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ARTICLE

3,4-Dimercapto-3-cyclobutene-1,2-dione-chelated Ruthenium Carbene Catalyst for *Z*-Stereoretentive/Stereoselective Olefin Metathesis

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A ruthenium carbene catalyst chelated with a 3,4-dioxocyclobut-1-ene-1,2-dithiolate ligand was synthesized and its molecular structure was determined by single-crystal X-ray diffraction. The Ru catalyst had excellent catalytic activity with high yields and good *Z/E* ratios for the ring opening metathesis polymerization (ROMP) of norbornene (yield:96%/*Z/E*:86:14) and 1,5-cyclooctadiene (yield:86%/*Z/E*:91:9) and for ring opening cross metathesis (ROCM) reactions of norbornene/5-norbornene-2-*exo*, 3-*exo*-dimethanol with styrene (yields:64%-92%/*Z/E*:97:3-98:2) or 4-fluorostyrene (yield: 46%-94%/*Z/E*:98:2). The catalyst also had high *Z*-stereoretentivity (91:9–98:2) for cross-metathesis (CM) reactions of terminal olefins with (*Z*)-2-butene-1,4-diol. More importantly, the catalyst had moderate *Z*-stereoselectivity for homometathesis reactions of terminal olefins giving *cis*-olefins as the major products (*Z/E* ratios of 70:30–77:23). Like other Ru carbene complexes, the catalyst tolerates many different functional groups. Presented data, supported with DFT calculations, show that our catalyst, bearing a chelating 3,4-dioxocyclobut-1-ene-1,2-dithiolate ligand, exhibits higher stability towards air than Hoveyda's stereoretentive complex systems.

Introduction

Olefin metathesis is an extremely important reaction that builds C-C bond skeletons.[1] Commercially available Ru carbene olefin metathesis catalysts (e.g., Grubbs I and II and Grubbs-Hoveyda I and II catalysts) usually produce high proportions of *E*-olefin products in cross-metathesis (CM), ring-opening metathesis (ROM), and ring-closing metathesis (RCM) reactions. Since many natural products, including oleic acid,[2a,b] civetone,[2c] and substances with anticancer activity,[2d-f] often contain *Z*-olefin frameworks. The design of metathesis catalysts that can selectively generate *Z*-olefin products has been an important and challenging pursuit[3] since the 21st century. One of the most significant achievements was the synthesis of Mo complex **1** which has a monopyrrole ligand (**Fig.** 1) in 2009 by Ibrahem et al.[4] This complex produces a high proportion of *Z*-olefin products in ring opening cross metathesis (ROCM) reactions. The structure of **1** has been incorporated and optimized in the design of other Mo and W complexes (**Fig**. 1) to give a series of *Z*-selective olefin metathesis catalysts.[5] These catalysts have been successfully applied to CM reactions and RCM reactions to form macrocyclic compounds.[6]

In 2011, Grubbs and co-workers reported a *Z*-selective Ru olefin metathesis catalyst **3** (**Fig.** 1)[7] containing an *N*-heterocyclic carbene (NHC) with a carbanion bidentate ligand. Complex **3** can efficiently catalyze the CM of terminal olefins in different solvents and at different temperatures with good *Z*-selectivities. In addition, like other Ru carbene catalysts, **3** has excellent functional group compatibility, which greatly broadens the scope of applications for *Z*-selective olefin metathesis reactions.[8]

The catalytic performance of these Ru complexes is substantially affected by the carboxylic acid ligand and aryl group on the NHC. For example, when the carboxylic acid ligand is replaced with a monodentate halogen ligand the stereoselectivity of the catalyst is markedly reduced. Changing the carboxylic acid ligand slightly affects the catalyst stereoselectivity. When the carboxyl ligand was replaced with a nitrate group to give complex **4** (**Fig.** 1), both the catalytic activity and selectivity improved greatly (turnover number (TON) ~ 1000).[9] When complex **4** was applied to the ring opening metathesis polymerization (ROMP) of norbornene, the ratio of *cis*-polymer largely depended on the monomer structure and the reaction temperature.[10] At low temperatures the ratios of *cis*-polymers were obtained as high as 96%. In 2013, Grubbs found that replacing the *Mes*- group of the NHC ligand with a more crowded 2,6-diisopropylbenzene group resulted in a catalyst with a higher activity and better *Z*-selectivity (*Z*-selectivity > 95%; TON = 7400).[11] Asymmetrically modified catalysts have been applied to the asymmetric ROM of cyclic

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olefins to give chiral structures containing *Z*-olefins (98% *Z*; 95% ee).[12]

In 2013, Hoveyda and co-workers found that complex **5** (**Fig.** 1) with a 1,2-benzenedithiolate ligand could catalyze ROCM and ROMP reactions to provide highly selective *Z*-olefin products.[13] In 2015, the addition of a benzene-1,2-dithiolate ligand with a 3,6-dichloro substitution (**Fig.** 1) was found to remarkably increase the stability and catalytic activity of the resulting Ru complex.[14] The CM reactions of (*Z*)-but-2-ene-1,4-diol and terminal olefins catalyzed by **6** selectively gave *Z*-products (>96% *Z*).[14] In addition, complex **6** can tolerate many common organic functional groups and allyl alcohol compounds did not need protection. Furthermore, the conversion rate and the *Z*-retentivity of the reaction system were greatly improved. Grubbs and co-workers have also used complex **6** to catalyze CM reactions of terminal olefins and *cis*- or t*rans*-olefins to produce the corresponding *cis*- and *trans*-products, indicating that **6** has good stereoretention.[15] Since, Ru complexes containing dithiolate ligands have the advantages of simple structures, easy syntheses, and good functional groups tolerance, Such as that they have great application prospects for producing *Z*-olefins.

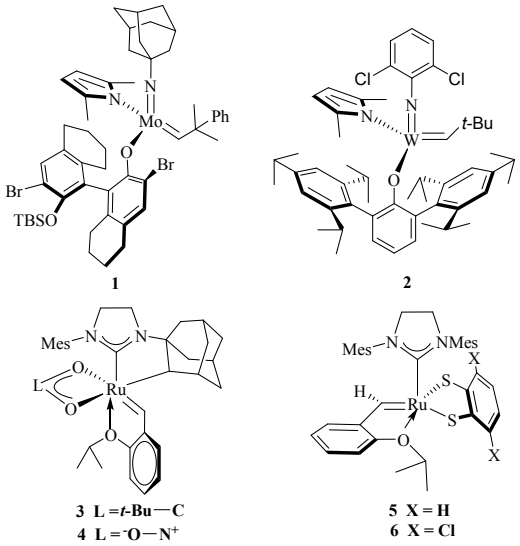


Fig. 1 Catalysts used previously to selectively generate *Z*-products.

In addition to ligand structure, the electron density of the Ru center also greatly influences the catalytic activity of a catalyst. For example, Slugovc and co-workers found that the catalytic activity of Grubbs-Hoveyda II (**Ru-1**, **Fig.** 2) was significantly reduced when chlorine atoms were replaced by bromine or iodine atoms.[16] As the electron density of the Ru atom increased (I > Br > Cl), the catalytic activity gradually decreased (**Fig**. 2). Hoveyda have proposed that the decomposition pathway of dithiolate catalysts involved a sulfide shift and enrich the electron density of anionic ligand would prone to deactivation.[14] Based on the above studies, we think that this nucleophilic addition of a sulfur anion to the carbon atom of the benzylidene carbene could be greatly inhibited by reducing the electron density of the sulfur ligand. This would increase the energy of the reaction barrier which should improve the stability of the Ru complex. In order to verify our inference, we need a ligand with low electronegativity and stable structure to coordinate with ruthenium. 3,4-Dimercaptocyclobut-3-ene-1,2-dione (**Fig.** 2, **L3**), as a stable ligand, is used to coordinate with Cu[17a-d], Ni[17e-h], In[17i], Pt[17j] and Pd[17c, j], but the coordination with Ru has not been studied. The pKa value of **L3** is 4.20, which is lower than those of benzene-1,2-dithiol (**L1**) and 3,6-dichlorobenzene-1,2-dithiol (**L2**). Therefore the use of **L3** as a ligand should reduce the electron density of the Ru center and thus improve the stability of the Ru complex. Herein, the synthesis of a new Ru carbene complex with 3,4-dimercaptocyclobut-3-ene-1,2-dione as a ligand is reported. The ability of this complex to catalyze ROMP, ROCM and CM reactions was investigated and the results are reported.

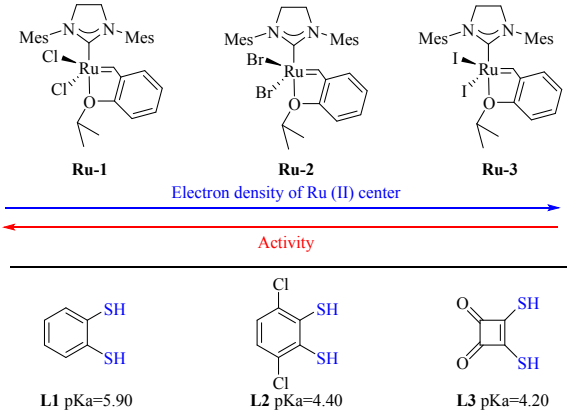
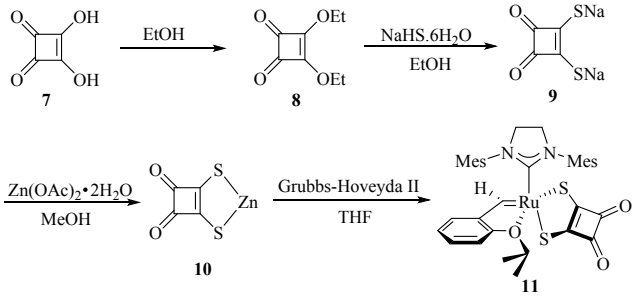


Fig. 2 Top: Correlation between electron density of Ru metal centers and their catalytic activities; Bottom: Structure and pKa values of ligands used in this work. These pKa values of the ligands were calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994-2019 ACD/Labs).

Results and discussion

The synthesis of the 3,4-dimercapto-3-cyclobutene-1,2-dione ligand and the corresponding Ru complex **11** are depicted in Scheme 1. First, the square acid (**7**) was converted to 3,4-diethoxycyclobut-3-ene-1,2-dione (**8**) in 78% yield using the method reported in the literature.[18] Next, **8** was reacted with sodium bisulfide in ethanol to give disodium 3,4-dioxocyclobut-1-ene-1,2-dithiolate (**9**) in 80% yield.[19] The zinc 3,4-dioxocyclobut-1-ene-1,2-dithiolate salt (**10**) was obtained by reacting ethylenediamine with a methanol solution of **9** and zinc acetate (yield, 94%). The zinc salt **10** and **Ru-1** were then reacted in tetrahydrofuran (THF) at 22 °C for 2 h to give the Ru-based complex **11** in 66% yield. The ^{1}H NMR spectra of the complex has a singlet peak at 15.36 ppm, which corresponds to the benzylidene carbene protons. This indicates that the ligand exchange was successful.



Scheme 1 Synthesis of 3,4-dioxocyclobut-1-ene-1,2-dithiolate-chelated ruthenium carbene complex **11**.

A single crystal of complex **11** was grown by slow evaporation from a CH_2Cl_2 solution at room temperature under N_2 atmosphere. The molecular structure of **11** was determined by single X-ray diffraction

and is shown in **Fig.** 3. The arrangement of the ligands around the metal center are similar to those in catalysts **5**[13] and **6**[14]. Complex **11** has a slightly deformed trigonal bipyramidal structure with an NHC, two sulfides, an isopropoxy moiety and the benzylidene carbene ligand seated around the Ru metal center. The bond distances between the Ru center and the S atoms are 2.3137 (5) and 2.3785 (5) Å for Ru (1)–S (1) and Ru (1)–S (2), respectively. Both of these are longer than those in catalyst **5** (Ru (1)–S (1), 2.2830 (6) Å and Ru (1)–S (2), 2.2933 (6) Å) and catalyst **6** (Ru (1)–S (1), 2.2706 (10) Å and Ru (1)–S (2), 2.2954 (9) Å). The bond angles of S (1)–Ru–S (2) (90.635° (19)), S (1)–Ru (1)–O (1) (170.49° (4)) and S (2)–Ru (1)–O (1) (90.68° (4)) in **11** are also larger than the corresponding angles in **5** and **6**. These results indicate that the introduction of the 3,4-dioxocyclobut-1-ene-1,2-dithiolate ligand to the catalyst slightly changed the structure of the Ru center, which may change the stability and catalytic activity of the complex.

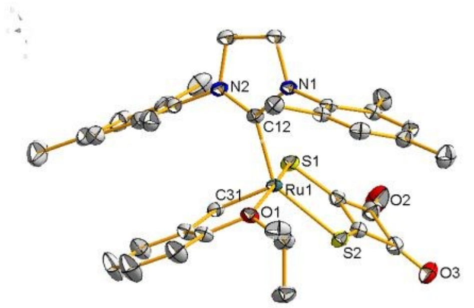


Fig. 3 Perspective views of **11**. Ellipsoids are drawn at 50% probability. For clarity, the hydrogen atoms were omitted. The supporting materials provide detailed bond lengths (Å) and angles (°).

In order to investigate the stability of complex **11**, the decomposition rate of the catalyst was monitored by sealing the complex as a solid in a vial at room temperature without N_2 protection for several days. For comparison, the same experiment was performed on complexes **5** and **6**. As catalysts decompose, their activities change, so the stored complexes were used to catalyze the CM reaction of hex-5-en-1-yl benzoate with (*Z*)-but-2-ene-1,4-diol. The results are shown in **Fig.** 4. After 10 or 18 days respectively, complexes **5** and **6** had no activity (0% yield) indicating that these catalysts were completely deactivated by this time. In comparison, after 18 days complex **11** still had a yield of 31% and did not totally lose its catalytic activity until 30 days. Clearly catalyst 11 has better stability than catalysts **5** and **6**. In addition, there were no significant changes in the stereoselectivity of the products over the course of the experiments (the catalysts maintained high *Z*-stereoretentivity). The ^{1}H NMR spectra for the products are given in the SI.

Density functional theory (DFT) calculations were performed in order to further validate the stability of complex **11**. The calculated energy profiles are shown in **Fig.** 5. Previously Hoveyda reported that the decomposition of a dithiolate catalyst was caused by the nucleophilic attack of S-ligand on the carbene carbon atom.[14] The ruthenium center must provide enough space for the transition of the hybrid orbitals of the carbene carbon atom from sp^2 to sp^3. We found that the Ru−O (alkoxy) linkage is the weakest coordination bond, because the oxygen atom is a hard donor atom and it has no negative charge to a soft Ru(II) center. This initial Ru-O bond dissociation process is supported by many studies.[9, 20] Indeed, we

The calculated energy profile shows that the reaction begins with the formation of intermediate 2 which occurs through transition state TS1 via the coordination dissociation of O (alkoxy) from the Ru(II) center. Next, intermediate 3 is produced by isomerization of intermediate 1. A subsequent nucleophilic attack of the sulfur atom on the carbene carbon atom to form Ru species intermediate 4 was absorbed (relative to intermediate 2) by 3.7, 14.3 and 14.4 kcal/mol (for **L1**, **L2** and **L3**, respectively). These results show that the nucleophilic addition is the rate-determining step. Therefore, complex **11** would be expected to have better stability than complexes **6** and **5**, which is consistent with the experiment results.

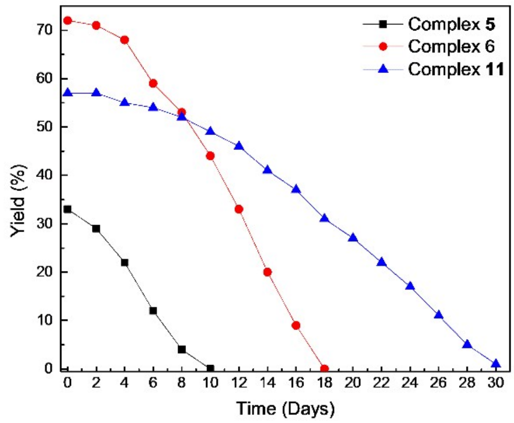


Fig. 4 The activity of catalysts **5**, **6** and **11** as a function of storage time. Reaction duration: 4 h; temperature: 55 °C; solvent: THF (0.5 mL); Ru complex **5**, **6** and **11**: 5 mol%; hex-5-en-1-yl benzoate(0.13 mmol), (*Z*)-but-2-ene-1,4-diol(0.26 mmol); Conversions and *Z/E* were determined by analysis of ^{1}H NMR spectra of the mixtures; Yields are based on isolated products.

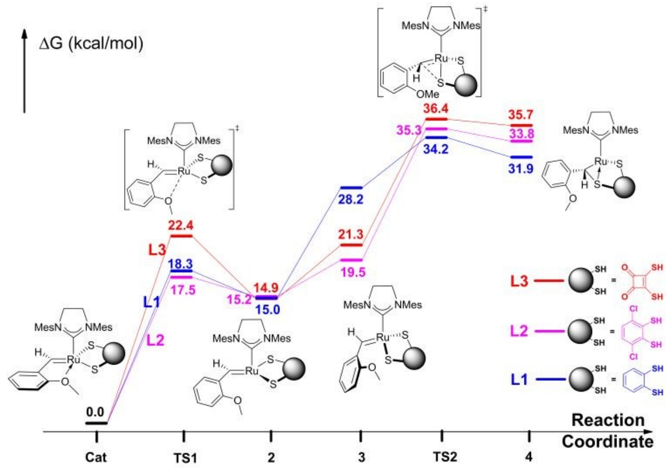


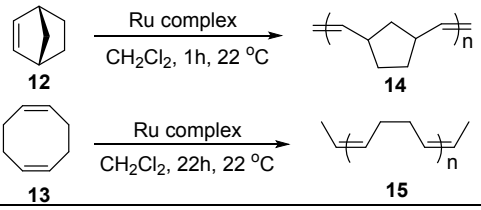
Fig. 5 Calculated energy profiles of all intermediate and transition states' for complexes **5**, **6** and **11**

Although no higher activity catalysts than complex **6** were obtained by ligand design, we found that the stability of the catalyst can be greatly improved by regulating ligands. This finding is related to the properties of 3,4-dioxocyclobut-1-ene-1,2-dithiolate, which illustrates low basicity and electron density of two S atoms involved in the coordination process. Such a strategy inhibits the decomposition process of the catalyst and could produce high-stability catalysts for olefin metathesis.

Complex **11** was used to catalyze ROMP reactions of norbornene (**12**) and 1,5-cyclooctadiene (**13**). The ROMP reactions were carried

out at room temperature, using dichloromethane as solvent without N_2 atmosphere. The complex **11** gives high yields and *Z/E* ratios which are shown in the Table 1. With a catalyst load of 0.1 mol%, the polymerization of **12** was achieved in 1 h with a total yield of 96%. The *cis*-product yield was 86%. When the catalyst load was reduced to 0.005 mol%, after 1 h of reaction, the TON was 17950 compared to 960 for the higher catalyst load. In contrast, the polymerization rate of **13** was much slower. It took 22 h to achieve a yield of 86% with a *Z/E* ratio of 91:9. The catalytic activities of catalyst **5** for these reactions were also investigated. The reaction of **12**, gave a yield of 94% with a *Z/E* ratio of 97:3 (**Table** 1, entry 2). Whereas, for monomer **13**, a yield of 73% with a *Z/E* ratio of 98:2 was obtained (**Table** 1, entry 5). These results are similar to those of Khan et al.[13]

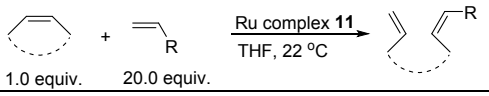
Table 1 Ru-based catalyst **11** in ROMP reactions[a]

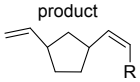
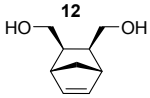
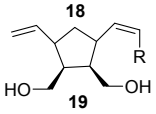


entry	monomer	cat.	mol%	time	yield/*Z*:*E*[b]	TON
1	**12**	**11**	0.1	1 h	96%/86:14	960
2	**12**	**5**	0.1	1 h	94%/97:3	940
3	**12**	**11**	0.005	1 h	85%/86:14	17950
4	**13**	**11**	0.1	22 h	86%/91:9	860
5	**13**	**5**	0.1	24 h	73%/98:2	730

[a] Solvent: CH_2Cl_2 (2 mL); temperature: 22 °C; [b] *Z/E* ratios were determined from ^{1}H NMR spectra of the pure products; [c] yields are based on pure products.

Table 2 Ru-based catalyst **11** in ROCM reactions.[a,b]



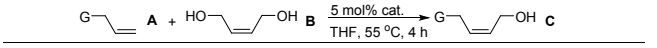
entry	substrate	R	cat.	product	yield	*Z/E*
1	 **12**	$R=C_6H_5$	1 mol%	 **18**	**18a** 78%	97:3
		$R=4\text{-}FC_6H_4$	1 mol%		**18b** 62%	98:2
2	 **16 (exo)**	$R=C_6H_5$	1 mol%	 **19**	**19a** 64%	98:2
			2 mol%		**19a** 92%	98:2
		$R=4\text{-}FC_6H_4$	1 mol%		**19b** 46%	98:2
			3 mol%		**19b** 94%	98:2
3	 **17 (endo)**	$R=C_6H_5$	1 mol%	non.	---	---
		$R=4\text{-}FC_6H_4$	1 mol%	non.	---	---

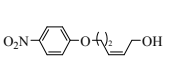
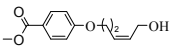
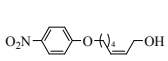
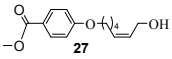
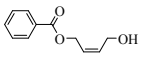
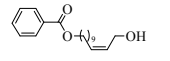
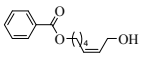
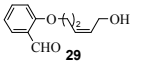
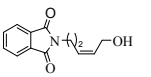
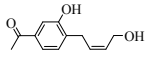
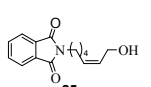
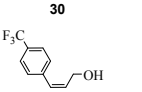
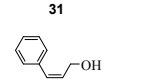
[a] Solvent: THF (0.5 mL); temperature: 22 °C; time: 4 h; [b] *Z/E* ratios were determined from ^{1}H NMR spectra of the pure products; [c] yields are based on pure products.

Next the reaction scope of complex **11** for catalyzing ROCM reactions was investigated and the results are shown in Table 2. With a catalyst load of 1.0 mol% the reactions of **12** with styrene and 4-fluorostyrene gave good yields (78% and 62%, respectively) and good *Z/E* ratios (97:3 and 98:2, respectively) (**Table** 2, entry 1). However with 1.0 mol% of complex **11**, the reactions of 5-norbornene-2-exo, 3-exo-dimethanol (**16**) with styrene and 4-fluorostyrene gave moderate yields (64%/46%) with high *Z/E* ratios (98:2). When the catalyst load was increased to 2.0 and 3.0 mol%, high *Z/E* ratios (98:2) and high yields (92%/94%) were obtained. When 5-norbornene-2-endo, 3-endo-dimethanol (**17**) was used as the substrate, no products were obtained. This is due to the steric hindrance of the hydroxymethyl.[21]

Complex **11** was then used to catalyze CM reactions of different terminal olefins and (*Z*)-but-2-ene-1,4-diol. The results are shown in **Table** 3. The CM reactions were carried out using 5 mol% of **11** in THF. Initially, 1-(but-3-en-1-yloxy)-4-nitrobenzene and (*Z*)-but-2-ene-1,4-diol were used as the substrates. When the reaction was carried out at 25 °C, a low conversion (33%) was obtained but as the temperature was increased to 55 °C, the yield gradually increased. from 33% to 49%. Further increasing temperature to 65 °C, did not significantly increase the activity of the catalyst. In order to better elucidate the temperature effect, five other substrates (1-(hex-5-en-1-yloxy)-4-nitrobenzene, allyl benzoate, hex-5-en-1-yl benzoate, 2-(but-3-en-1-yl)isoindoline-1,3-dione and 2-(hex-5-en-1-yl)isoindoline-1,3-dione) were also tested and the results are shown in Table 3. All the results indicate that 55 °C is the optimal reaction temperature. Complex **6** was also used for the CM reactions using the optimum conditions and relatively high yields (49-85%) with *Z/E* product ratios of 92:8–98:2 were obtained. This indicates that although the stability of catalyst **11** has been greatly improved by the introduction of the new ligand, the activity of catalyst **11** still

Table 3 Stereoretentivity and activity study of Ru-based catalyst **11** in CM reactions of different terminal alkenes and *(Z)*-but-2-ene-1,4-diol.[a, b,c,d]



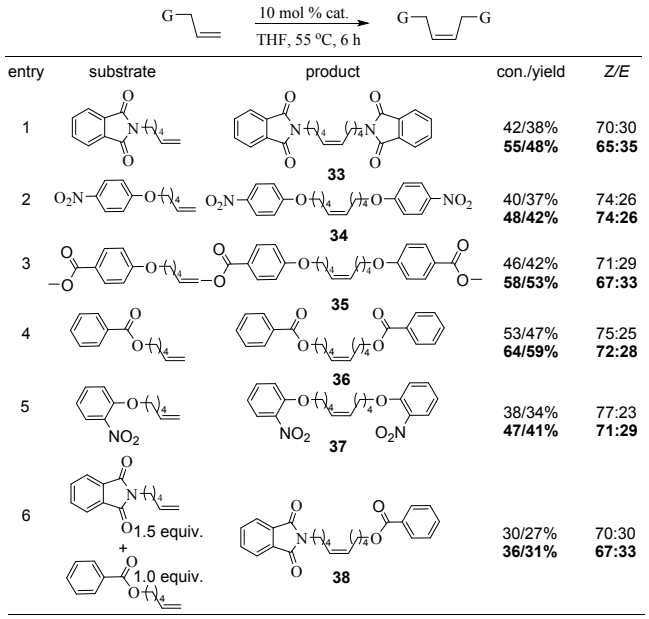
Product	con./yield	*Z/E*	Product	con./yield	*Z/E*
 **20**	33/28%	97:3(25 °C)	 **26**	47/40%	97:3(55 °C)
	38/33%	97:3(35 °C)		**64/56%**	**96:4(55 °C)**
	45/39%	96:4(45 °C)			
	49/45%	96:4(55 °C)			
	50/44%	95:5(65 °C)			
	85/78%	**95:5(55 °C)**			
 **21**	36/30%	98:2(25 °C)	 **27**	53/46%	97:3(55 °C)
	44/39%	98:2(35 °C)		**71/63%**	**97:3(55 °C)**
	50/44%	98:2(45 °C)			
	58/51%	98:2(55 °C)			
	57/52%	97:3(65 °C)			
	88/82%	**97:3(55 °C)**			
 **22**	18/13%	98:2(25 °C)	 **28**	66/60%	95:5(55 °C)
	24/19%	98:2(35 °C)		**92/85%**	**97:3(55 °C)**
	32/26%	97:3(45 °C)			
	39/33%	97:3(55 °C)			
	42/35%	97:3(65 °C)			
	57/50%	**96:4(55 °C)**			
 **23**	40/35%	98:2(25 °C)	 **29**	38/31%	96:4(55 °C)
	47/42%	98:2(35 °C)		**57/52%**	**95:5(55 °C)**
	58/52%	97:3(45 °C)			
	65/57%	96:4(55 °C)			
	67/61%	96:4(65 °C)			
	79/72%	**97:3(55 °C)**			
 24	33/27%	98:2(25 °C)	 **30**	49/43%	93:7(55 °C)
	37/33%	98:2(35 °C)		**81/72%**	**96:4(55 °C)**
	47/41%	97:3(45 °C)			
	51/44%	97:3(55 °C)			
	50/45%	96:4(65 °C)			
	68/62%	**97:3(55 °C)**			
 **25**	36/32%	98:2(25°C)	 **31**	35/29%	91:9(55 °C)
	44/39%	97:3(35°C)		**65/59%**	**92:8(55 °C)**
	53/48%	97:3(45°C)			
	59/53%	97:3(55°C)			
	62/55%	97:3(65°C)			
	78/71%	**98:2(55 °C)**			
			 **32**	29/23%	92:8(55 °C)
				54/49%	**93:7(55 °C)**

[a] Reaction duration: 4 h; solvent: THF (0.5 mL); Ru complex 11: 5 mol%; A:B = 1.0:2.0 equiv.; under N_2 atmosphere; [b] Conversions and *Z/E* ratios were determined from ^{1}H NMR spectra of the mixtures; [c] Yields are based on isolated products; [d] The catalytic results for catalyst **6** are shown in bold at the bottom of each set of data.

needs to be improved. The data from **Table** 3 also demonstrates the functional group tolerance of catalyst **11**. Like other Ru carbene catalysts, complex **11** tolerates many common functional groups, such as nitro (**20** and **21**), ketone (**30**) and aldehyde (**29**) groups. When terminal olefins with similar structures and different alkyl chain lengths were used, the terminal olefins with longer chains gave higher yields than those with shorter chains (like **22**, **23** and **28**). Furthermore, the activity of catalyst **11** did not decrease even without nitrogen protection.

Complex **11** was then used to catalyze the homometathesis reactions of terminal olefins and the results are shown in **Table** 4. These reactions gave low yields with *Z*-olefins selectivities from 70:30 to 77:23. The CM reaction of hex-5-en-1-yl benzoate and 2-(hex-5-en-1-yl)isoindoline-1,3-dione at a molecular ratio of 1:1.5 gave **38** in low yield, because the homometathesis reactions also resulted in by-products **33** (5%) and **36** (9%). The homometathesis products observed in this reaction system may contribute to the low yield of the CM reactions. However, the major product **38** still possessed a *Z/E* ratio of 70:30. This indicates that catalyst **11** can generate *Z*-olefin products without inheriting the original configuration of the substrates. In addition, complex **6** was used for the homometathesis reactions under the same conditions as complex **11** and the relatively yields (31-59%) with *Z/E* product ratios of 67:33–74:26 were obtained. This indicates that the catalytic activity of catalyst **6** is higher than those of **11**, but the *Z*-stereoselectivity not much difference between these two catalysts. Overall, these experiments demonstrate that the products obtained (**Table** 3, **20**-**32**) from the CM reactions of terminal olefins with (*Z*)-but-2-ene-1,4-diol generally inherit the *cis*-structure of (*Z*)-but-2-ene-1,4-diol even though catalyst **11** is a *Z*-selective catalyst.

Table 4 *Z*-selective CM reactions with terminal olefins catalyzed by the Ru-based catalyst **11**[a, b, c, d]



entry	substrate	product	con./yield	*Z/E*
1		**33**	42/38% **55/48%**	70:30 **65:35**
2		**34**	40/37% **48/42%**	74:26 **74:26**
3		**35**	46/42% **58/53%**	71:29 **67:33**
4		**36**	53/47% **64/59%**	75:25 **72:28**
5		**37**	38/34% **47/41%**	77:23 **71:29**
6		**38**	30/27% **36/31%**	70:30 **67:33**

[a] Reaction duration: 6 h; Solvent: THF (0.5 mL); Temperature: 55 °C; Ru complex: 10 mol%; [b] Conversions and *Z/E* ratios were determined by analysis of ^{1}H NMR spectra of the mixtures; [c] Yields are based on isolated products. [d] The catalytic results for catalyst **6** are shown in bold at the bottom of each set of data.

Conclusions

In summary, a new Ru carbene complex bearing a 3,4-dioxocyclobut-1-ene-1,2-dithiolate ligand with high *Z*-stereo-retentivity/stereoselectivity was synthesized. This new Ru carbene complex has a better stability than Hoveyda's stereoretentive complex systems, and excellent catalytic activities with high yields and good *Z/E* ratios for ROMP/ROCM reactions without the need for N_2 protection. The Ru carbene complex also has good *Z*-stereoretentivity for the reaction of terminal alkenes with (*Z*)-but-2-ene-1,4-diol. For the homometathesis and CM reactions of terminal olefins, *cis*-olefins products were the major products. Moreover, this Ru carbene complex has a high functional group tolerance which is similar to that of other Ru carbene olefin metathesis catalysts.

Experimental Section

General Information

^{1}H-NMR and ^{13}C-NMR spectra were acquired in $CDCl_3$ on a Bruker (AVANCE III) 400 MHz spectrometer. If not otherwise noted, chemical shift values are reported in ppm relative to residual $CDCl_3$ (*J* =7.26) for the ^{1}H-NMR spectra and relative to $CDCl_3$ (77.1 ppm) for the ^{13}C-NMR spectra. Multiplicities are described using the following abbreviations: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). The ^{1}H coupling constants (*J*) are given in Hz. High-resolution mass spectra were obtained on a JEOL JMS-DX303 mass spectrometer.

DFT calculations were performed using a Gaussian 09 package.[22] Geometry optimizations were performed at the BP86-D3BJ[23, 24, 25]/LanL2dz[26] levels for Ru and at the level 6-31G(d)[27] for other atoms. Single-point electronic energy calculations were performed at the BP86-D3BJ/def2-TZVP[28] levels for Ru and at the 6-311+G(2df,2p) levels for other atoms. The computed structures were illustrated using CYL View.[29]

Materials and Methods

Unless otherwise noted, all reactions were performed under an atmosphere of dry N_2 with oven-dried glassware and with anhydrous solvents using standard dry box or vacuum line techniques. Toluene, THF, hexane and Et_2O was distilled from sodium/benzophenone under a N_2 atmosphere. Ethanol was distilled over $MgSO_4$. CH_2Cl_2 was dried over CaH_2, and distilled prior to use. All other solvents were dried over 4-8 Å mesh molecular sieves (Aldrich) and were either saturated with dry argon or degassed before use. Reactions were monitored by analytical thin layer chromatography (TLC) using 0.20 mm Yantai Huagong silica gel plates. Silica gel (200-300 mesh) (from Yantai Huagong Company) was used for flash chromatography. $CDCl_3$ and CD_2Cl_2 were purchased from TCI (Shanghai) Development Co., Ltd. and used as received. All other chemicals or reagents were obtained from commercial sources.

Experimental details

3,4-diethoxycyclobut-3-ene-1,2-dione (**8**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (dq, *J* = 14.3, 7.2 Hz, 4H), 1.60 –1.35 (m, 6H) ppm; ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 189.2, 184.1, 70.5, 15.5 ppm.

3,4-dimercapto-3-cyclobutene-1,2-dione disodium salt (**9**): IR (KBr): *v* 3523, 3380, 2648, 2441, 2308,1883, 1713, 1624, 1429, 1356, 1215, 1123, 1007, 923, 673, 562, 471 cm^{-1}.

For the preparation of 3,4-dimercapto-3-cyclobutene-1,2-dione zinc salt (**10**), first 1,2-dithiosquaric acid disodium salt (1 g, 5.3 mmol, 1.0 equiv.) was added to a 100 mL single port round bottom flask equipped with a magnetic stirrer. Next, $Zn(OAc)_2 \bullet 2H_2O$ (4.03 g, 18.5 mmol, 3.5 equiv.) and 50 mL of methanol were added and the mixture was stirred at room temperature under a nitrogen atmosphere until the solid completely dissolved. Then ethylenediamine solution (1.8 mL, 6.0 equiv) was added to the reaction solution and a white solid gradually precipitated from the solution. After stirring for 30 min, the reaction solution was filtered and the collected solid was washed with methanol three times (10 mL x 3). The solid was then dried in a vacuum at 100 °C to give 0.93 g of the white powder **10** with a yield of 94.2%. The product was then directly reacted without further purification. IR (KBr): *v*: 3443, 3336,

3277, 2957, 1879, 1727, 1670, 1565, 1456, 1391, 1360, 1195, 1114, 1033, 940, 895, 851, 748, 663, 607, 521, 468 cm^{-1}.

For the preparation of Ru-Based dithiolate complex (**11**), first zinc 1,2-dithiosquaric acid (0.51 g, 2.4 mmol, 1.0 equiv.) and Grubbs-Hoveyda second-generation catalyst (1.5 g, 2.4 mmol, 1.0 equiv.) were added under N_2 atmosphere to a 25 mL round bottom flask equipped with a magnetic stirrer. Next 15 mL of dry THF was added and the reaction was stirred for 2 h at room temperature. After the reaction was complete, the solution turned from dark green to brown and then a yellow precipitate formed. The solution was filtered to give a yellow brown solid. The solid was washed with dried THF (10 mL x 3) and dried to give complex **11** as a yellow-brown solid, 1.21 g, yield 72%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 15.36 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 18.7 Hz, 2H), 6.86 (dd, *J* = 14.2, 6.3 Hz, 2H), 6.69 (d, *J* = 7.3 Hz, 1H), 6.08 (s, 1H), 5.20 – 5.11 (m, 1H), 4.11 – 3.82 (m, 4H), 2.53 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 1.74 (d, *J* = 6.5 Hz, 3H), 1.56 (s, 6H), 1.41 (d, *J* = 6.4 Hz, 3H).ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 223.7, 213.5, 206.9, 189.8, 154.3, 141.7, 138.8, 135.7, 129.2, 127.9, 124.3, 122.6, 120.3, 116.0, 114.2, 112.9, 112.4, 110.0, 84.1, 75.3, 75.1, 71.2, 67.8, 31.0, 25.9, 25.6, 24.2, 21.7, 21.6, 20.9, 20.8, 20.7 ppm. IR (KBr): *v* 3463, 3335, 3275, 2973, 2924, 1810, 1736, 1707, 1581, 1479, 1427, 1368, 1264, 1162, 1114, 1064, 1034, 945, 905, 871, 854, 823, 750, 715, 625, 572, 527, 420 cm^{-1}. ESI-MS $[M+Na]^+$calcd for $C_{35}H_{38}N_2O_3Ru_1S_2$: 700.1367; found: 723.1257. CCDC number: 1585252.

ROMP Reactions

An oven-dried 10 mL vial equipped with a magnetic stir bar was charged with 0.1 mL CH_2Cl_2 solution containing complex **11** (0.7 mg, 0.001 mmol). Then a solution of norbornene (94.1 mg, 1.0 mmol) in 1.5 mL CH_2Cl_2 was added and the solution was stirred for 1 h at room temperature. The solution became very viscous. Next MeOH (5 mL) was added and the white poly-norbornene settled out of the solution with vigorous stirring. The polymer was washed with MeOH (4 mL x 3) and dried under vacuum for 24 h to give a white solid **14** (90.0 mg, yield 96%) with a *Z/E* ratio of 86:14. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (d, *J* = 5.9 Hz, 2H), 2.79 (s, 2H), 2.00 – 1.85 (m, 1H), 1.82 (d, *J* = 13.3 Hz, 2H), 1.36 (s, 2H), 1.02 (dd, *J* = 22.2, 10.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 42.7, 38.6, 33.2.

An oven-dried 10 mL vial equipped with a magnetic stir bar was charged with 0.1 mL CH_2Cl_2 solution containing complex **11** (0.7 mg, 0.001 mmol). Then 1, 5-cyclooctadiene (108.1 mg, 1.0 mmol) was added and the solution was stirred for 22 hours at room temperature. Next MeOH (5 mL) was added and the formed polymer settled out of the solution with vigorous stirring. The polymer was washed with MeOH (4 mL x 3) and dried under vacuum for 22 h to give **15** (93.0 mg, yield 86%) with a *Z/E* ratio of 91:9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 4.1 Hz, 4H), 2.09 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.6, 27.4.

ROCM Reactions

General Procedure: An oven-dried 10 mL vial equipped with a magnetic stir bar was charged with the alkene substrate (1.0 equiv.) and a terminal olefin (20 equiv.) in a fume hood. To this vessel, a solution of complex **11** (1.0-3.0 mol%) in THF was added. The resulting solution was then stirred for 4 h at room temperature. The reaction mixture was then concentrated by vacuum and the product was purified using silica gel chromatography.

For ((*Z*)-2-((1*S*,3*R*)-3-vinylcyclopentyl)vinyl)benzene (**18a**), complex **11** (1.0 mol%) dissolved in 0.2 mL THF was used. The product was purified by column chromatography with hexane to give a colorless oil (24.6 mg, yield 78%) with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.13 (m, 5H), 6.36 (d, *J* = 11.5 Hz, 1H), 5.82 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.58 (dd, *J* = 11.4, 10.1 Hz, 1H), 5.07 – 4.82 (m, 2H), 3.14 – 2.96 (m, 1H), 2.64 – 2.44 (m, 1H), 2.10 – 1.96 (m, 1H), 1.96 – 1.76 (m, 2H), 1.54 – 1.44 (m, 2H), 1.28 – 1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.9, 128.6, 128.2, 127.6, 126.51, 112.6, 44.6, 41.5, 38.7, 33.0, 31.9.

For (*Z*)-1-fluoro-4-(2-((1S,3R)3-vinylcyclopentyl)vinyl)benzene (**18b**), complex **11** (1.0 mol%) dissolved in 0.2 mL THF was used. The product was purified by column chromatography with hexane to give a colorless oil (21.3 mg, yield 62%) with a *Z/E* ratio of 98:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 2H), 7.08 – 6.93 (m, 2H), 6.31 (d, *J* = 11.5 Hz, 1H), 5.82 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.56 (dd, *J* = 11.3, 10.1 Hz, 1H), 4.94 (dddd, *J* = 34.0, 10.2, 1.9, 1.1 Hz, 2H), 3.08 – 2.91 (m, 1H), 2.65 – 2.45 (m, 1H), 2.01 (dt, *J* = 13.1, 4.4 Hz, 1H), 1.93 – 1.78 (m, 2H), 1.54 – 1.44 (m, 2H), 1.22 (dt, *J* = 12.4, 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 160.3, 142.9, 137.8, 133.8, 130.1, 126.5, 115.1, 114.9, 112.6, 44.5, 41.4, 38.6, 33.0, 31.9.

For 3-((*Z*)-styryl)-5-vinylcyclopentane-1,2-diyl)dimethanol (**19a**), complex **11** (1.0 mol%) dissolved in 0.2 mL THF was used. The product was purified by column chromatography with hexane/ether (3/7) to give a colorless oil (16.0 mg, yield 64%) with a *Z/E* ratio of 98:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 2H), 7.23 (dt, *J* = 6.9, 5.6 Hz, 3H), 6.48 (d, *J* = 11.5 Hz, 1H), 5.74 (ddd, *J* = 17.7, 10.1, 7.8 Hz, 1H), 5.52 (dd, *J* = 11.4, 10.2 Hz, 1H), 5.08 – 4.92 (m, 2H), 3.58 (ddd, *J* = 16.9, 13.4, 8.2 Hz, 4H), 3.41 (s, 2H), 2.82 – 2.63 (m, 1H), 2.18 (dd, *J* = 13.7, 5.9 Hz, 1H), 2.15 – 2.07 (m, 2H), 2.01 (td, *J* = 12.0, 5.9 Hz, 1H), 1.36 (dd, *J* = 23.3, 11.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.4, 135.8, 129.8, 128.4, 126.7, 114.5, 61.9, 50.4, 48.5, 46.3, 40.1, 39.7.

For 3-((*Z*)-4-fluorostyryl)-5-vinylcyclopentane-1,2-diyl)dimethanol (**19b**), complex **11** (1.0 mol%) dissolved in 0.2 mL THF was used. The product was purified by column chromatography with hexane/ether (3/7) to give a colorless oil (12.4 mg, yield 46%) with a *Z/E* ratio of 98:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 2H), 7.06 – 6.93 (m, 2H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.74 (ddd, *J* = 17.7, 10.1, 7.9 Hz, 1H), 5.58 – 5.43 (m, 1H), 5.06 – 4.93 (m, 2H), 3.72 – 3.52 (m, 4H), 3.42 (d, *J* = 74.1 Hz, 2H), 2.76 – 2.60 (m, 1H), 2.28 – 2.15 (m, 1H), 2.15 – 2.05 (m, 2H), 1.97 (dt, *J* = 12.4, 6.1 Hz, 1H), 1.35 (dd, *J* = 23.3, 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 135.8, 133.4, 130.0, 128.7, 115.3, 115.1, 114.6, 61.9, 50.4, 48.4, 46.3, 40.0, 39.7.

***Z*-Stereoretentive/Stereoselective CM Reactions.**

General Procedure: An oven-dried 10 mL vial equipped with a magnetic stir bar was charged with the alkene substrate (0.12 mmol, 1.0 equiv.) and *Z*-2-butene-1,4-diol (0.24 mmol, 2.0 equiv.). To this vessel, a solution of complex **11** or **6** (4.9 mg, 5.0 mol%) in THF (0.5 mL) was added. The resulting solution was stirred for 4-6 h at 55 ºC. The reaction media was then concentrated by vacuum. Purification was performed using silica gel chromatography and the percent conversion was determined using ^{1}H NMR analysis.

For homometathesis reactions, an oven-dried 10 mL vial equipped with a magnetic stir bar was charged with alkene substrate (0.12 mmol, 1.0 equiv.). To this vessel, a solution of complex **11** or **6** (9.8 mg, 10.0 mol%) in THF (0.5 mL) was added. The resulting solution is allowed was stirred for 4-6 hours at 55 ºC. The reaction media was then concentrated by vacuum. Purification was performed using silica gel chromatography and the percent conversion was determined using ^{1}H NMR analysis.

For (*Z*)-5-(4-nitrophenoxy)pent-2-en-1-ol (**20**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was purified by column chromatography to provide a pale yellow oil (12.0 mg, yield 45%)

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with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.07 (m, 1H), 6.99–6.87 (m, 1H), 5.88–5.75 (m, 1H), 5.73 – 5.53 (m, 1H), 4.25 (d, *J* = 6.7 Hz, 1H), 4.08 (t, *J* = 6.4 Hz, 1H), 2.63 (q, *J* = 6.7 Hz, 1H), 1.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 131.7, 127.5, 125.9, 114.4, 67.9, 58.5, 27.4 ppm.

For (*Z*)-7-(4-nitrophenoxy)hept-2-en-1-ol (**21**), complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (15.4 mg, yield 51%) with a *Z/E* ratio of 98:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21–8.12 (m, 2H), 6.97–6.88 (m, 2H), 5.67–5.59 (m, 1H), 5.58–5.48 (m, 1H), 4.19 (d, *J* = 6.4 Hz, 2H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.82 (dd, *J* = 8.5, 6.9 Hz, 2H), 1.55 (dq, *J* = 15.0, 7.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1, 141.3, 132.2, 129.1, 125.9, 114.4, 68.6, 58.5, 28.5, 27.0, 25.9 ppm. ESI-MS [M+Na]$^+$ calcd for $C_{13}H_{17}NO_4$: 251.2820, found: 274.1042. Analytical Data. Found (calcd) for: $C_{13}H_{17}NO_4$ C, 62.14 (62.27); H, 6.82 (6.88); N, 5.57(5.50).

For (*Z*)-4-hydroxybut-2-en-1-yl benzoate (**22**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (7.6 mg, yield 33%) with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 5.92 (dt, *J* = 13.0, 7.7 Hz, 1H), 5.82–5.60 (m, 1H), 4.93 (d, *J* = 7.0 Hz, 1H), 4.34 (d, *J* = 6.5 Hz, 1H), 2.13 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 133.6, 133.1, 130.0, 129.6, 128.4, 125.6, 60.6, 58.5 ppm.

For (*Z*)-7-hydroxyhept-5-en-1-yl benzoate (**23**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (15.9 mg, yield 57%) with a *Z/E* ratio of 96:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 5.68–5.60 (m, 1H), 5.59 –5.50 (m, 1H), 4.33 (t, *J* = 6.6 Hz, 1H), 4.21 (d, *J* = 6.6 Hz, 1H), 2.16 (q, *J* = 7.3 Hz, 1H), 1.81–1.75 (m, 1H), 1.67 (s, 1H), 1.54 (dt, *J* = 15.0, 7.5 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 132.9, 132.3, 130.3, 129.5, 129.0, 128.4, 64.7, 58.5, 28.2, 26.9, 25.9 ppm.

For (*Z*)-2-(5-hydroxypent-3-en-1-yl)isoindoline-1,3-dione (**24**), complex **11** (4.9 mg, 5.0 mol%) was used. The product was a white solid (12.2 mg, yield 44%) with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.72–7.64 (m, 2H), 5.73–5.62 (m, 1H), 5.56–5.45 (m, 1H), 4.11 (d, *J* = 6.2 Hz, 2H), 3.72 (t, *J* = 7.1 Hz, 2H), 2.47 (q, *J* = 7.3 Hz, 2H), 1.95 (s, 1H). ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.4, 134.0, 132.0, 131.7, 127.90, 123.2, 58.3, 37.5, 26.5 ppm. ESI-MS[M+Na]$^+$ calcd for $C_{13}H_{13}NO_3$: 231.2510; found: 254.0744. Analytical Data. Found (calcd) for: $C_{13}H_{13}NO_3$ C, 67.52 (67.46); H, 5.67 (5.75); N, 6.06 (6.00).

For (*Z*)-2-(7-hydroxyhept-5-en-1-yl)isoindoline-1,3-dione (**25**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (16.5 mg, yield 53%) with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.69–5.60 (m, 1H), 5.54–5.44 (m, 1H), 4.21 (d, *J* = 6.8 Hz, 2H), 3.73 –3.64 (m, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.76 (s, 1H), 1.72 –1.65 (m, 2H), 1.49–1.40 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.5, 133.9, 132.1, 129.2, 123.2, 58.5, 37.6, 27.7, 26.5, 26.4 ppm.

For benzoic acid, 4-[[(3*Z*)-5-hydroxy-3-penten-1-yl]oxy]-, methyl ester (**26**), complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (11.3 mg, yield 40%) with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 2H), 6.94 – 6.81 (m, 2H), 5.84–5.70 (m, 1H), 5.62 (dtt, *J* = 10.2, 7.5, 1.2 Hz, 1H), 4.22 (d, *J* = 6.6 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.86 (s, 3H), 2.66–2.50 (m, 2H), 1.99 (s, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 162.4, 131.6, 131.5, 127.9, 122.8, 114.0, 67.2, 58.4, 51.9, 27.5 ppm. ESI-MS[M+Na]$^+$calcd for $C_{13}H_{16}O_4$: 236.2670; found: 259.0933. Analytical Data. Found (calcd) for: $C_{13}H_{16}O_4$ C, 66.09 (66.02); H, 6.83 (6.72).

For benzoic acid, 4-[[(5*Z*)-7-hydroxy-5-hepten-1-yl]oxy]-, methyl ester (**27**), complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (14.6 mg, yield 46%) with a *Z/E* ratio of 97:3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.93 (m, 1H), 6.90 (s, 1H), 5.66 (d, *J* = 3.1 Hz, 1H), 5.58–5.48 (m, 1H), 4.20 (t, *J* = 4.9 Hz, 1H), 4.0 –3.96 (m, 1H), 3.87 (d, *J* = 1.9 Hz, 1H), 2.20–2.10 (m, 1H), 1.83 (d, *J* = 6.2 Hz, 1H), 1.64 (d, *J* = 9.3 Hz, 1H), 1.60–1.49 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.9, 162.8, 132.3, 131.6, 129.0, 122.4, 114.0, 67.9, 58.5, 51.9, 28.6, 27.1, 26.0 ppm. ESI-MS[M+Na]$^+$calcd for $C_{15}H_{20}NO_4$: 264.3210; found: 287.1292. Analytical Data. Found (calcd) for: $C_{15}H_{20}NO_4$ C, 68.16 (68.12); H, 7.63 (6.68).

For (*Z*)-12-hydroxydodec-10-en-1-yl benzoate (**28**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (21.9 mg, yield 60%) with a *Z/E* ratio of 95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 5.65–5.55 (m, 1H), 5.55–5.43 (m, 1H), 4.30 (t, *J* = 6.6 Hz, 1H), 4.18 (t, *J* = 5.1 Hz, 1H), 2.05 (dd, *J* = 13.7, 6.8 Hz, 1H), 1.80–1.71 (m, 1H), 1.53 (s, 1H), 1.48–1.39 (m, 1H), 1.34 (s, 2H), 1.28 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 133.2, 132.8, 130.5, 129.5, 128.3, 65.1, 58.6, 29.6, 29.5 – 29.2, 29.2, 28.7, 27.4, 26.0 ppm.

For (*Z*)-2-((5-hydroxypent-3-en-1-yl)oxy)benzaldehyde(**29**), complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (7.7 mg, yield 31%) with a *Z/E* ratio of 96:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.82 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.80 (dt, *J* = 13.2, 6.7 Hz, 1H), 5.65 (dt, *J* = 10.9, 7.5 Hz, 1H), 4.26 (d, *J* = 6.6 Hz, 2H), 4.11 (t, *J* = 6.4 Hz, 2H), 2.66 (q, *J* = 6.7 Hz, 2H), 1.66 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.9, 161.0, 135.9, 131.5, 129.0, 127.7, 120.8, 112.6, 67.7, 58.5, 27.5 ppm. ESI-MS [M+Na]$^+$ calcd for $C_{12}H_{14}O_3$: 206.2410, found: 229.0835. Analytical Data. Found (calcd) for: $C_{12}H_{14}O_3$ C, 69.89 (69.96); H, 6.84 (6.87).

For (*Z*)-1-(3-hydroxy-4-(4-hydroxybut-2-en-1-yl)phenyl)e-than-1-one (**30**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a white solid (10.6 mg, yield 43%) with a *Z/E* ratio of 93:7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.0 Hz, 1H), 7.74 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.77 (dd, *J* = 11.6, 5.5 Hz, 1H), 5.67 (dd, *J* = 18.6, 8.0 Hz, 1H), 4.36 (d, *J* = 6.5 Hz, 1H), 3.52 (d, *J* = 7.9 Hz, 1H), 2.54 (d, *J* = 6.8 Hz, 1H), 1.36–1.19 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.7, 159.9, 131.8, 131.2, 129.7, 129.4, 127.6, 125.9, 115.8, 58.4, 29.7, 26.3 ppm.

For (*Z*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol(**31**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (7.0 mg, yield 29%) with a *Z/E* ratio of 91:9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 11.8 Hz, 1H), 6.05–5.94 (m, 1H), 4.42 (d, *J* = 6.4 Hz, 2H), 1.66 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.1, 133.2, 129.8, 129.0, 125.2, 59.5 ppm.

For (*Z*)-3-phenylprop-2-en-1-ol (**32**)[14], complex **11** (4.9 mg, 5.0 mol%) was used. The product was a pale yellow oil (3.7 mg, yield 23%) with a *Z/E* ratio of 92:8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.29–7.26 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.58 (d, *J* = 11.7 Hz, 1H), 5.88 (dt, *J* = 12.5, 6.4 Hz, 1H), 4.45 (d, *J* = 6.4 Hz, 2H), 1.55 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.5, 131.1, 128.8, 128.3, 127.3, 59.7 ppm.

For (*Z*)-2,2'-(dec-5-ene-1,10-diyl)bis(isoindoline-1,3-dione) (**33**), complex **11** (9.8 mg, 10.0 mol%) was used. The product was a pale yellow solid (9.8 mg, yield 38%) with a *Z/E* ratio of 70:30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.4, 3.1 Hz, 4H), 7.69 (dd, *J* = 5.4, 3.0 Hz, 4H), 5.32 (t, *J* = 4.6 Hz, 2H), 3.67 (dd, *J* = 8.5, 6.0 Hz, 4H), 2.06 (dd, *J* = 12.6, 7.1 Hz, 4H), 1.67 (dd, *J* = 15.1, 7.5 Hz, 4H), 1.38 (dt, *J* = 15.0,

7.5 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.4, 133.8, 132.2, 130.2, 129.6, 123.1, 37.9, 32.0, 28.1, 26.8 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{26}H_{26}N_2O_4$: 430.5040, found: 453.1781. Analytical Data. Found (calcd) for: $C_{26}H_{26}N_2O_4$ C, 72.54 (72.66); H, 6.09 (6.13); N, 6.51 (6.44).

For (*Z*)-1,10-bis(4-nitrophenoxy)dec-5-ene (**34**), complex **11** (9.8 mg, 10.0 mol%) was used. The product was a white solid (9.1 mg, yield 37%) with a *Z/E* ratio of 74:26. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23–8.15 (m, 4H), 7.01–6.89 (m, 4H), 5.42 (t, *J* = 4.6 Hz, 2H), 4.05 (t, *J* = 6.4 Hz, 4H), 2.13 (dd, *J* = 12.8, 7.3 Hz, 4H), 1.90–1.76 (m, 4H), 1.55 (dd, *J* = 6.7, 3.9 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1, 141.4, 130.3, 129.8, 125.9, 114.4, 68.7, 32.1, 28.5, 26.9, 25.9 ppm. ESI-MS$[M+Na]^+$ calcd for $C_{22}H_{26}N_2O_6$: 414.4580; found: 437.1720. Analytical Data. Found (calcd) for: $C_{22}H_{26}N_2O_6$ C, 63.76 (63.68); H, 6.32 (6.24); N, 6.76 (6.70).

For dimethyl 4,4'-(dec-5-ene-1,10-diylbis(oxy))(*Z*)-dibenzo-ate (**35**), complex **11** (9.8 mg, 10.0 mol%) was used. The product was a pale yellow solid (11.1 mg, yield 42%) with a *Z/E* ratio of 71:29. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 4H), 6.89 (d, *J* = 8.7 Hz, 4H), 5.42 (dd, *J* = 11.0, 6.4 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 4H), 3.88 (s, 6H), 2.12 (dd, *J* = 12.8, 7.0 Hz, 4H), 1.88–1.72 (m, 4H), 1.59–1.47 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 162.9, 131.6, 129.8, 114.0, 68.0, 51.8, 28.7, 26.9, 26.0 ppm. ESI-MS$[M+Na]^+$ calcd for $C_{26}H_{32}O_6$: 440.5360; found: 463.2089. Analytical Data. Found (calcd) for: $C_{26}H_{32}O_6$ C, 70.89 (70.81); H, 7.32 (7.24).

For (*Z*)-dec-5-ene-1,10-diyl dibenzoate (**36**), complex **11** (9.8 mg, 10.0 mol%) was used. The product was a pale yellow oil (10.7 mg, yield 47%) with a *Z/E* ratio of 75:25. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 4H), 5.56–5.31 (m, 2H), 4.32 (t, *J* = 6.5 Hz, 4H), 2.12 (dd, *J* = 12.8, 7.1 Hz, 4H), 1.78 (dd, *J* = 10.4, 4.7 Hz, 4H), 1.61–1.41 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.7, 132.8, 130.4, 129.8, 129.5, 128.3, 64.9, 32.1, 28.4, 28.2, 26.8, 26.1, 26.0 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{24}H_{28}O_4$: 380.4840, found: 403.1882. Analytical Data. Found (calcd) for: $C_{24}H_{28}O_4$ C, 75.76 (75.71); H, 7.42 (7.39).

For (*Z*)-1,10-bis(2-nitrophenoxy)dec-5-ene (**37**), complex **11** (9.8 mg, 10.0 mol%) was used. The product was a white solid (8.5 mg, yield 34%) with a *Z/E* ratio of 77:23. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.50 (ddd, *J* = 8.5, 7.5, 1.7 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.04–6.91 (m, 2H), 5.40 (t, *J* = 4.6 Hz, 2H), 4.10 (dd, *J* = 7.5, 5.2 Hz, 4H), 2.11 (dd, *J* = 12.8, 7.3 Hz, 4H), 1.92–1.74 (m, 4H), 1.58– 1.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.47, 133.96, 129.82, 125.49, 120.03, 114.49, 69.50, 28.56, 26.79, 25.91. ESI-MS $[M+H]^+$ calcd for $C_{22}H_{26}N_2O_6$: 414.1791, found: 415.1860. Analytical Data. Found (calcd) for: $C_{22}H_{26}N_2O_6$ C, 63.76 (63.77); H, 6.32 (6.31); N, 6.76 (7.75).

For (*Z*)-10-(1,3-dioxoisoindolin-2-yl)dec-5-en-1-yl benzoate (**38**), an oven-dried 10 mL vial equipped with a magnetic stir bar was charged with hex-5-en-1-yl benzoate (0.6 mmol) and 2-(hex-5-en-1-yl)isoindoline-1,3-dione (0.9 mmol). Complex **11** (4.9 mg, 10.0 mol%) was used. The product was a pale yellow oil (6.6 mg, yield 27%) with a *Z/E* ratio of 70:30. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.82 (dd, *J* = 5.3, 2.8 Hz, 2H), 7.69 (dd, *J* = 5.1, 3.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.49 –5.30 (m, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.15–1.98 (m, 4H), 1.75 (dt, *J* = 13.3, 6.8 Hz, 2H), 1.71–1.63 (m, 2H), 1.50 (dt, *J* = 14.7, 7.5 Hz, 2H), 1.40 (dt, *J* = 14.9, 7.5 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.4, 133.8, 132.8, 132.2, 130.3, 129.5, 128.3, 123.1, 65.0, 37.9, 32.1, 28.1, 26.7, 25.9 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{25}H_{27}NO_4$: 405.4940, found: 428.1836. Analytical Data. Found (calcd) for: $C_{25}H_{27}NO_4$ C, 74.05 (74.00); H, 6.71 (6.66); N, 3.45 (3.40).

Conflicts of interest

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There are no conflicts to declare.

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