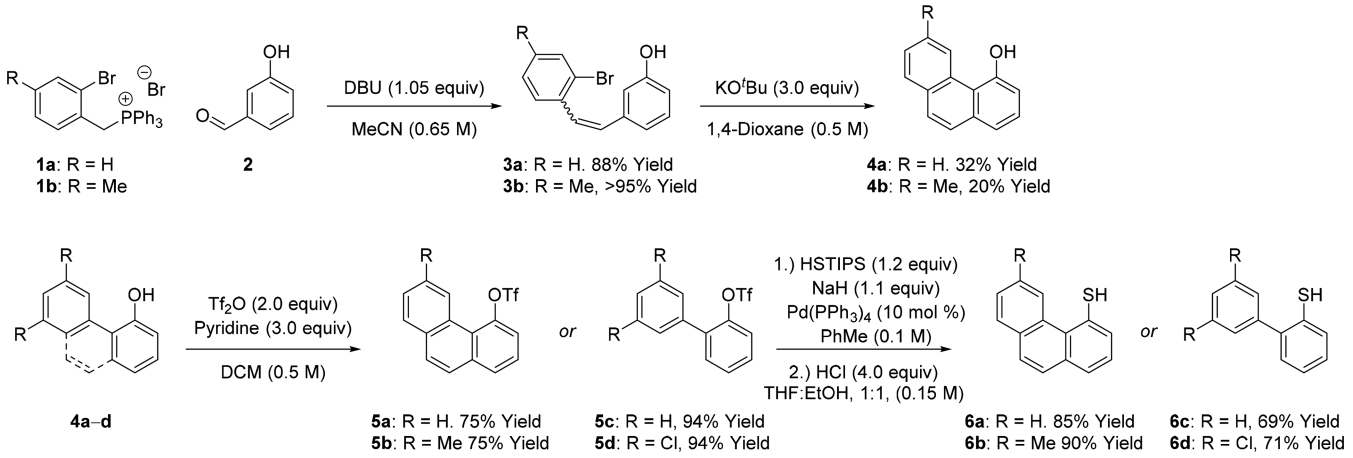

Figure 4. Synthesis of aryl thiols **6a–d** from aryl alcohols **4a–d**.

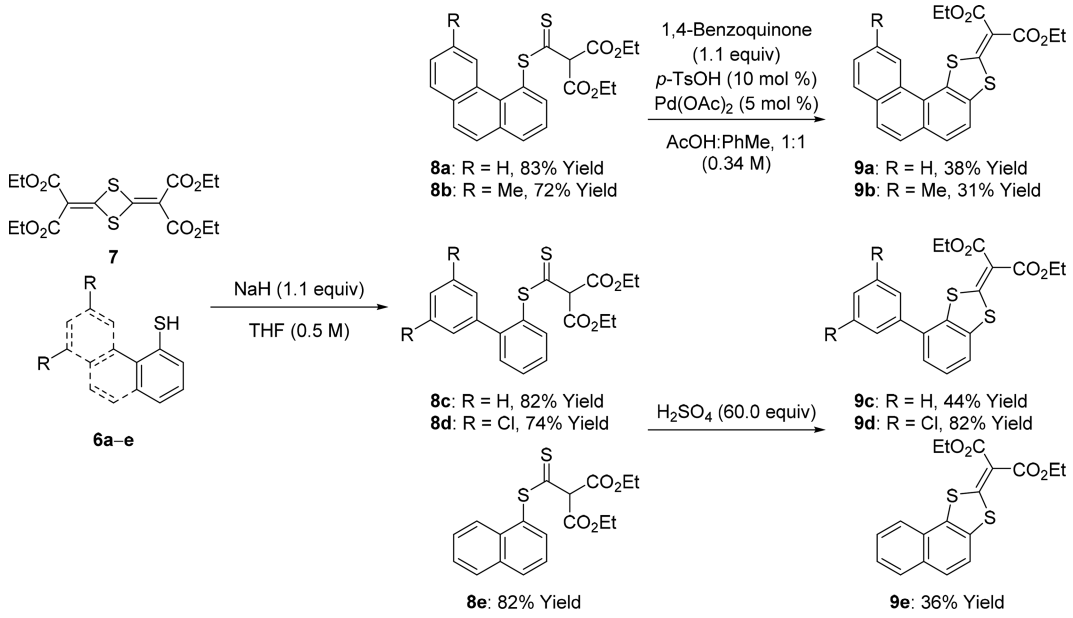

Figure 5. Synthesis of dthiolate precursors **9a–e** using a two-step method from thiols **6a–e**.

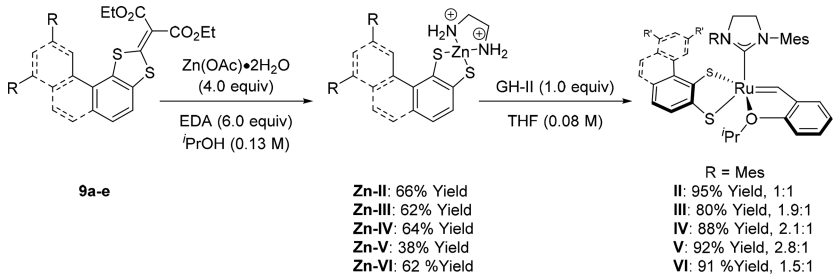

Figure 6. Synthesis of ruthenium dithiolates **II–VI** via transmetalation from the zinc salts. The up:down ratio of isomers detected by ^{1}H NMR is indicated.

electron density in the aromatic system caused overoxidation, leading to decomposition, as no starting material or product was ever recovered from the material. After a search of the literature, a palladium-catalyzed C–H sulfurylation to generate benzo[*d*][1,3]oxathiol-2-ones from thiocarbamates was identified.[64] This methodology provided access to 1,2-hydroxythiophenols; therefore, its application to generate analogous 1,2-dithiols was attempted. Initial efforts using **8a** delivered **9a** in poor yield. An abbreviated optimization increased the efficiency of this transformation with **8a** and led to the formation of **9a** in 38% yield. Application of these conditions to **8b** furnished **9b** in 31% yield (Figure 5).

With dithiolate precursors **9a–e** in hand, metalation onto zinc was attempted. Using a method adapted from Hoveyda and co-workers,[54] zinc dithiolates were formed in moderate yields (Figure 6). Transmetalation onto ruthenium proceeded smoothly using a known procedure,[54–56] furnishing ruthenium dithiolates **II–VI** (Figure 6).

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Studies of Catalyst Isomers. Upon characterization of catalysts **II**–**VI**, it was noticed that there were two benzylidene peaks in the ^{1}H NMR, due to the unsymmetrical dithiolates used in metalation. It was apparent that a mixture of the up (dithiolate bulk pointing toward the NHC) and down (dithiolate bulk pointing toward the ether chelate) isomers had been formed (Figure 6). Minimal selectivity was observed in the case of **II**, providing a mixture of the catalyst in a nearly 1:1 ratio. Likewise, **III** showed low preference for one isomer over the other. Complex **IV** had a slightly increased ratio of 2.1:1. When the more bulky phenanthrene-based dithiolate (**V**) was employed, a ratio of 2.8:1 was obtained. It is believed that the large bulk of the dithiolate interacts with the ligands on the ruthenium, favoring one isomer over the other. When the more sterically demanding Me-phenanthrene-based ligand (**VI**) was synthesized, it was believed that an enhanced effect would be observed, but to our surprise, a ratio of 1.5:1 was detected.

Our attention shifted to determine the major isomer of **V** formed. The two isomers of **V** could not be separated by crystallization. Attempts to separate the two isomers of **V** using chromatographic methods were also unsuccessful due to catalyst decomposition. Computational studies were undertaken to predict which isomer was favored by elucidating the interactions of the bulky dithiolate with the other ligands in the complex. Density functional theory (DFT) predicted that the up isomer of **V** was favored by 0.7 kcal/mol, leading to a predicted ratio of 3:1 up:down isomers (Figure 7a). Computations were also performed on **VI**. It was predicted that the two isomers were isoenergetic, leading to a 1:1 ratio (Figure 7b). These calculations are in very reasonable agreement with the 2.8:1 and the 1.5:1 ratios of up:down isomers found experimentally.

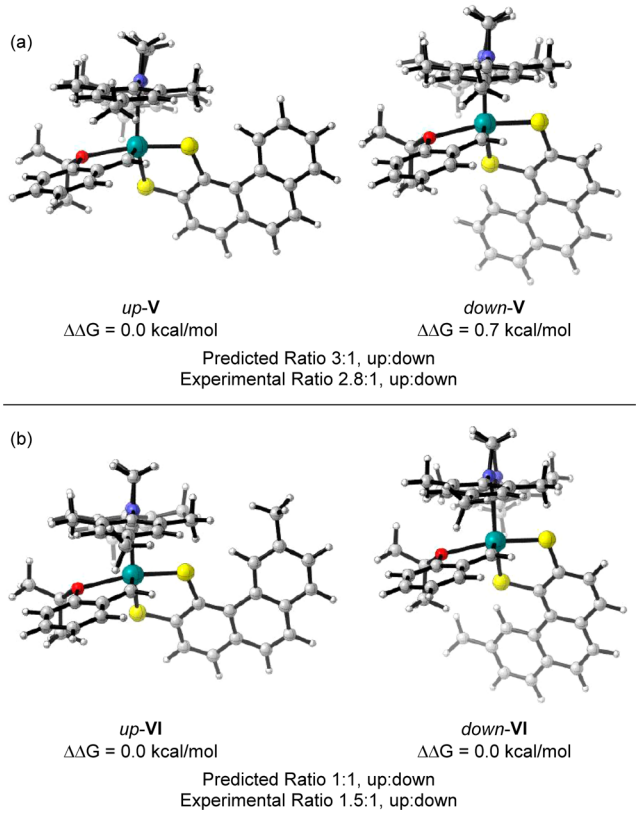

Figure 7. Computations to predict the up:down isomeric ratios: (a) computational predictions of the up:down ratio of **V**; (b) computational predictions of the up:down ratio of **VI**.

During crystallization attempts to separate the two isomers of **V**, an X-ray crystal structure was obtained of the up isomer, *up*-**V** (Figure 8). Unfortunately, ^{1}H NMR of this single crystal to determine the favored isomer of **V** was inconclusive. Additional NMR studies using the nuclear Overhauser effect (NOE)[65] indicated some through-space interaction between the proton at the 5-position of the phenanthrenedithiolate and the methyl groups of the NHC for the major isomer (Figure 9). Through-space interactions for the proton at the 5-position of the phenanthrenedithiolate and the methyl groups of the NHC for the minor isomer were absent. These results indicate that *up*-**V** is the major isomer of the catalyst formed. Furthermore, these findings indicate that computational calculations can not only predict the preferred isomer of ruthenium metathesis catalysts formed but also indicate the ratio of the two isomers generated. The major isomer as the up isomer for the other ruthenium dithiolate catalysts was assigned by analogy.

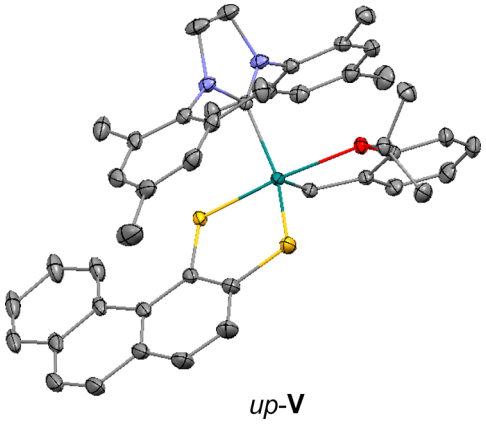

Figure 8. X-ray crystal structure of **V** indicating up geometry for the dithiolate ligand. Displacement ellipsoids are drawn at 50% probability. Ruthenium is shown in teal, sulfur in yellow, oxygen in red, nitrogen in blue, and carbon in gray. Hydrogen atoms have been omitted for clarity.

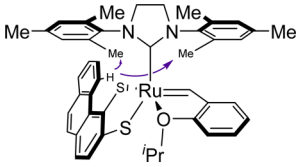

Figure 9. Illustration of the proton interactions observed in NOE.

Modifications to **V** were undertaken to affect the isomeric ratio of up to down. The aryl groups on the NHC used in **V** were changed from *N*-2,4,6-trimethylphenyl (Mes) to *N*-2,6-diisopropylphenyl (DIPP) (**VII**), which are sterically more demanding than the Mes groups. It was postulated that the DIPP groups would cause a greater steric clash on the dithiolate in the up position, favoring *down*-**VII**. Upon characterization of **VII**, it was found that the up:down ratio of isomers had changed, and in fact, when the DIPP groups were employed on the NHC, the down isomer was now slightly favored (Figure 10). Although the benzylidene peaks of each isomer no longer separate in ^{1}H NMR, the relative ratios of protons at the 5-

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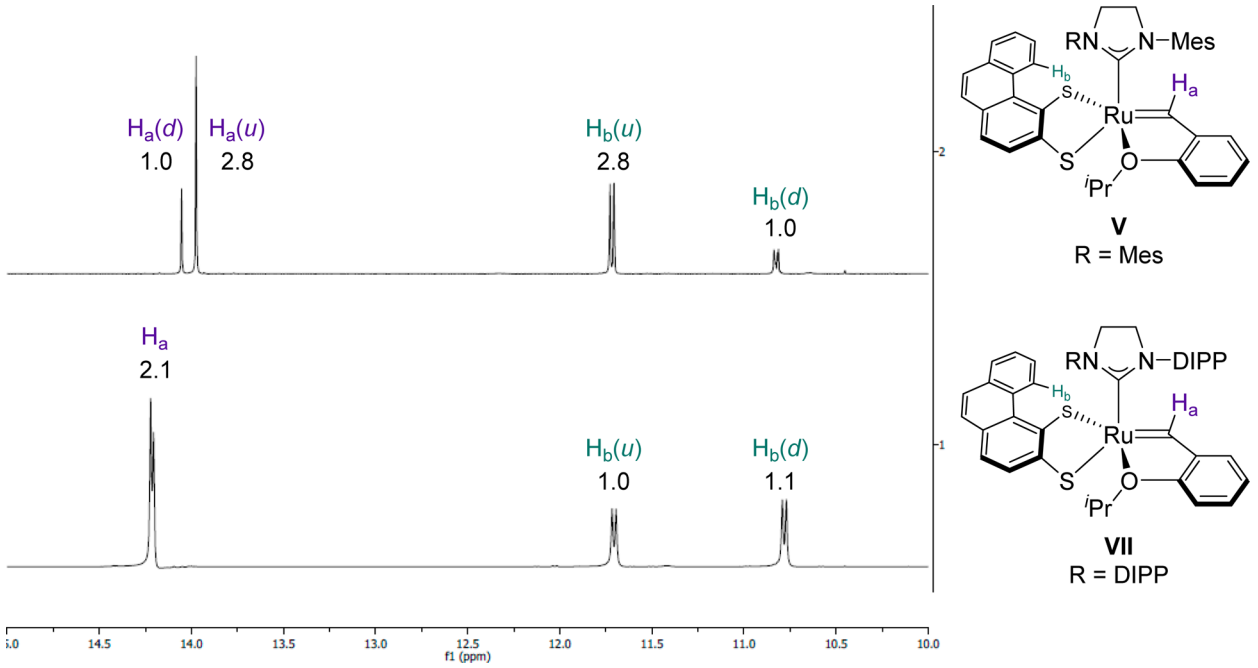

Figure 10. Probing the steric demands of the dithiolate in **V** by changing the *N*-aryl groups from Mes to DIPP.

position of the phenanthrene dithiolate could be compared to determine the up:down ratio of isomers (Figure 10).

Catalyst Robustness to Isomerization. After identifying the up/down isomers of the ruthenium dithiolate catalysts, studies on the robustness of these species to isomerization commenced. For these catalysts to isomerize, it was thought that one of the sulfurs from the dithiolate would need to dissociate, allowing ligand rotation to the opposite isomer. Recent work from Hoveyda and co-workers have shown that this process is not facile, and in order to observe ligand rotation, a strong σ-donating ligand, such as triisopropyl phosphite, must be used.[66] **III** was subjected to variable-temperature ^{1}H NMR (Figure 11a). ^{1}H NMR spectra were obtained at ambient temperature, 30 °C, and every 10 °C until 70 °C to see if the benzylidene signals would coalesce. This catalyst displayed incredible robustness to ligand isomerization and elevated temperature. No coalescence was observed. Even after the sample was left overnight at 100 °C, the relative ratio remained the same, and the ^{1}H NMR appeared unchanged from before. Examination of **V** using variable-temperature ^{1}H NMR was also performed, and again, no coalescence was observed (Figure 11b), indicating that each isomer of these catalysts is stable to isomerization to +70 °C.

Initiation Rates. Having a catalyst with two different isomers could prove problematic when olefin metathesis is performed. If one of the isomers reacts faster than the other, metathesis selectivity differences could be an issue. With a suite of ruthenium dithiolate catalysts containing a mixture of up/down isomers available, initiation rates of the different isomers were evaluated. Many initiation studies for ruthenium olefin metathesis catalysts employ UV–vis spectroscopy because of that technique's ability to withstand high olefin concentrations so that saturation kinetics can be achieved,[67,68] but concern for the detection of each specific isomer using this technique arose. Ultimately, ^{1}H NMR spectroscopy was employed so that each isomer's benzylidene peak could easily be monitored. Initiation studies were performed with 5, 10, and 20 equiv of phenyl vinyl ether. Phenyl vinyl ether was used due to the observation that

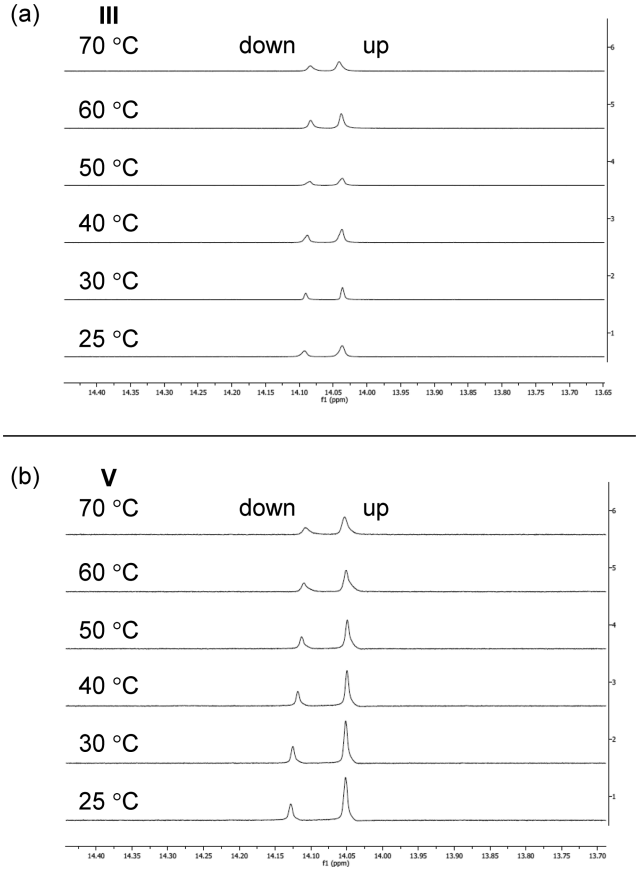

Figure 11. Catalyst isomerization studies at various temperatures: (a) variable-temperature ^{1}H NMR of **III** indicating no isomeric interconversion; (b) variable-temperature ^{1}H NMR of **V** indicating no isomeric interconversion.

the phenyl group is sterically larger than methyl, ethyl, and *n*-butyl. It was hoped that a larger vinyl ether could differentiate the rate of initiation for both the up/down catalysts.

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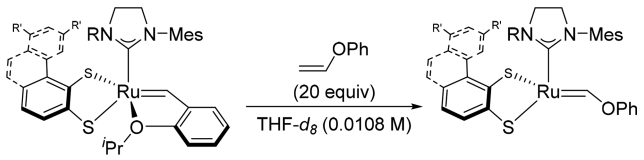
Surprisingly, the up/down isomers had similar initiation rates. A 20 equiv amount of phenyl vinyl ether was used as a way to gain saturation kinetics for the initiation of each catalyst (Table 1). On the basis of the initiation studies conducted, it appears that these catalysts adhere to an interchange type mechanism with associative character, which follows trends previously noted for second-generation ruthenium metathesis catalysts (GH-II).[68,69] These results also suggest that, overall, each isomer of a given catalyst has a similar initiation rate. **II** displayed one of the lower observed initiation rates (Table 1, entry 1), while **V** exhibited the highest observed initiation rate (Table 1, entry 4). It is thought that the larger dithiolate ligands could promote dissociation of the ether chelate. Given these results, each isomer of the catalyst is thought to perform similarly for a given ruthenium dithiolate. This allows employment of a mixture of catalyst isomers without the worry of competing reactivity differences between the catalyst isomers.

Table 1. Initiation Studies of II–VI with Phenylvinyl Ether[a]



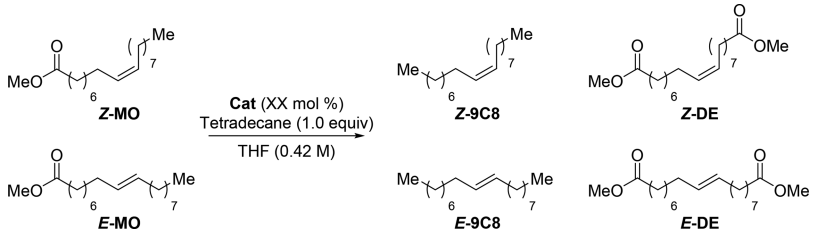
R = Mes

entry	cat.	k_{obs}(up)	k_{obs}(down)
1	**II**	0.0147	0.0152
2	**III**	0.0174	0.0201
3	**IV**	0.0109	0.0176
4	**V**	0.0229	0.0242
5	**VI**	0.0186	0.0161

[a]Full results from initiation studies including studies with 5 and 10 equiv of phenylvinyl ether can be found in the Supporting Information.

Catalysts Metathesis Activity. Continuing studies of **II–VI** probed the ability of these catalysts to engage in olefin metathesis. Previous generations of ruthenium dithiolate species have been examined using the self-metathesis of methyl 9-octadecenoate (**MO**),[55,56] allowing for a profile to be generated on the basis of both activity and stereoretentive ability. This system was used to evaluate the metathesis properties of **II–VI** (Table 2). All catalyst followed the trends observed in previous studies for the self-metathesis of **MO** using ruthenium dithiolate catalysts.[55,56] The catalysts were more reactive with (*Z*)-olefins than with (*E*)-olefins, and they appeared to be stereoretentive. Catalyst **III** seemed to perform the best in the self-metathesis of *Z*-**MO**, displaying the highest rate of metathesis while remaining highly stereoretentive (Table

Table 2. Self-Metathesis of Methyl 9-Octadecenoate[a]



entry	cat.	XX (mol %)	MO	time (h)	MO (%) (*Z*:*E*)	DE (%) (*Z*:*E*)	9C8 (%) (*Z*:*E*)
1	**II**	0.5	*Z*	1	70 (83:1)	15 (>99:1)	15 (74:1)
				2	50 (59:1)	25 (>99:1)	25 (82:1)
2	**III**	0.5	*Z*	1	50 (68:1)	25 (>99:1)	25 (>99:1)
3	**IV**	0.5	*Z*	1	58 (>99:1)	21 (>99:1)	21 (>99:1)
				2	50 (>99:1)	25 (>99:1)	25 (>99:1)
4	**V**	0.5	*Z*	1	88 (22:1)	11 (>99:1)	11 (>99:1)
				2	54 (47:1)	23 (4:1)	23 (>99:1)
				3	50 (14:1)	25 (4:1)	25 (>99:1)
5	**VI**	0.5	*Z*	1	60 (30:1)	20 (8:1)	20 (>99:1)
				2	50 (16:1)	25 (5:1)	25 (>99:1)
6	**II**	3.0	*E*	8	94 (1:38)	3 (1:>99)	3 (1:8)
				24	56 (1:51)	22 (1:15)	22 (1:20)
				48	50 (1:15)	25 (1:12)	25 (1:17)
7	**III**	3.0	*E*	8	92 (1:>99)	4 (1:>99)	4 (1:>99)
				24	56 (1:>99)	22 (1:>99)	22 (1:>99)
				48	50 (1:>99)	25 (1:>99)	25 (1:>99)
8	**IV**	3.0	*E*	8	74 (1:>99)	13 (1:>99)	13 (1:>99)
				24	50 (1:99)	25 (1:>99)	25 (1:>99)
9	**V**	3.0	*E*	8	60 (1:>99)	20 (1:>99)	20 (1:>99)
				24	50 (1:>99)	25 (1:>99)	25 (1:84)
10	**VI**	3.0	*E*	8	92 (1:>99)	4 (1:>99)	4 (1:>99)
				24	60 (1:>99)	20 (1:>99)	20 (1:>99)
				48	50 (1:>99)	25 (1:>99)	25 (1:>99)

[a]Tetradecane was added as an internal standard so that conversions could be accurately assigned.

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2, entry 2). Interestingly, **V**, which shows the lowest rate of conversion and stereoretention with *Z*-**MO**, displayed the highest rate of conversion with *E*-**MO** (Table 2, entries 4 and 9). It is believed that the large phenanthrene ligand is able to adopt a configuration in which the metathesis of *Z*-**MO** is less favored relative to the other catalyst, whereas the metathesis of *E*-**MO** is more favored relative to the other catalysts. **VI**, which contains a dithiolate even more sterically demanding than that of **V**, was expected to show an increased rate of reaction with *E*-**MO** relative to the other catalysts, but this catalyst performed similarly to the catalysts containing less sterically demanding dithiolates (Table 2, entries 5 and 10). DFT was used to compute the unsubstituted metallacycle structure of **VI**-down. Figure 12 shows that there is 4.68 Å between the β-position and

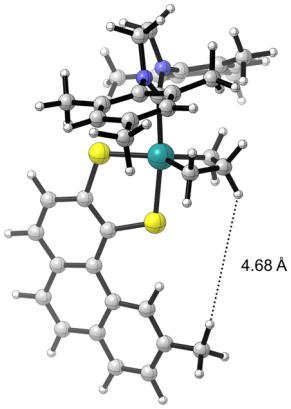

Figure 12. DFT computed structure of the unsubstituted metallacycle of **VI**.

the methyl substituent. This allowed us to predict that even the down isomer of **VI** would have little influence on the forming metallacycle to favor *E*-selective metathesis.

CONCLUSION

In summary, we have developed a route to sterically demanding zinc dithiolate ligands, offering entry into 1,2-dithiol structures previously unknown in the literature. The transmetalation of the dithiolate ligands onto ruthenium provided access to sterically demanding ruthenium dithiolate species. Characterization of **II**–**VII** revealed that the unsymmetrical dithiolates formed two different catalytic isomers, up and down. DFT calculations predicted that the up isomer would be the favored isomer for catalyst **V** by 0.7 kcal/mol, furnishing a 3:1 up:down ratio. These predictions were proven through NOE spectroscopy, as through-space interactions were detected between aromatic protons of the dithiolate and the Mes groups on the NHC. Furthermore, manipulation of the *N*-aryl groups on the NHC provided a mechanism to flip the isomeric ratio of the dithiolate catalysts. When DIPP was substituted for Mes as the *N*-aryl groups on the NHC, *down*-**VII** was favored over *up*-**VII**. The robustness of **III** and **V** to isomerization was probed through variable-temperature ^{1}H NMR experiments. Even at 70 °C, no coalescence was observed, and **III** remained unchanged after prolonged exposure to high temperatures. Initiation rates of **II**–**VI** were studied, and although the isomers place the dithiolate bulk in much different proximities to the ruthenium carbene, the initiation rates were similar for each isomer of a given catalyst. Furthermore, an interchange mechanism with associative character appears to be operative for ruthenium dithiolate catalysts. Finally, the stereoretentive abilities of these bulky dithiolate catalysts were probed. **II**–**VI** displayed stereoretentive abilities in the self-metathesis of both *Z*- and *E*-**MO**. Although these catalysts as a whole performed self-metathesis on *Z*-**MO** at a higher rate in comparison to *E*-**MO**, **V** (relative to the other catalysts) displayed a higher affinity for (*E*)-olefins, showing stereoretention and a higher reaction rate for *E*-**MO**. This suggests that sterically demanding dithiolate ligands can influence stereoselectivity in olefin metathesis. Continued investigations into stereoselective olefin metathesis are focusing on manipulations to the catalytic scaffold in an effort to uncover a kinetically *E* selective catalyst, which promotes *E* selectivity between two terminal olefins. Additionally, strategies for separating the isomers and resolving enantiomers of each catalytic isomer for use in asymmetric olefin metathesis are underway.

EXPERIMENTAL SECTION

General Information. General solvents were purified by passing through solvent purification columns. Commercially available substrates were used as received. Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)-ruthenium(II) (GH-II) and dichloro[1,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II) (**711**) were used as received from Materia, Inc. **7** was synthesized according to the literature procedure.[70] All solvents and substrates were sparged with argon before being brought into the glovebox, and solvents were filtered over basic alumina (Brockmann I) prior to use. Tetrahydrofuran-d_8 was dried over sodium metal and benzophenone and distilled to a Schlenk flask under an argon atmosphere. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Dynanmic Absorbents F_{254}). Visualization was accomplished with UV light. Purification of ligand precursors was carried out by flash chromatography using Silacycle silica gel (40–63 μm).

Spectroscopy, Spectrometry, and Data Collection. Infrared spectra were recorded on a Nicolet iS5 spectrometer equipped with an iD5 ATR accessory. Kinetic NMR experiments were performed on a Varian 600 MHz spectrometer with a penta inverse probe. ^{1}H and ^{13}C NMR characterization data were obtained on a Bruker 400 MHz spectrometer with Prodigy broad-band cryoprobe and a Varian 500 MHz spectrometer with an AutoX probe. Samples were referenced to residual protio solvent. ^{19}F and ^{31}P NMR data were acquired on a Varian 300 MHz spectrometer. Spectra were analyzed using MestReNova Ver. 11.0.2. X-ray crystallographic data were collected by the California Institute of Technology Beckman Institute X-ray Crystallographic Facility using a Bruker KAPPA APEXII X-ray diffractometer. GC conversion and selectivity data for the self-metathesis of methyl 9-octadeconate were obtained using an HP-5 capillary column with an Agilent 6850 FID gas chromatograph. Accurate conversion and yield data were generated by determining response factors by making solutions of varying concentrations of the desired compound to be analyzed and internal standard as described by Grubbs et al.[41] High-resolution mass spectrometry (HRMS) was performed using FAB+ ionization on a JEOL MSRoute mass spectrometer.

Representative Procedure for the Synthesis of Phosphonium Bromides 1a,b. This procedure was adapted from Gilheany et al.[71] To a flame-dried round-bottom flask equipped with a magnetic stir bar and under an argon atmosphere was added triphenylphosphine (1.0 equiv), and the mixture was stirred at 100 °C until the triphenylphosphine had melted. Bromobenzyl bromide (1.1 equiv) was added to neat triphenylphosphine, and the reaction mixture was stirred for 15 min. During this time, the reaction mixture solidified, indicating salt formation. The solid phosphonium bromide salt was dissolved in chloroform and precipitated with ethyl acetate to provide the desired phosphonium bromide salt.

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*(2-Bromobenzyl)triphenylphosphonium Bromide (**1a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a a 90 mmol scale. Phosphonium bromide **1a** was formed as a white solid (53.0 g, >95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80−7.74 (m, 3H, Ar-H), 7.68−7.57 (m, 12H, Ar-H), 7.48 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, Ar-H), 7.38−7.29 (m, 1H, Ar-H), 7.17−7.08 (m, 2H, Ar-H), 5.66−5.48 (m, 2H, methylene). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 135.30, 134.38 (d, J = 9.8 Hz), 133.11 (d, J = 6.1 Hz), 133.04 (d, J = 3.4 Hz), 130.33 (d, J = 12.3 Hz), 128.52 (d, J = 3.7 Hz), 127.64 (d, J = 8.6 Hz), 127.27 (d, J = 6.5 Hz), 117.77 (d, J = 5.9 Hz), 116.92 (d, J = 5.9 Hz), 77.38, 31.03 (d, J = 48.8 Hz). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 22.54 (s). HRMS (FAB+): $[M]^+$ $C_{25}H_{21}BrP$ calculated 431.0564, found 431.0581. FTIR (neat): 3419, 3061, 2997, 2848, 2784, 2360, 2343, 1472, 1429, 1111, 751, 690 cm^{-1}.

*(2-Bromo-4-methylbenzyl)triphenylphosphonium Bromide (**1b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 47 mmol scale. Phosphonium bromide **1b** was formed as a white solid (23.6 g, >95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79−7.75 (m, 3H, Ar-H), 7.66−7.59 (m, 12H, Ar-H), 7.34 (dd, $^{3}J_{HH}$ = 7.9, 2.7 Hz, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 6.94 (d, $^{3}J_{HH}$ = 10 Hz, 1H, Ar-H), 5.48 (d, $^{2}J_{HP}$ = 14.0 Hz, 2H, methylene), 2.23 (d, $^{4}J_{HH}$ = 2.6 Hz, 3H, methyl). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 140.83 (d, J = 4.2 Hz), 135.24 (d, J = 3.1 Hz), 134.41, 133.35 (d, J = 3.1 Hz), 132.72 (d, J = 4.9 Hz), 130.30 (d, J = 12.6 Hz), 129.36 (d, J = 3.6 Hz), 126.96 (d, J = 6.7 Hz), 124.19 (d, J = 9.0 Hz), 117.45 (d, J = 85.5 Hz), 30.68 (d, J = 48.5 Hz), 20.90 (d, J = 1.6 Hz). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 22.08. HRMS (FAB+): $[M]^+$ $C_{26}H_{23}BrP$ calculated 445.0721, found 445.0719. FTIR (neat): 3392, 3052, 2841, 2788, 1489, 1437, 1111, 747, 690 cm^{-1}.

Representative Procedure for the Synthesis of Alcohols 3a,b. To a flame-dried round-bottom flask equipped with a magnetic stir bar were added **1** (1.0 equiv) and 3-hydroxybenzaldehyde (**2**; 1.0 equiv). The flask was capped with a septum and purged with argon. Acetonitrile (0.65 M with respect to **1**) and 1,8-diazabicylo[5.4.0]-undec-7-ene (1.05 equiv) were added, and the reaction mixture was refluxed for 14 h. Upon cooling to ambient temperature, the reaction was quenched with aqueous HCl (1 M). The solution was extracted with ethyl acetate (three times). The combined organics were washed with water and brine, dried (Na_2SO_4), and concentrated. The crude residue was purified by flash column chromatography (SiO_2, dichloromethane) to deliver the desired product.

*3-(2-Bromostyryl)phenol (**3a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 90 mmol scale. Alcohol **3a** was formed as a pale yellow oil (21.9 g, 88% yield) as a mixture of E and Z isomers. TLC (SiO_2): R_f = 0.43 (dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, $^{3}J_{HH}$ = 7.8, $^{4}J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.59−7.53 (m, 2H), 7.42 (d, $^{3}J_{HH}$ = 16.2 Hz, 1H, Ar-H), 7.28 (t, $^{3}J_{HH}$ = 7.9 Hz, 1H, Ar-H), 7.25−7.20 (m, 1H, Ar-H), 7.19−7.16 (m, 1H, Ar-H), 7.12−7.09 (m, 2H, Ar-H), 7.09−7.03 (m, 3H), 7.01 (dd, J = 2.6, 1.6 Hz, 1H), 6.95 (d, J = 16.2 Hz, 1H), 6.75 (ddd, J = 8.1, 2.5, 1.0 Hz, 1H), 6.72 (ddd, J = 7.6, 1.5, 0.9 Hz, 1H), 6.64 (ddd, J = 8.1, 2.6, 1.0 Hz, 1H), 6.60 (s, 2H, Ar-H), 6.59 (dd, J = 2.6, 1.5 Hz, 1H, vinylic-H), 5.00 (s, 2H, OH). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 155.79, 155.20, 138.84, 138.03, 137.87, 137.01, 133.18, 132.77, 131.04, 131.02, 131.01, 130.09, 129.99, 129.61, 129.03, 128.89, 128.03, 127.68, 127.17, 126.84, 124.28, 123.93, 121.96, 120.01, 115.64, 115.27, 114.54, 113.30. HRMS (FAB+): $[M]^+$ $C_{14}H_{11}BrO$ calculated 273.9993, found 274.0021. FTIR (neat): 3344, 3056, 1581, 1447, 1246, 1157, 1024, 958, 747 cm^{-1}.

*3-(2-Bromo-4-methylstyryl)phenol (**3b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 45 mmol scale. Alcohol **3b** was formed as a pale yellow oil (13.3 g, >95% yield) as a mixture of E and Z isomers. TLC (SiO_2): R_f = 0.57 (dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 1H, Ar-H), 7.45−7.39 (m, 3H, Ar-H), 7.24 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.14−7.05 (m, 4H, Ar-H), 7.04−7.01 (m, 1H, Ar-H), 6.97−6.88 (m, 2H), 6.80−6.73 (m, 2H,), 6.69−6.62 (m, 2H, vinylic-H), 6.60 (s, 2H, Ar-H), 5.16 (s, 1H, OH), 4.96 (s, 1H, OH), 2.34 (s, 3H, methyl), 2.31 (s, 3H, methyl). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 155.85, 155.26, 139.39, 139.14, 139.02, 138.25, 134.74, 134.07, 133.56, 133.15, 130.64, 130.59, 130.07, 130.04, 129.90, 129.57, 128.60, 128.07, 127.89, 126.47, 124.10, 123.72, 121.91, 119.87, 115.62, 115.07, 114.43, 113.20, 20.97, 20.95. HRMS (FAB+): $[M]^+$ $C_{15}H_{13}BrO$ calculated 288.0150, found 288.0137. FTIR (neat): 3350, 3022, 2907, 1580, 1484, 1447, 1227, 1039, 959, 872, 837, 781, 675 cm^{-1}.

Representative Procedure for the Synthesis of Alcohols 4a,b. This procedure was adapted from Daugulis et al.[60] To a flame-dried pressure vessel equipped with a magnetic stir bar was added potassium *tert*-butoxide (3.0 equiv). The vessel was capped with a septum and purged with argon. 1,4-Dioxane (0.5 M with respect to **3**) and **3** (1.0 equiv) were added to the vessel. The reaction vessel was sealed, and the contents were stirred at 140 °C for 8 h. Upon cooling to ambient temperature, the reaction was quenched with aqueous HCl (1 M). The solution was extracted with ethyl acetate (three times). The combined organics were washed with water and brine, dried (Na_2SO_4), and concentrated. The crude residue was purified by flash column chromatography (SiO_2, dichloromethane) to deliver the desired product.

*Phenanthren-4-ol (**4a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 80 mmol scale. Alcohol **4a** was formed as a white solid (5.0 g, 32% yield). TLC (SiO_2): R_f = 0.57 (dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, Ar-H), 7.94 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.79−7.71 (m, 3H, Ar-H), 7.67−7.64 (m, 1H, Ar-H), 7.55 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.44 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ar-H), 6.93 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, Ar-H), 5.75 (d, $^{6}J_{HH}$ = 3.0 Hz, 1H, OH). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 154.41, 135.01, 132.65, 130.37, 128.63, 128.33, 128.09, 127.14, 126.63, 126.44, 126.09, 121.77, 119.47, 113.34. HRMS (FAB+): $[M]^+$ $C_{14}H_{10}O$ calculated 194.0732, found 194.0772. FTIR (neat): 3519, 3037, 2924, 1570, 1441, 1415, 1310, 1224, 1003, 826, 741, 713 cm^{-1}.

*6-Methylphenanthren-4-ol (**4b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 45 mmol scale, and the mixture stirred at 140 °C for 11 h. Alcohol **4b** was formed as a white solid (1.9 g, 20% yield). TLC (SiO_2): R_f = 0.71 (dichloromethane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.46 (dq, $^{4}J_{HH}$ = 1.5 Hz, $^{6}J_{HH}$ = 0.8 Hz, 1H, Ar-H), 7.80 (d, J = 8.0 Hz, 1H, Ar-H), 7.71 (d, J = 8.7 Hz, 1H, Ar-H), 7.64 (d, J = 8.8 Hz, 1H, Ar-H), 7.50 (dd, J = 7.9 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.44 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.41 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, Ar-H), 6.95 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, Ar-H), 5.69 (s, 1H, OH), 2.64 (s, 3H, methyl). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 154.47, 136.33, 135.27, 130.61, 130.46, 128.38, 128.18, 127.96, 127.73, 126.32, 126.20, 121.81, 119.33, 113.15, 22.59. HRMS (FAB+): $[M]^+$ $C_{15}H_{12}O$ calculated 208.0888, found 208.0884. FTIR (neat): 3522, 3055, 2916, 1603, 1572, 1418, 1341, 1304, 1227, 1140, 1003, 836, 754, 712 cm^{-1}.

Experimental Procedure for the Preparation of 3′,5′-Dichloro-[1,1′-biphenyl]-2-ol (4d). To a 250 mL round-bottom flask equipped with a magnetic stir bar was added acetonitrile/water 4/1 (0.2 M with respect to iodide, 26:6.5 mL), and the flask was sparged with argon for 10 min. 3,5-Dichloroiodobenzene (1.77 g, 6.5 mmol, 1.0 equiv), 2-hydroxyphenylboronic acid (1.3 g, 9.75 mmol, 1.5 equiv), K_3PO_4 (2.76 g, 13 mmol, 2.0 equiv), $Pd(OAc)_2$ (73 mg, 0.325 mmol, 5 mol %), and PPh_3 (170 mg, 0.65 mmol, 10 mol %) were placed in the flask. The flask was purged with argon for 5 min and then heated at 50 °C for 20 h. The reaction mixture was concentrated, diluted with water, and extracted with ethyl acetate (3 × 50 mL). The combined organics were washed with brine, dried (Na_2SO_4), and concentrated. The crude residue was purified by flash column chromatography (SiO_2, 1/3 dichloromethane/hexanes) to deliver **4d** (1.546 g, >95% yield) as a clear oil. TLC (SiO_2): R_f = 0.38 (1/1, dichloromethane/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, $^{4}J_{HH}$ = 1.9 Hz, 2H, Ar-H), 7.37 (t, $^{4}J_{HH}$ = 1.9 Hz, 1H, Ar-H), 7.28 (ddd, $^{3}J_{HH}$ = 8.1, 7.4 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.24 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.02 (td, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, Ar-H), 6.93 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1H, Ar-H), 5.08 (s, 1H, OH). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 152.30, 140.53, 135.40, 130.43, 130.10, 127.77, 127.70, 125.85, 121.44, 116.41. HRMS (FAB+): $[M]^+$

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$C_{12}H_8Cl_2O$ calculated 237.9952, found 237.9953. FTIR (neat): 3561, 3418, 2348, 2326, 1588, 1556, 1491, 1454, 1407, 1285, 1181, 1109, 847, 800, 751 cm^{-1}.

Representative Procedure for the Synthesis of Triflates 5a–d. To a flame-dried flask equipped with a magnetic stir bar was added **4** (1.0 equiv). The flask was capped with a septum and purged with argon. Dichloromethane (0.5 M with respect to the **4**) and pyridine (3.0 equiv) were placed in the flask. The reaction mixture was cooled to 0 °C, and trifluoromethylsulfonic anhydride (2.0 equiv) was added dropwise. The flask was slowly warmed to ambient temperature, and the contents were stirred overnight. The reaction was quenched with aqueous HCl (1 M). The solution was extracted with dichloromethane (two times). The combined organics were washed with water and brine, dried ($MgSO_4$), and concentrated. The crude residue was purified by flash column chromatography (SiO_2, 1/9 dichloromethane/hexanes) to deliver the desired product.

*Phenanthren-4-yl Trifluoromethanesulfonate (**5a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 25.9 mmol scale. Triflate **5a** was formed as a white solid (6.33 g, 75% yield). TLC (SiO_2): R_f = 0.54 (1/6, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 9.17 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 7.95–7.91 (m, 2H, Ar-H), 7.81 (d, $^3J_{HH}$ = 8.6 Hz, 1H, Ar-H), 7.74–7.59 (m, 5H, Ar-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 147.35, 135.27, 133.35, 129.36, 129.19, 129.03, 127.77, 127.54, 127.40, 127.30, 126.40, 126.30, 123.22, 120.66 (d, $^4J_{CF}$ = 1.7 Hz), 118.77 (q, $^1J_{CF}$ = 321.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −73.11 – −73.13 (m, 3F, CF_3). HRMS (FAB+): $[M]^+$ $C_{15}H_9F_3O_3S$ calculated 326.0225, found 326.0224. FTIR (neat): 3061, 2360, 2324, 1418, 1207, 1136, 977, 855, 827, 755 cm^{-1}.

*6-Methylphenanthren-4-yl Trifluoromethanesulfonate (**5b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 9.17 mmol scale. Triflate **5b** was formed as a white solid (2.33 g, 75% yield). TLC (SiO_2): R_f = 0.29 (1/9, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 8.99 (s, 1H, Ar-H), 7.89 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, Ar-H), 7.83 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.77 (d, $^3J_{HH}$ = 5.6 Hz, 1H, Ar-H), 7.67 (d, $^3J_{HH}$ = 8.8 Hz, 1H, Ar-H), 7.62–7.56 (m, 2H, Ar-H), 7.51 (ddd, J = 8.0, 1.6, 0.6 Hz, 1H, Ar-H), 2.63 (s, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 147.31, 137.35, 135.47, 131.24, 129.36, 129.32, 128.97, 128.78, 127.62, 127.15, 126.12, 125.46, 123.00, 120.52, 118.79 (q, $^1J_{CF}$ = 320.6 Hz). 22.19. ^{19}F NMR (282 MHz, $CDCl_3$): δ −73.34 (d, $^6J_{FH}$ = 1.9 Hz, 3F, CF_3). HRMS (FAB+): $[M]^+$ $C_{16}H_{11}F_3O_3S$ calculated 340.0381, found 340.0376. FTIR (neat): 2911, 2359, 2341, 1419, 1211, 1139, 978, 857 cm^{-1}.

*[1,1′-Biphenyl]-2-yl Trifluoromethanesulfonate (**5c**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 11.8 mmol scale. Triflate **5c** was formed as a white solid (3.36 g, 94% yield). TLC (SiO_2): R_f = 0.43 (1/4, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.50–7.39 (m, 9H, Ar-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 146.94, 135.70, 132.12, 129.51, 129.13, 128.68, 128.63, 128.45, 122.24, 118.47 (q, $^1J_{CF}$ = 320.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.09 – −74.11 (m, 3F, CF_3). HRMS (FAB+): $[M]^+$ $C_{13}H_9F_3O_3S$ calculated 302.0225, found 302.0219. FTIR (neat): 3068, 3035, 2384, 2331, 1477, 1421, 1241, 1207, 1137, 1100, 885, 765, 698 cm^{-1}.

*3′,5′-Dichloro-[1,1′-biphenyl]-2-yl Trifluoromethanesulfonate (**5d**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 5.82 mmol scale. Triflate **5d** was formed as a white solid (2.03 g, 94% yield). TLC (SiO_2): R_f = 0.38 (1/4, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.51–7.40 (m, 5H, Ar-H), 7.39 (d, $^4J_{HH}$ = 1.9 Hz, 2H, Ar-H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 146.39, 138.48, 135.23, 132.92, 131.70, 130.32, 128.94, 128.51, 127.94, 122.51, 118.46 (q, $^1J_{CF}$ = 320.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.00 – −74.03 (m, 3F, CF_3). HRMS (FAB+): $[M]^+$ $C_{13}H_7Cl_2F_3O_3S$ calculated 369.9445, found 369.9448. FTIR (neat): 3073, 2375, 2346, 1580, 1559, 1502, 1423, 1265, 1204, 1136, 1106, 1056, 888, 814, 766 cm^{-1}.

Representative Procedure for the Synthesis of Silyl Thioethers 10a–d. To a flame-dried pressure vessel equipped with a magnetic stir bar was added sodium hydride (1.1 equiv). The flask was capped with a septum and purged with argon. Toluene (0.2 M with respect to **5**) and triisopropylsilanethiol (1.2 equiv) were placed in the flask. The heterogeneous mixture was stirred for 30 min (until the solution became clear and homogeneous, indicating that all the hydride had been quenched). **5** (1.0 equiv) was added as a solution in toluene (0.2 M with respect to **5**). Tetrakis(triphenylphosphine)-palladium(0) (10.0 mol %) was added, the reaction vessel was sealed, and the contents were stirred at 120 °C for 14 h. Upon cooling to ambient temperature, the reaction mixture was filtered through a plug of silica gel with dichloromethane. The crude mixture was concentrated and purified by flash column chromatography (SiO_2, 1/19 dichloromethane/hexanes) to deliver the desired product.

*Triisopropyl(phenanthren-4-ylthio)silane (**10a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 19.4 mmol scale. Silyl thioether **10a** was formed as a clear oil (6.33 g, 89% yield). TLC (SiO_2): R_f = 0.43 (1/20, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 10.77 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, Ar-H), 7.94 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.87 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, Ar-H), 7.77 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.71 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ar-H), 7.67–7.57 (m, 3H, Ar-H), 7.38 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 1.19–1.08 (m, 3H, methine), 0.92 (d, $^3J_{HH}$ = 7.4 Hz, 18H, ^{i}Pr-methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.70, 134.56, 133.44, 131.37, 129.14, 129.04, 128.89, 128.17, 127.75, 127.60, 126.59, 126.59, 125.18, 124.85, 18.36, 13.34. HRMS (FAB+): $[M]^+$ $C_{23}H_{30}SSi$ calculated 366.1838, found 366.1851. FTIR (neat): 2931, 2865, 2360, 2341, 1653, 1559, 1507, 1457, 750 cm^{-1}.

*Triisopropyl((6-methylphenanthren-4-yl)thio)silane (**10b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 6.84 mmol scale. Silyl thioether **10b** was formed as a white solid (2.54 g, >95% yield). TLC (SiO_2): R_f = 0.57 (1/19, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 10.66 (dq, $^4J_{HH}$ = 1.7 Hz, $^9J_{HH}$ = 0.8 Hz, 1H, Ar-H), 7.91 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.77–7.73 (m, 2H, Ar-H), 7.66 (d, $^3J_{HH}$ = 8.6 Hz, 1H, Ar-H), 7.58 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ar-H), 7.43 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.6 Hz, $^7J_{HH}$ = 0.6 Hz, 1H, Ar-H), 7.35 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 2.62 (s, 3H, Ar-methyl), 1.14 (sep, $^3J_{HH}$ = 5.0 Hz, 1H, methine), 0.92 (d, $^3J_{HH}$ = 7.4 Hz, 18H, ^{i}Pr-methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 138.67, 134.77, 134.52, 133.12, 131.46, 131.36, 128.94, 128.91, 128.17, 128.04, 127.57, 126.69, 125.04, 22.36, 18.39, 13.30. HRMS (FAB+): $[M]^+$ $C_{24}H_{32}SSi$ calculated 380.1994, found 380.1982. FTIR (neat): 3045, 2943, 2865, 2360, 2348, 1458, 836 cm^{-1}.

*([1,1′-Biphenyl]-2-ylthio)triisopropylsilane (**10c**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 11.1 mmol scale. Silyl thioether **10c** was formed as a clear oil (3.26 g, 86% yield). TLC (SiO_2): R_f = 0.42 (1/9, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.64 (ddd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, $^5J_{HH}$ = 0.5 Hz, 1H, Ar-H), 7.52–7.48 (m, 2H, Ar-H), 7.44–7.38 (m, 2H, Ar-H), 7.36–7.33 (m, 1H, Ar-H), 7.31–7.28 (m, 2H, Ar-H), 7.20 (ddd, $^3J_{HH}$ = 7.7, 6.8 Hz, $^4J_{HH}$ = 2.1 Hz, 1H, Ar-H), 1.21–1.07 (m, 3H, methine), 0.92 (d, $^3J_{HH}$ = 7.4 Hz, 18H, ^{i}Pr-methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 146.81, 141.98, 137.08, 131.01, 130.41, 130.21, 127.65, 127.28, 127.05, 126.99, 18.35, 13.42. HRMS (FAB+): $[M + H]^+$ $C_{21}H_{31}SSi$ calculated 343.1916, found 343.1916. FTIR (neat): 3044, 2944, 2865, 2360, 2342, 1460, 880, 748, 698 cm^{-1}.

*((3′,5′-Dichloro-[1,1′-biphenyl]-2-yl)thio)triisopropylsilane (**10d**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 5.03 mmol scale. Silyl thioether **10d** was formed as a clear oil (1.58 g, 76% yield). TLC (SiO_2): R_f = 0.71 (1/9, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.64–7.60 (m, 1H, Ar-H), 7.37 (d, $^4J_{HH}$ = 1.9 Hz, 2H, Ar-H), 7.34 (t, $^4J_{HH}$ = 1.9 Hz, 1H, Ar-H), 7.28–7.26 (m, 1H, Ar-H), 7.25–7.21 (m, 2H, Ar-H), 1.17–1.06 (m, 3H, methine), 0.94 (d, $^3J_{HH}$ = 7.4 Hz, 18H, ^{i}Pr-methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 144.77, 143.91, 137.09, 134.12, 130.60, 128.88, 128.30, 127.22, 127.02, 18.36, 13.48. HRMS (FAB+): $[M + H]^+$ $C_{21}H_{29}Cl_2SSi$ calculated

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411.1136, found 411.1131. FTIR (neat): 2945, 2867, 1591, 1556, 1463, 1421, 1391, 1298, 881, 803, 757 cm^{-1}.

Representative Procedure for the Synthesis of Thiols 6a–d. To a round-bottomed flask equipped with a magnetic stir bar were added **10** (1.0 equiv), tetrahydrofuran (0.3 M with respect to **10**), ethanol (0.3 M with respect to **10**), and concentrated HCl (12 M, 4 equiv). The reaction mixture was stirred for 5 h. The crude mixture was concentrated and purified by flash column chromatography (SiO_2, 1/9 dichloromethane/hexanes) to deliver the desired product.

*Phenanthrene-4-thiol (**6a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 17.3 mmol scale. Thiol **6a** was formed as a clear oil (3.74 g, >95% yield). TLC (SiO_2): R_f = 0.43 (1/6, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 9.31 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 7.93 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, Ar-H), 7.78–7.62 (m, 5H, Ar-H), 7.58 (ddd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$= 1.3 Hz, $^5J_{HH}$ = 0.8 Hz, 1H, Ar-H), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 4.17 (s, 1H, SH). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 134.54, 133.29, 130.89, 130.54, 129.76, 128.89, 128.65, 127.87, 127.65, 127.13, 126.91, 126.48, 126.00, 125.71. HRMS (FAB+): $[M]^+$ $C_{14}H_{10}S$ calculated 210.0503, found 210.0499. FTIR (neat): 2917, 2849, 2213, 2030, 823 cm^{-1}.

*6-Methylphenanthrene-4-thiol (**6b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 6.68 mmol scale. Thiol **6b** was formed as a clear oil (1.57 g, >95% yield). TLC (SiO_2): R_f = 0.4 (1/4, toluene:hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 9.07 (s, 1H, Ar-H), 7.81 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.70–7.68 (m, 2H, Ar-H), 7.61 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ar-H), 7.56 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 7.46 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.39–7.34 (m, 1H, Ar-H), 4.15 (s, 1H, SH), 2.67 (s, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 135.54, 134.76, 131.25, 130.67, 129.78, 128.77, 128.51, 128.12, 127.72, 127.68, 127.12, 126.87, 126.72, 125.91, 22.50. HRMS (FAB+): $[M]^+$ $C_{15}H_{12}S$ calculated 224.0660, found 224.0667. FTIR (neat): 3047, 2914, 2567, 1441, 1190, 834, 754 cm^{-1}.

*[1,1′-Biphenyl]-2-thiol (**6c**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 9.50 mmol scale. Thiol **6c** was formed as a clear oil (1.42 g, 80% yield). TLC (SiO_2): R_f = 0.28 (1/9, dichloromethane/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.51–7.46 (m, 2H, Ar-H), 7.46–7.41 (m, 3H, Ar-H), 7.40–7.37 (m, 1H, Ar-H), 7.28–7.25 (m, 1H, Ar-H), 7.25–7.21 (m, 2H, Ar-H), 3.42 (s, 1H, SH). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 140.94, 140.56, 130.91, 130.60, 129.55, 129.24, 128.59, 128.02, 127.79, 125.63. HRMS (FAB+): $[M+H-H_2]^+$ $C_{12}H_9S$ calculated 185.0425, found 185.0425. FTIR (neat): 3056, 3009, 2924, 2881, 2360, 2328, 1465, 747, 700 cm^{-1}.

*3′,5′-Dichloro-[1,1′-biphenyl]-2-thiol (**6d**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 2.88 mmol scale. Thiol **6d** was formed as a clear oil (0.681 g, 93% yield).TLC (SiO_2): R_f = 0.69 (1/2, toluene:hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (t, $^4J_{HH}$ = 1.9 Hz, 1H, Ar-H), 7.38–7.34 (m, 1H, Ar-H), 7.31 (d, $^4J_{HH}$ = 1.9 Hz, 2H, Ar-H), 7.27–7.16 (m, 3H, Ar-H), 3.36 (s, 1H, SH). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 143.63, 137.99, 135.07, 130.67, 130.37, 130.17, 128.93, 127.91, 127.83, 125.98. HRMS (FAB+): $[M]^+$ $C_{12}H_8Cl_2S$ calculated 253.9724, found 253.9712. FTIR (neat): 3066, 2579, 1583, 1556, 1476, 1407, 1121, 1096, 1047, 857, 802, 751, 688 cm^{-1}.

Representative Procedure for the Synthesis of Thioesters 8a–e. This procedure was adapted from Klein et al.[63] To a flame-dried round-bottom flask equipped with a magnetic stir bar under an atmosphere of argon were added **6** (1.0 equiv) and tetrahydrofuran (0.5 M with respect to **6**). The mixture was cooled to 0 °C, and sodium hydride (1.1 equiv) was added. The reaction mixture was stirred for 30 min at 0 °C. **7** (0.55 equiv) was added, and the reaction mixture was stirred at ambient temperature for 5 h and 45 °C for 2 h. The reaction was quenched with aqueous HCl (1 M). The solution was extracted with chloroform (two times). The combined organics were dried ($MgSO_4$) and concentrated. The crude residue was purified by flash column chromatography (SiO_2, chloroform) to deliver the desired product.

*Diethyl 2-((Phenanthren-4-ylthio)carbonothioyl)malonate (**8a**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 17.8 mmol scale. Thioester **8a** was formed as a red-orange oil (6.08 g, 83% yield). TLC (SiO_2): R_f = 0.57 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 9.58–9.53 (m, 1H, Ar-H), 8.04 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.90–7.85 (m, 1H, Ar-H), 7.79–7.72 (m, 3H, Ar-H), 7.65–7.60 (m, 3H, Ar-H), 5.34 (s, 1H, methine), 4.32 (q, ^3J = 7.1 Hz, 4H, methylene), 1.33 (d, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.31 (d, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 219.43, 164.60, 138.67, 134.69, 133.45, 133.03, 131.92, 129.68, 128.65, 128.41, 127.44, 127.41, 126.97, 126.84, 126.66, 126.57, 69.64, 62.65, 14.07. HRMS (FAB+): $[M + H]^+$ $C_{22}H_{21}S_2O_4$ calculated 413.0881, found 413.0881. FTIR (neat): 2987, 2906, 2360, 2342, 1734, 1653, 1559, 1507, 1276, 748 cm^{-1}.

*Diethyl 2-(((6-Methylphenanthren-4-yl)thio)carbonothioyl)-malonate (**8b**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 7.00 mmol scale. Thioester **8b** was formed as a red-orange oil (2.14 g, 72% yield). TLC (SiO_2): R_f = 0.37 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 9.32 (s, 1H, Ar-H), 8.03 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.78 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.76–7.72 (m, 2H, Ar-H), 7.68 (d, $^3J_{HH}$ = 8.8 Hz, 1H, Ar-H), 7.63–7.58 (m, 1H, Ar-H), 7.45 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 5.30 (s, 1H, methine), 4.28 (q, $^3J_{HH}$ = 7.2 Hz, 4H, methylene), 2.60 (s, 3H), 1.30 (d, $^3J_{HH}$ = 7.1 Hz, 3H, methyl) 1.28 (d, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 219.83, 164.63, 138.48, 136.58, 134.92, 133.02, 131.73, 131.45, 129.84, 129.19, 128.56, 128.29, 127.12, 126.56, 126.54, 126.52, 69.70, 62.63, 22.28, 14.08. HRMS (FAB+): $[M + H]^+$ $C_{23}H_{23}S_2O_4$ calculated 427.1038, found 427.1047. FTIR (neat): 2981, 2919, 2360, 2336, 1734, 1289, 1234, 1162, 1031, 838 cm^{-1}.

*Diethyl 2-(([1,1′-Biphenyl]-2-ylthio)carbonothioyl)malonate (**8c**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 7.60 mmol scale. Thioester **8c** was formed as a red-orange oil (2.42 g, 82% yield). TLC (SiO_2): R_f = 0.34 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (ddd, $^3J_{HH}$ = 7.7, 7.0 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, Ar-H), 7.54–7.44 (m, 3H, Ar-H), 7.38–7.34 (m, 3H, Ar-H), 7.31–7.29 (m, 2H, Ar-H), 5.11 (s, 1H, methine), 4.21 (q, $^3J_{HH}$ = 7.1 Hz, 4H, methylene), 1.25 (t, $^3J_{HH}$ = 7.1 Hz, 6H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 220.41, 164.35, 146.73, 139.77, 136.85, 131.35, 131.29, 128.87, 128.81, 128.75, 127.92, 127.86, 69.39, 62.49, 13.97. HRMS (FAB+): $[M + H]^+$ $C_{20}H_{21}O_4S_2$ calculated 389.0881, found 389.0870. FTIR (neat): 2981, 1738, 1465, 1300, 1221, 1145, 1018, 753 cm^{-1}.

*Diethyl 2-(((3′,5′-Dichloro-[1,1′-biphenyl]-2-yl)thio)-carbonothioyl)malonate (**8d**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 2.00 mmol scale. Thioester **8d** was formed as a red-orange oil (0.699 g, 74% yield). TLC (SiO_2): R_f = 0.53 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 7.61–7.55 (m, 1H, Ar-H), 7.52–7.48 (m, 2H, Ar-H), 7.44–7.40 (m, 1H, Ar-H), 7.35 (t, $^4J_{HH}$ = 1.9 Hz, 1H), 7.16 (d, $^4J_{HH}$ = 1.9 Hz, 2H), 5.11 (s, 1H, methine), 4.22 (q, $^3J_{HH}$ = 7.1 Hz, 4H, methylene), 1.26 (d, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.25 (d, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 219.68, 164.24, 144.21, 142.56, 136.96, 134.41, 131.54, 131.05, 129.80, 128.82, 127.99, 127.41, 69.51, 62.65, 14.00. HRMS (FAB+): $[M + H]^+$ $C_{20}H_{19}Cl_2O_4S_2$ calculated 457.0102, found 457.0100. FTIR (neat): 2982, 2914, 2360, 2342, 1734, 1653, 1558, 1276, 758 cm^{-1}.

*Diethyl 2-((Naphthalen-1-ylthio)carbonothioyl)malonate (**8e**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 2.88 mmol scale. Thioester **8e** was formed as a red-orange oil (0.854 g, 82% yield). TLC (SiO_2): R_f = 0.47 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 8.18–8.13 (m, 1H, Ar-H), 8.03 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar-H), 7.96–7.89 (m, 1H, Ar-H), 7.73 (dd, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Ar-H), 7.59–7.52 (m, 3H, Ar-H), 5.28 (s, 1H, methine), 4.34–4.28 (m, 4H, methylene), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 6H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 220.19, 164.71, 135.12, 134.32, 133.33, 132.34, 132.31, 128.97, 127.91, 126.91, 125.91, 124.94, 69.75, 62.67, 14.07. HRMS (FAB+): $[M + H]^+$ $C_{18}H_{19}O_4S_2$ calculated 363.0725, found

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363.0732. FTIR (neat): 2981, 2942, 1735, 1367, 1301, 1236, 1145, 1030, 799, 771 cm^{-1}.

Representative Procedures for the Synthesis of Dithiomalonates 9a–e. *Method 1.* This procedure was adapted from Klein et al.[63] To a flame-dried round-bottom flask equipped with a magnetic stir bar under an atmosphere of argon was added H_2SO_4 (60.0 equiv). The mixture was cooled to 0 °C, and **8** (1.0 equiv) was added. The reaction mixture was stirred for 10 min at 0 °C and 4 h at ambient temperature. The reaction was quenched with ice and brine, and the contents were stirred for 30 min. The solution was extracted with chloroform (two times). The combined organics were dried ($MgSO_4$) and concentrated. The crude residue was purified by flash column chromatography (SiO_2, chloroform) to deliver the desired product.

Method 2. This procedure was adapted from Huang et al.[64] To a flame-dried pressure vessel equipped with a magnetic stir bar were added **8** (1.0 equiv), 1,4-benzoquinone (1.1 equiv), *p*-toluenesulfonic acid monohydrate (10 mol %), and palladium(II) acetate (5 mol %). The vessel was purged with argon, and acetic acid (0.67 M with respect to **8**) and toluene (0.67 M with respect to **8**) were added. The reaction vessel was sealed, and the contents were stirred at 120 °C for 4 h. Upon cooling to ambient temperature, the crude mixture was concentrated and purified by flash column chromatography (SiO_2, chloroform) to deliver the desired product.

*Diethyl 2-(Phenanthro[3,4-d][1,3]dithiol-2-ylidene)malonate (**9a**).* This compound was synthesized according to method 2; the reaction was conducted on a 14.2 mmol scale. Dithiomalonate **9a** was formed as a white solid (2.24 g, 38% yield). TLC (SiO_2): R_f = 0.65 (1/2, ethyl acetate:hexanes). ^1H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 7.94 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.85–7.71 (m, 5H, Ar-H), 7.67 (ddd, $^3J_{HH}$ = 8.0, 7.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 4.42 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 4.38 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 1.45 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.41 (q, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 173.82, 166.35, 165.93, 163.30, 137.47, 133.37, 132.53, 132.00, 129.17, 128.98, 128.35, 128.17, 127.39, 127.30, 127.16, 126.84, 119.87, 103.93, 61.32, 61.25, 14.47. HRMS (FAB+): $[M]^+$ $C_{22}H_{18}S_2O_4$ calculated 410.0647, found 410.0666. FTIR (neat): 2983, 2911, 2360, 2341, 1734, 1419, 1275 cm^{-1}.

*Diethyl 2-(10-Methylphenanthro[3,4-d][1,3]dithiol-2-ylidene)malonate (**9b**).* This compound was synthesized according to method 2; the reaction was conducted on a 5.04 mmol scale. Dithiomalonate **9b** was formed as a white solid (0.657 g, 31% yield). TLC (SiO_2): R_f = 0.35 (chloroform). ^1H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H, Ar-H), 7.90–7.82 (m, 2H, Ar-H), 7.82–7.75 (m, 2H, Ar-H), 7.70 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ar-H), 7.52 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar-H), 4.43 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 4.38 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 2.73 (s, 3H, Ar-methyl), 1.46 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.41 (t, $^3J_{HH}$ = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 173.47, 166.44, 165.69, 163.34, 137.24, 132.40, 132.20, 131.39, 129.05, 128.92, 128.35, 128.00, 126.78, 126.59, 126.41, 122.56, 119.82, 104.00, 61.36, 61.23, 22.75, 14.57, 14.48. HRMS (FAB+): $[M]^+$ $C_{23}H_{20}S_2O_4$ calculated 424.0803, found 424.0807. FTIR (neat): 2981, 2924, 2361, 2341, 1726, 1671, 1517, 1419, 1393, 1368, 1273, 1230, 1191, 1173, 1093, 1032, 839 cm^{-1}.

*Diethyl 2-(4-Phenylbenzo[d][1,3]dithiol-2-ylidene)malonate (**9c**).* This compound was synthesized according to method 1; the reaction was conducted on a 6.23 mmol scale. Dithiomalonate **9c** was formed as a white solid (1.06 g, 44% yield). TLC (SiO_2): R_f = 0.43 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, Ar-H), 7.57–7.53 (m, 2H, Ar-H), 7.48 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Ar-H), 7.45–7.41 (m, 1H, Ar-H), 7.40 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-H), 7.28 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, Ar-H), 4.34 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 4.28 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 1.37 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 173.85, 166.14, 165.89, 139.60, 138.03, 137.88, 136.17, 129.12, 128.65, 128.36, 127.37, 127.02, 120.87, 104.63, 61.28, 61.18, 14.40, 14.34. HRMS (FAB+): $[M + H]^+$ $C_{20}H_{19}O_4S_2$ calculated 387.0725, found 387.0735. FTIR (neat): 2980, 2927, 1702, 1653, 1425, 1397, 1265, 1034, 757 cm^{-1}.

*Diethyl 2-(4-(3,5-Dichlorophenyl)benzo[d][1,3]dithiol-2-ylidene)-malonate (**9d**).* This compound was synthesized according to method 1; the reaction was conducted on a 1.48 mmol scale. Dithiomalonate **9d** was formed as a white solid (0.555 g, 82% yield). TLC (SiO_2): R_f = 0.46 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 7.44–7.37 (m, 4H, Ar-H), 7.21 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 4.33 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 4.30 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene), 1.36 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 172.78, 166.01, 165.66, 142.35, 138.42, 135.97, 135.71, 134.96, 128.82, 127.28, 127.08, 126.96, 121.85, 105.28, 61.40, 61.37, 14.39, 14.34. HRMS (FAB+): $[M + H]^+$ $C_{20}H_{17}Cl_2O_4S_2$ calculated 454.9945, found 454.9963. FTIR (neat): 2977, 2372, 2358, 1739, 1671, 1648, 1435, 1416, 1284, 1041, 779 cm^{-1}.

*Diethyl 2-(Naphtho[1,2-d][1,3]dithiol-2-ylidene)malonate (**9e**).* This compound was synthesized according to method 1; the reaction was conducted on a 2.35 mmol scale. Dithiomalonate **9e** was formed as a white solid (0.302 g, 36% yield). TLC (SiO_2): R_f = 0.48 (chloroform). ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 7.90 (d, $^3J_{HH}$ = 8.2 Hz, 1H, Ar-H), 7.79 (d, $^3J_{HH}$ = 8.6 Hz, 1H, Ar-H), 7.64 (d, $^3J_{HH}$ = 8.7 Hz, 1H, Ar-H), 7.60 (ddd, $^3J_{HH}$ = 8.3, 6.9 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.54 (ddd, $^3J_{HH}$ = 8.1, 7.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, Ar-H), 4.38 (q, $^3J_{HH}$ = 7.2 Hz, 2H, methylene), 4.36 (q, $^3J_{HH}$ = 7.1 Hz, 2H, methylene) 1.40 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl), 1.39 (t, $^3J_{HH}$ = 7.1 Hz, 3H, methyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 174.44, 166.19, 134.82, 133.28, 131.52, 128.98, 128.15, 127.96, 127.61, 126.59, 124.30, 119.13, 104.37, 61.29, 14.45, 14.44. HRMS (FAB+): $[M]^+$ $C_{18}H_{16}O_4S_2$ calculated 360.0490, found 360.0482. FTIR (neat): 3047, 2982, 2931, 1669, 1647, 1420, 1287, 1034, 798, 782 cm^{-1}.

Representative Procedures for the Synthesis of Zinc Dithiolates Zn-II–Zn-VI. This procedure was adapted from Hoveyda et al.[54] To a pressure vessel equipped with a magnetic stir bar were added **9** (1.0 equiv), zinc(II) acetate dihydrate (4.0 equiv), and isopropyl alcohol (0.13 M with respect to **9**). The reaction mixture was put under an argon atmosphere, and ethylenediamine (6.0 equiv) was added. The vessel was sealed and heated at 120 °C for 5 days. Upon cooling to ambient temperature, the solid precipitate was isolated by filtration. The solid was washed with methanol and chloroform to deliver the desired product.

*Zinc Naphthalene-1,2-dithiolate (**Zn-II**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.83 mmol scale. Zinc dithiolate **Zn-II** was formed as a white powder (0.172 g, 66% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 8.50 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 7.59 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar-H), 7.54 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 7.33–7.29 (m, 1H, Ar-H), 7.15 (dd, $^3J_{HH}$ = 8.1, 6.7 Hz, 1H, Ar-H), 7.11 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 4.07 (s, 4H, $2NH_2$), 2.69 (s, 4H, alkyl backbone). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 142.65, 140.60, 134.52, 130.39, 130.10, 127.56, 127.52, 124.46, 121.95, 119.60, 40.51. HRMS (FAB+): $[M]^+$ $C_{12}H_{14}N_2S_2Zn$ calculated 313.9890, found 313.9916. FTIR (neat): 3308, 3191, 2936, 2889, 1569, 1322, 1294, 1109, 1030, 1012, 853, 810, 767, 736 cm^{-1}.

*Zinc [1,1′-Biphenyl]-2,3-dithiolate (**Zn-III**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 2.74 mmol scale. Zinc dithiolate **Zn-III** was formed as a white powder (0.580 g, 62% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 7.39–7.36 (m, 3H, Ar-H), 7.29 (t, $^3J_{HH}$ = 8.3, 6.7 Hz, 2H, Ar-H), 7.24–7.16 (m, 1H, Ar-H), 6.59 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 6.51 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-H), 3.94 (s,4H, $2NH_2$), 2.62 (s, 4H, alkyl backbone). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 147.03, 145.86, 144.26, 141.97, 129.38, 129.23, 127.05, 125.62, 122.78, 119.74, 40.47. HRMS (FAB+): $[M]^+$ $C_{14}H_{16}N_2S_2Zn$ calculated 340.0046, found 340.0061. FTIR (neat): 3302, 3235, 3127, 2953, 2896, 1475, 1493, 1428, 1372, 1231, 1180, 1134, 1018, 790, 761, 731, 698 cm^{-1}.

*Zinc 3′,5′-Dichloro-[1,1′-biphenyl]-2,3-dithiolate (**Zn-IV**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.44 mmol scale. Zinc dithiolate **Zn-IV** was formed as a white powder (0.115 g, 64% yield). ^1H NMR (400

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MHz, DMSO-d_6): δ 7.45 (t, $^4J_{HH}$ = 1.9 Hz, 1H, Ar-H), 7.40 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.37 (d, $^4J_{HH}$ = 1.9 Hz, 2H, Ar-H), 6.62 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 6.55 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-H), 3.98 (s, 4H, 2NH$_2$), 2.63 (s, 4H, alkyl backbone). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 149.09, 147.60, 144.08, 139.02, 132.72, 130.06, 128.21, 125.26, 122.40, 120.02, 40.44. HRMS (FAB+): [M]$^+$ $C_{14}H_{14}Cl_2N_2S_2Zn$ calculated 407.9267, found 407.9269. FTIR (neat): 3498, 3293, 3227, 3196, 3106, 2981, 1594, 1561, 1414, 1368, 1281, 1094, 1030, 855, 783, 771, 693, 660 cm^{-1}.

*Zinc Phenanthrene-3,4-dithiolate (**Zn-V**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 5.46 mmol scale. Zinc dithiolate **Zn-V** was formed as a white powder (0.759 g, 38% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.15 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-H), 7.77 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Ar-H), 7.61−7.31 (m, 4H, Ar-H), 7.16 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar-H), 4.10 (s, 4H, 2NH$_2$), 2.72 (s, 4H, alkyl backbone). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 147.45, 141.87, 133.09, 131.92, 131.05, 129.82, 129.57, 128.65, 127.86, 127.16, 124.95, 123.91, 122.71, 120.77, 40.52. HRMS (FAB+): [M]$^+$ $C_{16}H_{16}N_2S_2Zn$ calculated 364.0046, found 364.0039. FTIR (neat): 3318, 3241, 3191, 3120, 3062, 2947, 1570, 1442, 1281, 1189, 1165, 1129, 1030, 838, 794, 748 cm^{-1}.

*Zinc 6-Methylphenanthrene-3,4-dithiolate (**Zn-VI**).* This compound was synthesized according to the representative procedure; the reaction was conducted on a 1.56 mmol scale. Zinc dithiolate **Zn-VI** was formed as a white powder (0.365 g, 62% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.04 (s, 1H, Ar-H), 7.74 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.67 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 7.43 (s, 2H, Ar-H), 7.30 (dd, $^3J_{HH}$ = 8.0, 4.0 Hz, 1H, Ar-H), 7.13 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar-H), 4.10 (s, 4H, 2NH$_2$), 2.71 (s, 4H, alkyl backbone), 2.49 (s, 3H, Ar-methyl). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 147.17, 141.89, 132.02, 131.61, 131.08, 130.89, 129.78, 128.54, 127.08, 126.97, 126.43, 123.79, 120.79, 40.47, 22.07. HRMS (FAB+): [M]$^+$ $C_{17}H_{18}N_2S_2Zn$ calculated 378.0203, found 378.0201. FTIR (neat): 3328, 3221, 2952, 1594, 1525, 1378, 1300, 1190, 1047, 843 cm^{-1}.

Representative Procedures for the Synthesis of Ruthenium Dithiolates II−VII. This procedure was adapted from Hoveyda et al.[54] In a nitrogen-filled glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with GH-II (1.0 equiv), **Zn-xx** (2.0 equiv), and tetrahydrofuran (0.08 M with respect to GH-II). The reaction mixture was stirred for 5 h at ambient temperature. The reaction mixture was concentrated, dissolved in dichloromethane, filtered through a Celite plug, and concentrated to deliver the desired product.

*Ruthenium Catalyst **II**.* This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.0253 mmol scale. Ruthenium catalyst **II** was formed as a brown solid (18 mg, 95% yield) and a mixture of isomers. ^{1}H NMR (400 MHz, THF-d_8): δ 14.21 (s, 0.5H, *down*-benzylidene H), 14.11 (s, 0.5H, *up*-benzylidene, H), 8.81 (d, $^3J_{HH}$ = 8.3 Hz, 0.5H, Ar-H), 8.32 (d, $^3J_{HH}$ = 8.3 Hz, 0.5H, Ar-H), 7.59 (d, $^3J_{HH}$ = 8.0 Hz, 0.5H, Ar-H), 7.54 (d, $^3J_{HH}$ = 8.1 Hz, 0.5H, Ar-H), 7.50 (d, $^3J_{HH}$ = 8.5 Hz, 0.5H, Ar-H), 7.32 (d, $^3J_{HH}$ = 8.3 Hz, 0.5H, Ar-H), 7.28−7.21 (m, 1H, Ar-H), 7.21−7.11 (m, 3H, Ar-H), 7.06 (d, $^3J_{HH}$ = 8.3 Hz, 0.5H, Ar-H), 7.04−7.01 (m, 0.5H, Ar-H), 6.93 (s, 2H, Ar-H), 6.76 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.59−6.56 (m, 1H, Ar-H), 6.35 (s, 2H, Ar-H), 5.34 (hept, $^3J_{HH}$ = 6.6 Hz, 0.5H, *down*-methine), 5.26 (hept, $^3J_{HH}$ = 6.5 Hz, 0.5H, *up*-methine), 3.92 (s, 4H, NHC-methylenes), 2.54 (s(br), 8H, Ar-methyl), 2.22−2.08 (m, 8H, Ar-methyl), 1.66 (dd, J = 22.9 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, ^{i}Pr-methyl), 1.50 (dd, J = 24.6 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, ^{i}Pr-methyl). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ 249.38, 248.47, 220.63, 220.37, 155.67, 152.30, 150.00, 143.07, 139.82, 138.64, 137.68, 137.32, 136.48, 134.71, 131.57, 131.48, 130.57, 130.03, 129.21, 129.07, 128.95, 128.50, 128.31, 128.02, 127.45, 127.36, 125.32, 125.10, 125.07, 124.89, 124.83, 124.78, 123.63, 122.84, 122.75, 122.04, 120.73, 116.27, 116.20, 81.63, 81.57, 52.25, 24.32, 24.20, 22.11, 22.06, 21.22, 19.81, 18.09. HRMS (FAB+): [M]$^+$ $C_{41}H_{44}N_2OS_2Ru$ calculated 746.1939, found 746.1932.

*Ruthenium Catalyst **III**.* This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.29 mmol scale. Ruthenium catalyst **III** was formed as a brown solid (180 mg, 80% yield) and mixture of isomers. ^{1}H NMR (400 MHz, THF-d_8): δ 14.10 (s, 0.35H, *down*-benzylidene H), 14.05 (s, 0.65H, *up*-benzylidene H), 7.79−7.68 (m, 1H, Ar-H), 7.45−7.34 (m, 2H, Ar-H), 7.32−7.03 (m, 5H, Ar-H), 6.91 (s(br), 2H, Ar-H), 6.76 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar-H), 6.74−6.69 (m, 1H, Ar-H), 6.65 (d, $^3J_{HH}$ = 4.5 Hz, 1H, Ar-H), 6.61−6.57 (m, 1H, Ar-H), 6.57−6.52 (m, 1H, Ar-H), 6.19 (s, 1H, Ar-H), 5.26 (hept, $^3J_{HH}$ = 6.6 Hz, 0.35H, *down*−methine), 5.15 (hept, J = 6.6 Hz, 0.65H, *up*-methine), 3.97−3.69 (m, 4H, NHC-methylenes), 2.51 (s, 3H, Ar-methyl), 2.45−2.33 (m, 5H, Ar-methyl), 2.25−2.17 (m, 7H, Ar-methyl), 2.11 (s, 3H, Ar-methyl), 1.62 (d, $^3J_{HH}$ = 6.6 Hz, 1H, ^{i}Pr-methyl), 1.57 (d, $^3J_{HH}$ = 6.5 Hz, 2H, ^{i}Pr-methyl), 1.45 (t, $^3J_{HH}$ = 6.5 Hz, 2H, ^{i}Pr-methyl), 1.31 (d, $^3J_{HH}$ = 6.5 Hz, 1H, ^{i}Pr-methyl). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ 248.29, 246.95, 220.61, 220.44, 156.21, 155.68, 155.36, 151.95, 145.07, 144.97, 144.04, 143.04, 142.99, 141.14, 140.86, 140.39, 139.27, 139.08, 137.87, 137.75, 136.90, 136.34, 131.11, 130.82, 130.28, 129.84, 128.34, 128.04, 127.71, 127.30, 127.21, 126.99, 126.65, 126.49, 125.07, 124.77, 123.31, 122.82, 122.77, 122.53, 122.13, 120.78, 116.52, 115.96, 82.06, 80.74, 52.15, 26.02, 24.46, 23.92, 22.29, 21.60, 21.28, 19.98, 19.38, 17.95. HRMS (FAB+): [M]$^+$ $C_{43}H_{46}N_2OS_2Ru$ calculated 772.2096, found 772.2080.

*Ruthenium Catalyst **IV**.* This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.0253 mmol scale. Ruthenium catalyst **IV** was formed as a brown solid (19 mg, 88% yield) and mixture of isomers. ^{1}H NMR (500 MHz, THF-d_8): δ 14.21 (s, 0.33H, *down*-benzylidene H), 14.07 (s, 0.67H, *up*-benzylidene H), 7.75 (d, $^3J_{HH}$ = 2.0 Hz, 1H, Ar-H), 7.46−7.42 (m, 1H, Ar-H), 7.38 (t, $^3J_{HH}$ = 2.0 Hz, 1H, Ar-H), 7.30−7.23 (m, 1.67H, Ar-H), 7.23−7.20 (m, 0.33H, Ar-H), 7.18−7.15 (m, 1H, Ar-H), 6.94 (s(br), 2H, Ar-H), 6.82−6.72 (m, 1.67H, Ar-H), 6.71−6.65 (m, 1H, Ar-H), 6.64−6.60 (m, 1H, Ar-H), 6.56 (dd, $^3J_{HH}$ = 7.5, 1.6 Hz, 0.33H, Ar-H), 6.21 (s, 1H, Ar-H), 5.30 (hept, $^3J_{HH}$ = 6.5 Hz, 0.33H, *down*-methine), 5.14 (hept, $^3J_{HH}$ = 6.5 Hz, 0.67H, *up*-methine), 4.08−3.69 (m, 4H, NHC-methylenes), 2.76 (s, 1H, Ar-methyl), 2.52 (s, 2H, Ar-methyl), 2.50−2.40 (m, 5H, Ar-methyl), 2.23 (s, 5H, Ar-methyl), 2.18 (s, 2H, Ar-methyl), 2.12 (s, 2H, Ar-methyl), 1.83−1.75 (m, 1H, Ar-methyl), 1.69 (d, $^3J_{HH}$ = 6.7 Hz, 1H, ^{i}Pr-methyl), 1.59 (d, $^3J_{HH}$ = 6.5 Hz, 2H, ^{i}Pr-methyl), 1.45 (d, $^3J_{HH}$ = 6.5 Hz, 2H, ^{i}Pr-methyl), 1.35 (d, $^3J_{HH}$ = 6.5 Hz, 1H, ^{i}Pr-methyl). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8): δ 249.55, 248.67, 219.92, 157.08, 155.76, 155.35, 152.03, 148.27, 144.83, 142.95, 140.38, 139.09, 138.16, 137.84, 137.35, 137.01, 136.32, 134.61, 134.24, 130.91, 130.37, 129.93, 129.70, 129.49, 129.38, 129.17, 128.27, 127.58, 127.29, 126.62, 126.41, 125.15, 124.83, 123.20, 122.93, 122.36, 122.03, 121.05, 116.84, 116.07, 82.69, 81.20, 52.23, 41.75, 24.00, 22.24, 21.62, 21.27, 20.02, 19.83, 19.41, 17.92. HRMS (FAB+): [(M]$^+$ $C_{43}H_{44}Cl_2N_2OS_2Ru$ calculated 840.1316, found 840.1349.

*Ruthenium Catalyst **V**.* This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.68 mmol scale. Ruthenium catalyst **V** was formed as a brown solid (502 mg, 92% yield) and mixture of isomers. H NMR (400 MHz, $CDCl_3$): δ 14.05 (s, 0.28H, *down*-benzylidene H), 13.97 (s, 0.72H, *up*-benzylidene H), 11.72 (d, $^3J_{HH}$ = 8.6 Hz, 0.75H, Ar-H), 10.87−10.78 (m, 0.29H, Ar-H), 7.83 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 0.83H, Ar-H), 7.71 (d, $^3J_{HH}$ = 8.2 Hz, 0.26H, Ar-H), 7.69−7.66 (m, 0.27H, Ar-H), 7.64−7.60 (m, 1H, Ar-H), 7.59 (d, $^3J_{HH}$ = 6.0 Hz, 0.85H, Ar-H), 7.56−7.49 (m, 2H, Ar-H), 7.38 (d, $^3J_{HH}$ = 8.6 Hz, 0.28H, Ar-H), 7.34−7.18 (m, 4H, Ar-H), 7.16 (d, $^3J_{HH}$ = 8.4 Hz, 0.83H, Ar-H), 7.06−6.89 (m, 2H, Ar-H), 6.82−6.71 (m, 1H, Ar-H), 6.59 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.7 Hz, 0.72H, Ar-H), 6.55 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.6 Hz, 0.28H, Ar-H), 6.25 (s, 1H, Ar-H), 5.43 (hept, $^3J_{HH}$ = 6.6 Hz, 0.3H, *down*-methine), 5.19 (hept, $^3J_{HH}$ = 6.5 Hz, 0.83H, *up*-methine), 4.07−3.85 (m, 4H, NHC-methylenes), 2.94 (s, 2H, Ar-methyl), 2.73−2.34 (m, 4H, Ar-methyl), 2.14 (d, J = 57.4 Hz, 10H, Ar-methyl), 1.77 (d, $^3J_{HH}$ = 6.5 Hz, 1H, Ar-methyl), 1.62−1.59 (m, 4H, Ar-methyl, ^{i}Pr-methyl), 1.47 (d, $^3J_{HH}$ = 6.4 Hz, 3H, ^{i}Pr-methyl). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 248.94, 248.61, 220.27, 220.06, 157.07, 155.71, 155.52, 151.58, 143.90, 143.01, 142.96, 139.15, 138.67, 137.85, 137.30, 136.99, 136.52, 134.51, 134.38, 133.40, 132.58, 131.44, 131.20, 131.07, 130.63, 130.56, 130.27, 130.00, 129.56, 129.19, 128.98, 128.95, 128.48, 128.29, 128.15, 128.11, 127.54, 127.46, 125.46, 125.37, 125.33, 125.14, 125.00, 124.32, 124.18, 124.08, 123.48, 122.90, 122.81, 122.39, 116.31, 116.05, 81.67, 80.92, 52.29, 52.24, 24.35, 24.09, 22.26, 22.17, 21.25,

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21.20, 19.84, 18.04. HRMS (FAB+): $[M]^+$ $C_{45}H_{46}N_2OS_2Ru$ calculated 796.2096, found 796.2104.

Ruthenium Catalyst ***VI.*** This compound was synthesized according to the representative procedure; the reaction was conducted on a 0.053 mmol scale. Ruthenium catalyst **VI** was formed as a brown solid (39 mg, 91% yield) and mixture of isomers. ^{1}H NMR (400 MHz, THF-d_8): δ 14.04 (s, 0.4H, *down*-benzylidene H), 13.99 (s, 0.6H, *up*-benzylidene H), 11.57 (s, 0.6H, Ar-H), 10.74 (s, 0.4H, Ar-H), 7.73 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.6 Hz, 0.6H, Ar-H), 7.68 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.7 Hz, 0.4H, Ar-H), 7.57 (d, $^3J_{HH}$ = 8.0 Hz, 0.4H, Ar-H), 7.53 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.48 (d, $^3J_{HH}$ = 8.5 Hz, 0.6H, Ar-H), 7.35 (d, $^3J_{HH}$ = 16.0 Hz, 0.6H, Ar-H), 7.33 (d, J = 20.0 Hz, 0.4H, Ar-H), 7.28−7.20 (m, 2H, Ar-H), 7.19−7.16 (m, 2H, Ar-H), 7.04−6.84 (m, 2H, Ar-H), 6.77−6.72 (m, 1H, Ar-H), 6.58−6.50 (m, 1H, Ar-H), 6.43 (s, 1.4H, Ar-H), 6.15 (s, 0.6H, Ar-H), 5.49−5.40 (m, 0.4H, *up*-methine), 5.40−5.29 (m, 0.6H, *down*-methine), 4.06 (s, 1.6H, NHC-methylenes), 3.98−3.78 (s, 2.4H, NHC-methylenes), 2.87 (s, 2H, Ar-H), 2.73 (s, 2H, Ar-H), 2.66−2.39 (m, 5H, Ar-H), 2.29−2.04 (m, 9H, Ar-H), 1.84−1.46 (m, 9H, methyl). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ 248.22, 247.39, 220.38, 220.01, 156.65, 155.51, 155.47, 151.73, 143.44, 143.02, 142.99, 139.11, 138.99, 138.57, 138.04, 137.70, 137.28, 136.92, 136.37, 136.04, 133.55, 133.49, 133.26, 132.57, 132.47, 132.36, 131.33, 131.28, 130.82, 130.72, 130.55, 130.36, 130.19, 130.04, 129.65, 129.15, 128.77, 128.23, 128.03, 127.99, 127.60, 127.40, 127.35, 127.05, 126.94, 125.14, 125.04, 124.98, 124.04, 123.54, 122.82, 122.26, 116.35, 116.26, 81.67, 81.33, 52.36, 52.23, 52.15, 24.28, 24.18, 22.89, 22.50, 22.18, 21.24, 21.18, 20.14, 19.80, 17.94. HRMS (FAB+): $[M]^+$ $C_{46}H_{48}N_2OS_2Ru$ calculated 810.2252, found 810.2240.

Ruthenium Catalyst ***VII.*** This compound was synthesized according to the representative procedure; but using **711**, the reaction was conducted on a 0.03 mmol scale. Ruthenium catalyst **VII** was formed as a brown solid (25 mg, 95% yield) and mixture of isomers. ^{1}H NMR (400 MHz, THF-d_8): δ 14.38−13.94 (m, 1H, benzylidene H), 11.71 (d, $^3J_{HH}$ = 8.6 Hz, 0.47H, Ar-H), 10.78 (d, $^3J_{HH}$ = 8.4 Hz, 0.53H, Ar-H), 7.86 (d, $^3J_{HH}$ = 7.8 Hz, 0.47H, Ar-H), 7.81 (d, $^3J_{HH}$ = 8.2 Hz, 0.53H, Ar-H), 7.74−7.43 (m, 4H, Ar-H), 7.42−7.18 (m, 7H, Ar-H), 7.17−6.99 (m, 2H, Ar-H), 6.80−6.69 (m, 2H, Ar-H), 6.55−6.45 (m, 0.53H, Ar-H), 6.45−6.35 (m, 0.47H, Ar-H), 5.07 (hept, $^3J_{HH}$ = 5.8 Hz, 1H, ^{i}PrO-methine), 4.60−4.47 (m, 1H), 4.42−4.29 (m, 1H), 4.23−3.81 (m, 3H), 3.61−3.60 (m, 1H), 3.18 (td, J = 14.8, 13.6, 7.9 Hz, 1H, Ar-methine), 2.80−2.52 (m, 1H, Ar-methine), 1.96 (d, J = 6.4 Hz, 2H, methyl), 1.60 (d, J = 5.8 Hz, 2H, methyl), 1.55−1.23 (m, 11H, methyl), 1.17 (t, J = 5.9 Hz, 3H, methyl), 0.97 (t, J = 6.2 Hz, 6H, methyl), 0.48 (dd, J = 20.5, 5.6 Hz, 3H, methyl), 0.07 (d, J = 6.9 Hz, 3H, methyl). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ 256.21, 254.70, 222.56, 222.03, 156.46, 156.07, 150.82, 150.21, 149.28, 147.61, 146.22, 144.52, 142.75, 140.09, 139.48, 137.31, 134.40, 133.17, 132.38, 131.50, 131.11, 130.97, 130.59, 130.00, 129.17, 129.05, 128.94, 128.84, 128.70, 128.53, 128.03, 127.68, 126.40, 126.22, 126.07, 125.99, 125.84, 125.46, 125.34, 125.28, 125.08, 124.67, 124.19, 124.00, 123.60, 122.90, 122.33, 115.45, 115.40, 76.51, 76.41, 55.30, 54.89, 30.83, 30.48, 29.70, 29.47, 29.29, 27.55, 27.28, 27.10, 26.91, 24.49, 24.31, 24.11, 23.77, 22.46, 22.35, 21.15, 21.10, 20.88, 20.53. HRMS (FAB+): $[M]^+$ $C_{51}H_{58}N_2OS_2Ru$ calculated 880.3035, found 880.3024.

Representative Procedure for Catalyst Initiation Studies. In a nitrogen-filled glovebox, an oven-dried NMR tube was charged with ruthenium catalyst (0.00648 mmol) and tetrahydrofuran-d_8 (0.0108 M with respect to ruthenium catalyst). The NMR tube was capped with a septum and removed from the glovebox. The sample was used to set up the NMR probe. Phenyl vinyl ether was placed in the NMR tube, and data points were collected over the appropriate period of time using the Varian array function. The disappearance of the benzylidene peaks was measured on the basis of integrations normalized to the respective peaks starting at time 0 s and every 30 s thereafter.

Representative Procedure for Self-Metathesis of (*Z*)-Methyl 9-Octadecenoate. In a nitrogen-filled glovebox, an oven-dried vial equipped with a magnetic stir bar was charged with ruthenium catalyst (0.00119 mmol, 0.5 mol %) and tetrahydrofuran (567 μL, 0.42 M with respect to (*Z*)-methyl 9-octadecenoate). (*Z*)-Methyl 9-octadecenoate (*Z*-**MO**; 0.238 mmol, 80.7 μL, 1.0 equiv) and tetradecane (0.238 mmol, 61.8 μL, 1.0 equiv) were added to the catalyst solution, and the vial was capped. At the specified time points, 20 μL aliquots were taken out and quenched with ethyl vinyl ether, and the product distribution was analyzed using gas chromatography.

Representative Procedure for Self-Metathesis of (*E*)-Methyl 9-Octadecenoate. In a nitrogen-filled glovebox, an oven-dried vial equipped with a stir bar was charged with ruthenium catalyst (0.00378 mmol, 3.0 mol %) and tetrahydrofuran (300 μL, 0.42 M with respect to (*E*)-methyl 9-octadecenoate). (*E*)-Methyl 9-octadecenoate (*E*-**MO**; 0.126 mmol, 42.5 μL, 1.0 equiv) and tetradecane (0.126 mmol, 33.0 μL, 1.0 equiv) were added to the catalyst solution, and the vial was capped. At the specified time points, 20 μL aliquots were taken out and quenched with ethyl vinyl ether, and the product distribution was analyzed using gas chromatography.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00555.

Experimental details, NMR spectra, crystallographic data, details of computational methods, and complete references to Gaussian 09 (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1563880 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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