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ARTICLE

Synthesis, Catalysis, and DFT Study of A Ruthenium Carbene Complex Bearing A 1,2-Dicarbadodecaborane (12)-1,2-Dithiolate Ligand

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Ruthenium carbene catalyst containing a 1,2-dicarbadodecaborane(12)-1,2-dithiolate ligand was synthesized, and the structure was determined by single crystal x-ray diffraction. This new ruthenium carbene catalyst can catalyze ring opening metathesis polymerization (ROMP) reaction of norbornene to give the corresponding *Z*-polymer (*Z*/*E* ratio, 98:2) in high yield (93%); ring opening cross metathesis (ROCM) reactions of norbornene/5-norbornene-2-*exo*, 3-*exo*-dimethanol with styrene or 4-fluorostyrene to give the corresponding *Z*-olefin products (*Z*/*E* ratios, 97:3-98:2), respectively, in high yields (73%-88%); Cross metathesis (CM) reactions of terminal alkenes with (*Z*)-but-2-ene-1,4-diol to give high *Z*-olefin products in low yields. Homometathesis reactions of terminal alkenes to give olefin products in low yields. Like other ruthenium carbene catalysts, the new complex tolerates many different functional groups. DFT calculation was also performed in order to understand the process of forming *Z*-olefin products and the decomposition process of catalysts.

Introduction

The olefin metathesis reaction is a simple, fast, and efficient tool for constructing complex molecules. These reactions usually produce few by-products, which is important from a green chemistry standpoint. Olefin metathesis has been widely applied to many synthetic fields, including synthetic chemicals,[1] pharmaceuticals and biotechnology,[2] functional polymer materials.[3] The success of olefin metathesis has stemmed from the discovery of air and moisture stable ruthenium carbene catalysts which are tolerant to many different functional groups.[4] These catalysts are highly selective for *E*-olefin products in cross metathesis (CM) reactions and in the construction of macrocyclic compounds *via* ring closing metathesis (RCM) reactions. However, since many natural products and pharmaceutical molecules[5] contain *Z*-olefin structures, a critical challenge for olefin metathesis reactions is the production of *Z*-olefin products.

In this context, some new metathesis catalysts with *Z*-selectivity have been developed. For example, a molybdenum aryloxy complex **1** (Chart 1) with a pyrryl ligand has been found to give some *Z*-olefin products in ring-opening cross-metathesis (ROCM) reactions.[6] Subsequently, a series of *Z*-selective complexes containing molybdenum or tungsten were developed using a similar structure,[7] and these complexes were successfully applied to the synthesis of macrocyclic molecules through CM and RCM reactions[8a, 8b]. Some molybdenum- and tungsten-based catalysts show excellent *Z*-selectivity and high reactivity, especially in sterically hindered systems. In addition to biological products, a tungsten oxo alkylidene catalyst has been demonstrated to promote ring-closing metathesis reactions to form 45-membered macrocycle compounds with *Z*-selectively.[8c] These works on molybdenum and tungsten catalysts has enhanced the development of ruthenium carbene catalysts. In 2011, a ruthenium-based *Z*-selective olefin metathesis catalyst **2** (Chart 1) was developed.[9] Complex **2** can catalyze CM reactions of terminal olefins to give *Z*-olefin dimer products with excellent selectivity. Further studies have shown that complex **3** (Chart 1),[10] which is formed by replacing the carboxyl in **2** with a nitrate ligand, has better catalytic activity and selectivity than **2**. Using a more hindered NHC ligand also increases the activity and Z-selectivity of the catalyst.[11] These *Z*-selective catalysts can be used in a wide variety of CM reactions, including the synthesis of industrial products.[12] In addition these ruthenium based

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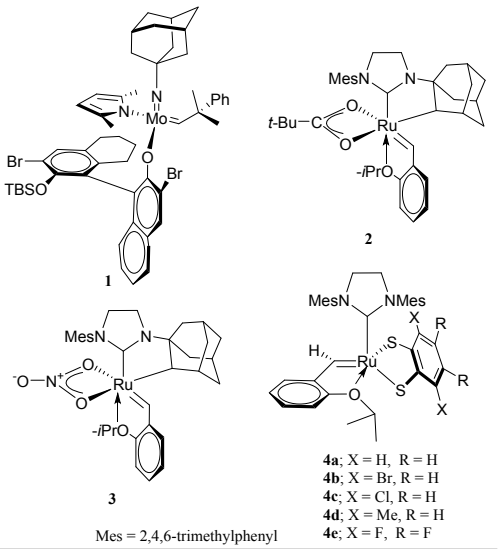
catalysts tolerate many functional groups, and efficiently convert olefins in different solvents and at various temperatures while maintaining excellent *Z*-selectivity.[13] The development of these *Z*-selective ruthenium carbene catalysts has further expanded the range of olefin metathesis reactions.

In the quest to further expand the scope of metathesis reactions, complex **4a** (Chart 1), in which the two chlorides of the Hoveyda-Grubbs second generation catalyst were substituted with a benzene dithiolate ligand was developed in 2013.[14] This catalyst was found to catalyze the ring opening metathesis reaction of a substrate with a highly strained cyclic olefin to give a *Z*-selective product. Later on, complexes **4b**-**e** (Chart 1) with substituted benzene dithiolate ligands were found to have even better stabilities and catalytic activities.[15] These complexes all have good functional group tolerance and give highly *Z*-olefin products in the CM reactions of (*Z*)-but-2-ene-1,4-diol and terminal alkenes. These ruthenium dithiolate catalysts have simple structures which are easily constructed and they have good functional groups tolerance. Thus they have good prospects for future applications.[15-18]

Chart 1. *Z*-selective catalysts for olefin metathesis

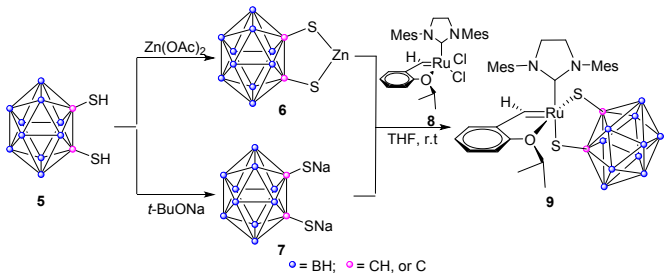


Carborane is a polyhedron composed of carbon and boron atoms. Due to the special bonding characteristics of boron, the electrons are delocalized over the whole polyhedron and the compound is as stable as benzene. However, the electron deficient property of borane gives caborane a stronger electron withdrawing property than benzene when functionalized at carbon atoms.[19, 20] For example, the acidity of 1-hydroxy-1,2-dicarbadodecaborane, in which the hydroxyl group is linked to a 1,2-dicarbadodecaborane, is between 4-nitrophenol and 2,4-dinitrophenol.[21] Moreover, carborane possesses a three-dimensional polyhedron structure which is more sterically hindered that the planar structure of a benzene ring,[22] and carboranes were often used in ligand design and catalysis.[23] 1,2-dicarbadodecaborane has large space constraints, and plays an electron withdrawing effect when contacting at carbon atoms. These two properties may increase the stability of the catalyst by weakening the nucleophilic properties of sulfur atoms and inhibiting the nucleophilic reaction of sulfur atoms to benzylidene carbon. Similar example for steric protection against nucleophilic attack at the benzylidene carbon has been reported by Fogg et al.[24] Under this context, a new ruthenium carbene catalyst bearing a 1,2-dicarbadodecaborane(12)-1,2-dithiolate ligand was synthesized and the catalytic activity of this complex is reported herein.

Results and discussion

The new Ru complex containing 1,2-dicarbadodecaborane (12)-1,2-dithiolate ligand could be synthesized *via* two different pathways, which are depicted in Scheme 1. In the first pathway, 1,2-dicarbadodecaborane(12)-1,2-dithiol was first converted to the corresponding zinc salt (**6**) in high yield (87%). The zinc salt **6** was then treated with the Hoveyda-Grubbs second generation catalyst (**8**) in THF at room temperature to give the desired product **9** in a 65% yield. In the second pathway, 1,2-dicarbadodecaborane(12)-1,2-dithiol was treated with sodium tert-butoxide (1:2 equivalent) in CH_3OH at room temperature to quantitatively give sodium 1,2-dicarbadodecaborane(12)-1,2-dithiolate (**7**) in a high yield (93%). The sodium dithiolate **7** and **8** were stirred in THF at 22 °C for two hours to give the ruthenium based complex **9** as an orange-brown solid in good yield (72%). The ^{1}H NMR spectra of the complex contained singlet peaks at values of δ1.43-2.60 ppm, and 15.55 ppm which correspond to the carborane and benzylidene carbene protons respectively. This indicates that the ligand exchange was successful.

Scheme 1. Synthesis of 1,2-dicarbadodecaborane(12)-1,2-dithiolate chelating ruthenium carbene catalyst **9**



A single crystal of the complex **9** was grown by slow evaporation from a CH_2Cl_2/*n*-hexane mixture solution at -5 °C under N_2. The structure of **9** determined by single X-ray diffraction is shown in Figure 1. The arrangement of the ligand around the metal center is similar to that found in Hoveyda complexes.[18] Compound **9** has a slightly deformed trigonalbipyramidal structure with the NHC carbene, two sulfide, the phenyl oxide, and the benzylidene carbene ligand seated around the Ru metal center. The bond distance between the sulfur and the Ru center Ru1-S1 is 2.2813 (7) Å which is longer than that in **4b** [2.247 (2) Å], **4c** [2.2706 (10) Å] and **4e** [2.2759 (5) Å], but little short than **4a** [2.2830 (6) Å]. Ru1-S2 [2.3215 (7) Å] is longer than that in **4a** [2.2933 (6) Å]， **4b** [2.295 (2) Å], **4c** [2.2954 (9) Å] and **4e** [2.3160 (5) Å]. The S1-Ru1-S2 [91.75 (2)°] bond angles is larger than the corresponding angles in **4a** [87.98 (2)°], **4b** [88.17 (7)°], **4c** [88.23 (3)°] and **4e** [88.740 (16)°]. These results show that the introduction of a 1,2-dicarbadodecaborane (12)-1,2-dithiol tag changed the structure of the catalytic center.

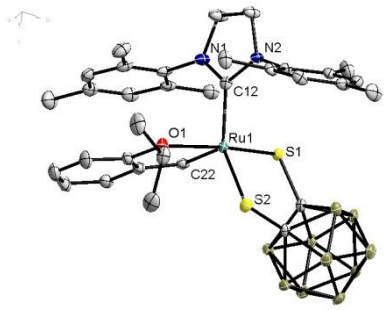
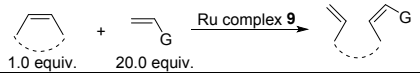
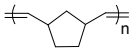
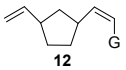
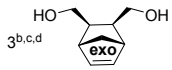
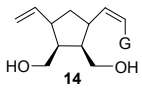
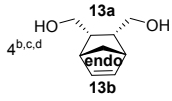


Figure 1 Perspective view of **9**. Ellipsoids are drawn at the 50% probability. For clarity, the solvents and all hydrogen atoms have been omitted. See the supporting materials for detailed bond lengths and angles (Å).

The catalytic activity of **9** to the ring opening metathesis polymerization (ROMP) reaction of norbornene (**10**) was initially detected. The results were shown in Table 1. ROMP of **10** in the presence of **9** (0.1 mol%) gave the corresponding *Z*-polymer (**11**)(*Z*/*E* ratio, 98:2) in high yield (93%). When the loading of catalyst was reduced to 0.005 mol%, the turnover number (TON) of the catalyst **9** reached up to 5900. Next, the ring opening cross metathesis (ROCM) reaction of **10** with styrene or 4-fluorostyrene

Table 1 *Z*-selective ROMP and ROCM of Ru-based catalyst for norbornene and 5-norbornene-2-*exo*, 3-*exo*-dimethanol



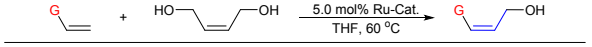
entry	substrate	G	cat.	product	con./yield	*Z*/*E*
1[a,c,d]	 **10**	------	0.1 mol% 0.005 mol%	 **11**	>99%/93% 44%/28%	98:2 98:2
2[b,c,d]	 **10**	a. C_6H_5	1 mol% 3 mol%	 **12**	>99%/42% >99%/73%	98:2 98:2
		b. 4-FC_6H_4	1 mol% 3 mol%		>99%/36% >99%/77%	98:2 98:2
3[b,c,d]	 **13a**	a. C_6H_5	1 mol% 3 mol%	 **14**	>78%/51% >99%/88%	97:3 98:2
		b. 4-FC_6H_4	1 mol% 3 mol%		>83%/46% >99%/80%	98:2 98:2
4[b,c,d]	 **13b**	a. C_6H_5	5 mol%	------	---/---	------
		b. 4-FC_6H_4	5 mol%	------	---/---	------

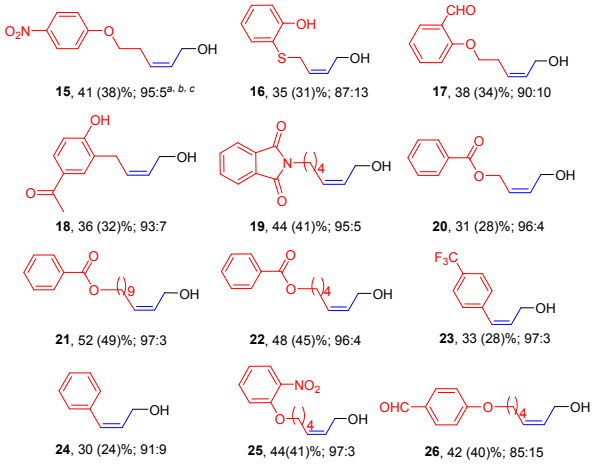
[a] Solvent: CH_2Cl_2; time: 1h; temperature: 22 °C; [b] Solvent: THF; time: 1h; temperature: 40 °C; [c] Conversions and Z/E were determined by analysis of ^{1}H NMR spectra of the mixtures; [d] Yields are based on isolated pure products.

using **9** as the catalyst in THF at 40 °C were studied. The desired olefin products with high *Z*/*E* ratios (98:2) were obtained in 42% and 36%, respectively, at low loading of **9** (1.0 mol%). However, it respectively gave 73% and 77% yields of olefin products with high *Z*/*E* ratios (98:2) when the catalyst loading was increased to 3.0 mol%. Similarly, the ROCM reactions of 5-norbornene-2-*exo*, 3-*exo*-dimethanol (**13a**) with styrene or 4-fluorostyrene using complex **9** (3 mol%) as the catalyst also gave the desired *Z*-products in 88% and 80% respectively. These results are comparable to those of **4a**.[14] However, 5-norbornene-2-*endo*, 3-*endo*-dimethanol does not undergo ROCM reactions with styrene or 4-fluorostyrene, even using considerable amount of **9** at elevated temperatures. The results indicate that the steric hindrance of the substrate plays an important role in the catalytic reaction.

Next, the catalytic activity and *Z*-stereoretentive of **9** for CM reactions of terminal olefins and (*Z*)-but-2-ene-1,4-diol were tested and the results are shown in Table 2. The CM reactions in THF at 60 °C in the presence of **9** (5.0 mol%) under N_2 proceeded smoothly to give an array of *Z*-alkenyl alcohols. The products all had high stereoretentives (*Z*:*E* 85:15 to 97:3). Like other ruthenium based olefin metathesis catalysts, **9** tolerate many different functional groups. For example, CM occurred between (*Z*)-but-2-ene-1,4-diol and terminal alkenes with hydroxyl (**16** and **18**), ketone (**18**), and aldehyde (**17**, **26**) groups. In addition the CM reaction was successful for olefins with different chain lengths (**20**-**22**) and longer chains gave higher yield. Non-conjugated olefins with alkyl chains (**15**-**22**) were more active and had better *Z*-product selectivity than conjugated olefins with aryl groups (**23** and **24**).

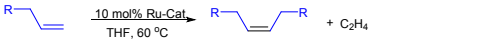
Table 2 *Z*-stereoretentive study of Ru-based catalyst 9 in CM reactions of different terminal alkenes and (*Z*)-but-2-ene-1,4-diol

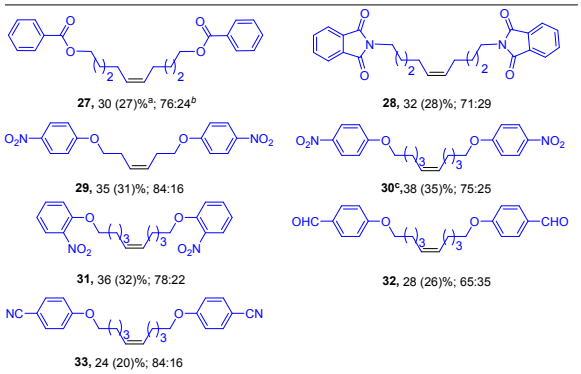




[a] Reaction duration: 6 h; Solvent: THF (0.5 mL); Temperature: 60 °C; Ru complex: 5 mol%; Terminal alkenes: 1.0 equiv.; (Z)-but-2-ene-1,4-diol: 2.0 equiv., under N_2; [b] Conversions and Z/E were determined by analysis of ^{1}H NMR spectra of the mixtures; [c] Yields are based on isolated pure products.

Table 3 *Z*-selective cross-metathesis of Ru-based catalyst for terminal olefins





[a] Except where noted, the catalytic reactions were performed in THF (0.5 mL) at 60 °C for 8 h under nitrogen in the presence of **9** (5 mol%). [b] Conversions and Z/E were determined by analysis of ^{1}H NMR spectra of the unpurified mixtures. [c] Yields are based on isolated pure products.

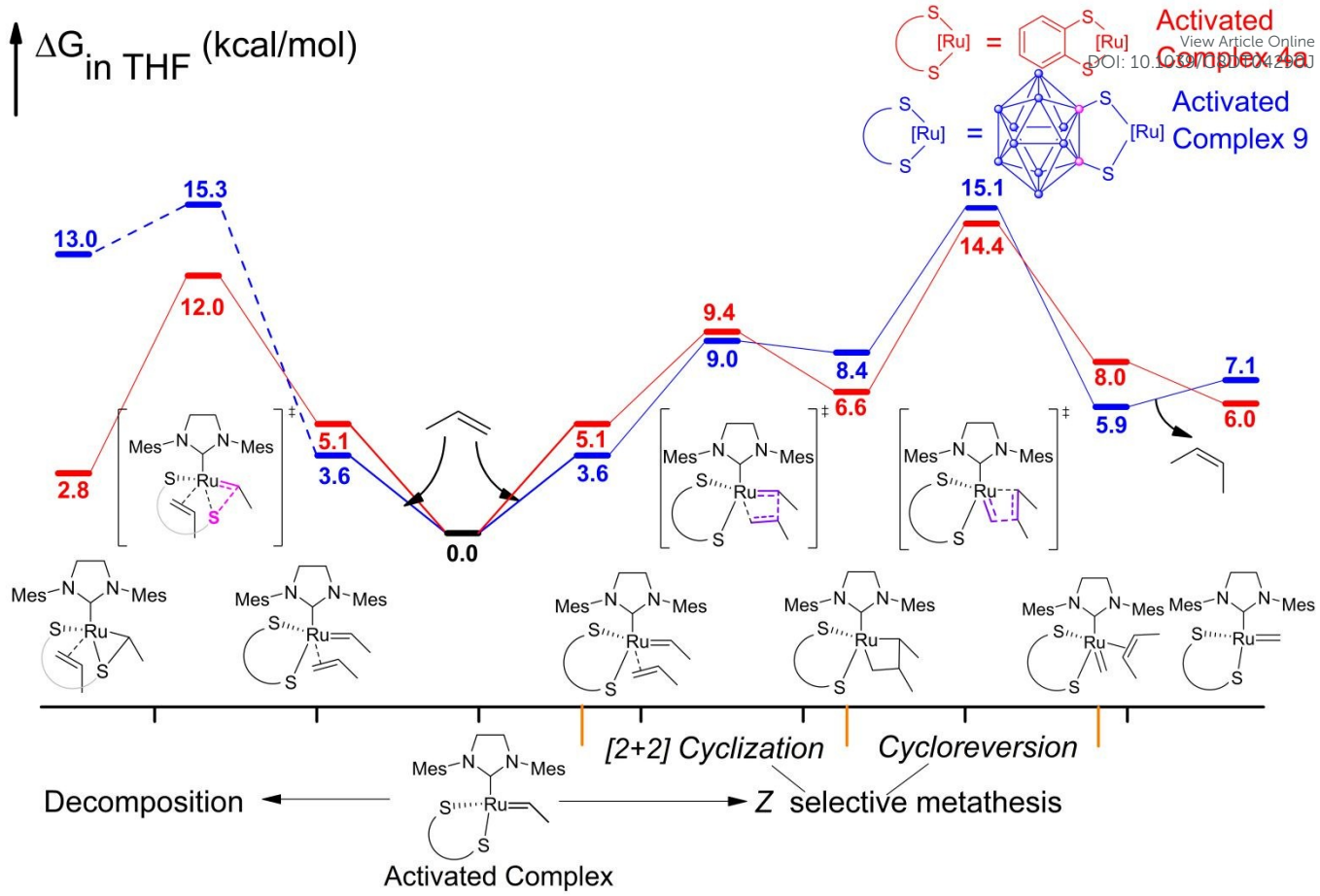


Figure 2 Reaction pathway of propene convert to (*Z*)-2-butene and S-shift decomposition with Gibbs free energy of all intermediates and transition states by calculated

During the catalyst **9**-mediated CM reactions between terminal olefins and (*Z*)-but-2-ene-1,4-diol, occasionally small amounts of the terminal olefins homocoupled products were observed. So, homometathesis reactions of terminal olefins were investigated using **9** as the catalyst (Table 3, **27** to **33**). Although the dimeric olefin products were obtained in relatively low yields, the *Z*-olefin products were found as the major isomers (*Z*:*E* 65:35 to 84:16). The homocoupling metathesis yields of olefins with aldehyde (**32**) and cyano (**33**) substituent are lower than that of olefin having other substituents. However, *Z*-olefin isomers were found as the major product in these reactions, indicating that catalyst **9** is able to selectively generate *Z*-olefin products without inheriting the original configuration of the substrates.

For simplification, propene was selected as the model molecule for the metathesis reactions and the activated catalyst **9** and **4a** as CH_3CH=[Ru] carbene complex was considered to represent complex **9** and **4a**. The schematic pathways of the continuous coupling metathesis of complex **9** with propene leading to (*Z*)-2-butene are indicated as the blue line in Figure 2. We sought to determine whether replacement of catechothiolate by *o*-carboranedithiol as the catalyst ligand could reduce the rate of catalyst decomposition; thus, complex **4a**, which was previously studied by Hoveyda's group[15], was also considered here, as indicated by the red line in Figure 2. Acidity is an evident difference between the two ligands, and the low electron density of *o*-carboranedithiol causes low endergonicity during olefin coordination (3.6 kcal/mol vs. 5.1 kcal/mol).

In 2015, Hoveyda's group[15] suggested that the catalyst decomposition pathway may involve a sulfide shift leading to generation of a catalytically inactive Ru-alkyl species. Figure 2 also shows this decomposition mechanism after propene coordinates to the Ru (II) center of complexes **9** and **4a**. The free-energy barrier of the sulfide shift in complex **9** with *o*-carboranedithiol as the ligand is 11.7 kcal/mol, which is larger than the corresponding barrier of the product of *Z*-selective (6.7 kcal/mol) metathesis; the latter further presents advantages in $\Delta G^{\neq}$ compared with the sulfide shift process (15.1 kcal/mol vs. 15.3 kcal/mol). In addition, the product of *Z*-selective metathesis is more thermodynamically stable than that of sulfide-shift decomposition (7.1 kcal/mol vs. 13.0 kcal/mol). However, when catechothiolate is applied as the catalyst ligand, the free-energy barrier of the sulfide shift is only 6.9 kcal/mol, which is lower than the free-energy barrier of *Z*-selective metathesis (6.9 kcal/mol vs. 7.8 kcal/mol). The same finding is obtained by inspecting the $\Delta G^{\neq}$ of the sulfide-shift decomposition and *Z*-selective metathesis pathways (12.0 kcal/mol vs. 14.4 kcal/mol). The product of *Z*-selective metathesis is more thermodynamically unstable than that obtained from sulfide-shift decomposition (6.0 kcal/mol vs. 2.8 kcal/mol), resulting in side reactions and deactivation of the *Z*-selective metathesis catalyst.

Interestingly, replacement of catechothiolate with *o*-carboranedithiol could substantially improve the stability of the

catalyst. A catalyst is more prone to decomposition with catechothiolate as a ligand, and its stability and *Z*-selectivity may decrease during reaction.

Conclusions

In summary, a 1,2-dicarbadodecaborane(12)-1,2-dithiolate chelating Ru carbene catalyst **9** with high activity and *Z*-selectivity was synthesized. Although the core structure of **9** is similar to those of reported benzene disulfide chelated analogues, the activity and selectivity of **9** is different which is due to the strongly electron deficient nature and steric bulkiness of the 1,2-dicarbadodecaborane(12) ligand. Catalyst **9** can catalyze the ROMP/ROCM reactions to give high yields and *Z/E* ratios. The CM reactions of terminal alkenes with (*Z*)-but-2-ene-1,4-diol, or homo-metathesis of terminal alkenes using **9** as catalyst also gave *Z*-olefins as major products. Like other ruthenium-based catalysts, **9** is able to tolerate many different functional groups and is suitable for many substrates. The introduction of a 1,2-dicarbadodecaborane(12)-1,2-dithiolate ligand to the Ru center improved the stability and reactivity of the catalyst, which were consistent with the DFT calculations. In addition, this work provides a theoretical basis for the synthesis and design of other efficient metal catalysts. Further, studies on the application of this 1,2-dicarbadodecaborane (12)-1,2-dithiolate chelating Ru carbene catalyst to the synthesis of functional molecules and polymers is currently ongoing in our this laboratories.

Experimental

General Procedures

^{1}H-NMR and ^{13}C-NMR spectra were acquired in $CDCl_3$ on Bruker (AVANCE III) 600 MHz or Bruker (AVANCE III) 400 MHz spectrometers. If not otherwise noted, chemical shift values of are reported as values in ppm relative to residual $CDCl_3$ (*J* =7.26) for ^{1}H-NMR spectra, relative to $CDCl_3$ (77.1 ppm) for ^{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). Coupling constants (*J*) are quoted in Hz. at 400 MHz or 600 MHz for ^{1}H. High-resolution mass spectra were provided using Bruker Daltonics matrix assisted laser desorption tandem time of flight mass spectrometry the (Autoflex tof/tof III). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303 instrument. Elemental analyses were performed by the Elemental Analysis Section of Tianjin University.

Materials and Methods

Unless otherwise noted, all reactions were performed under an atmosphere of dry N_2 with oven-dried glassware and anhydrous solvents with standard dry box or vacuum line techniques. Toluene, THF, hexane and Et_2O was distilled from sodium/benzophenone under a N_2 atmosphere. Methanol 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 on 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 DMSO-d_6 were purchased from TCI and used as received. 1-(but-3-enoxyl)-4-nitrobenzoate[25], N-(5-hexenyl)phthalimide[26], 1-[4-hydroxy-3-(2-propen-1-yl)phenyl]ethanone[27], 2-propenyl benzoate[28], 5-hexenyl benzoate[29], 10-undecenyl benzoate[30], 1,2-dicarbadodecaborane(12)-1,2-dithiol (**5**)[31], 2-(allylthio)phenol[32], 2-(but-3-en-1-yloxy)benzaldehyde[33]. All other chemicals or reagents were obtained from commercial sources.

In order to evaluate the stability of the catalyst in the reaction, the formation of *Z*-products, and the decomposition of catalysts were performed by using DFT calculations. All calculations were performed using Gaussian 09 package[34]. Geometry optimizations were performed at the theory level of B3LYP-D3BJ[35-37]/LanL2dz[38] for Ru and 6-31G(d)[39] for other atoms in the gas phase. Frequency correction factors[40] were used for thermal corrections to Gibbs free energy after frequency calculations at the same level. Single-point electronic energy calculations were performed at the level of M06-D3[41]/def2-TZVP[42] for Ru and 6-311+G (2df, 2p) for other atoms, and in conjunction with the SMD[43] model to account for the solvation effect of THF. The Computed structures were illustrated by using CYL View[44].

Experimental details

Preparation of zinc 1,2-dicarbadodecaborane(12)-1,2-dithiolate (**6**): In an N_2 filled glove box, a solution of $Zn(OAc)_2 \bullet 2H_2O$ (878 mg, 4.00 mmol, 2.0 equiv.) andethylenediamine (0.40 mL, 6.00 mmol, 3.0 equiv.) in *i*-PrOH (8 mL) is transferred to a vial containing 5 (416.6 mg, 2.00 mmol, 1.0 equiv.), and the resulting mixture is allowed to stir for 1h at 22 °C. The precipitated solid was filtered, washed with methanol (5.0 mL) and hot chloroform (5.0 mL), and dried in a vacuum to afford zinc 1,2-dicarbadodecaborane(12)- 1,2-dithiolate (**6**) (472.7 mg, 1.74 mmol, 87% yield) as white solid.

Preparation of sodium 1,2-dicarbadodecaborane(12)-1,2-dithiolate (**7**): In an N_2 filled glove box, a solution of sodium tert-butoxide (427.1 mg, 4.40 mmol, 2.2 equiv.) in methanol (8.2 mL) is transferred to a vial containing **5** (416.6 mg, 2.00 mmol, 1.0 equiv.), and the resulting mixture is allowed to stir for 30 minutes at 50 °C. The mixture is cooled to room temperature followed by evaporation of solvent under vacuum. The residue is transferred to a fritted funnel and washed with tetrahydrofuran (10 mL). After removal of solvents in vacuo, **7** is obtained as white solid (469.1 mg, 1.86 mmol, 93% yield). **7** may contain a small amount of impurities, such as boric acid and deboronated cluster $\{C_2B_9\}$. These impurities are difficult to separate, but they do not affect the next reaction, so the sodium salt can be directly carried out in the next reactions without further purification. ^{1}H{^{11}B} (400 MHz, MeOD) δ 2.53 (s, 4H), 2.14 (s, 2H), 1.69-1.63 (d, *J* = 23.0 Hz, 4H). ^{13}C{^{1}H} NMR

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(100 MHz, MeOD-d_4) δ 102.20 ppm. ^{11}B NMR (128 MHz, MeOD-d_4) δ -2.60, -3.75, -6.89, -7.84, -9.98, -11.05, -12.14, -13.30 ppm. δ IR (KBr): *v* 3608, 3539, 2588, 2561, 2060, 1626, 1444, 1305, 1067, 1050, 1006, 972, 944, 889, 727, 516 cm^{-1}.

Preparation of Ru-based dithiolate complex **(9)**: To a 2-dram vial charged with a stir bar and sodium 1,2-dicarbadodecaborane(12)-1,2-dithiolate (60.5 mg, 0.24 mmol, 1.2 equiv.) under N_2 atmosphere, a solution of Ru complex **8** (125.2 mg, 0.20 mmol, 1.0 equiv.) in tetrahydrofuran (4.0 mL) is added. The resulting mixture is allowed to stir at 22 °C for three hours, and then the solvent is evaporated under vacuum. Residual tetrahydrofuran is removed through co-evaporation with pentane (2 x 4 mL). The resulting solid is dissolved in dichloromethane and passed through a short column of Celite (4 cm in height), placed in a pipette (0.5 cm diameter), with dichloromethane (10 mL). The filtrate is adsorbed onto fresh Celite and subjected to vacuum until complete dryness. The adsorbed material is loaded onto a second short column of Celite (4 cm in height) and washed with Et_2O (20 mL), after which Ru-based complex is collected upon elution with dichloromethane. After removal of solvents and co-evaporation with pentane, Ru-Based dithiolate complex (**9**) is isolated as an orange-brown solid (109.8 mg, 0.14 mmol, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.55 (s, 1H, Ru=CH), 7.32 – 7.27 (m, 1H, PhH), 7.12 (d, $^3J_{H,H}$ = 6.1 Hz, 2H, PhH), 7.01 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, PhH), 6.88 (s, 1H, PhH), 6.82 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, PhH), 6.71 (d, $^3J_{H,H}$ = 6.6 Hz, 1H, PhH), 5.95 (s, 1H, PhH), 5.16 – 5.02 (m, 1H, $CH(CH_3)_2$), 3.96 (dd, $^3J_{H,H}$ = 22.1, 10.7 Hz, 2H, N-CH_2), 3.73 (t, $^3J_{H,H}$ = 9.8 Hz, 2H, N-CH_2), 2.58 (d, $^3J_{H,H}$ = 15.9 Hz, 6H, $PhCH_3$), 2.44 (s, 3H, $PhCH_3$), 2.17 (d, $^3J_{H,H}$ = 4.1 Hz, 6H, $PhCH_3$), 1.69 (d, $^3J_{H,H}$ = 6.7 Hz, 3H, $CH_3(CHCH_3)$), 1.64 (s, 3H, $PhCH_3$), 1.44 (d, $^3J_{H,H}$ = 6.6 Hz, 3H, $CH_3(CHCH_3)$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 259.35, 214.90, 154.52, 141.23, 139.41, 138.37, 136.12, 135.74, 135.13, 134.51, 130.88, 129.96, 129.16, 128.06, 123.83, 122.12, 115.66, 96.97 (C-*o*-carborane), 86.14, 83.26, 51.84, 51.21, 23.92, 21.29, 21.09, 20.28, 19.17, 18.26, 17.06 ppm. ^{11}B NMR (128 MHz, CD_3CN) δ -3.16, -7.63, -8.65, -10.08, -11.12, -12.21 ppm. ^{11}B{^{1}H} NMR (128 MHz, acetone-d_6) δ -3.03, -6.47, -7.76, -9.36, -11.03 ppm. ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$) δ 15.53 (s, 1H, Ru=CH), 7.26 (m, 1H, PhH), 7.09 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, PhH), 6.98 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, PhH), 6.86 (s, 1H, PhH), 6.79 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, PhH), 6.68 (d, $^3J_{H,H}$ = 7.3 Hz, 1H, PhH), 5.93 (s, 1H, PhH), 5.06 (dt, $^3J_{H,H}$ = 13.4, 6.6 Hz, 1H, $CH(CH_3)_2$), 3.94 (dd, $^3J_{H,H}$ = 23.7, 10.4 Hz, 2H, N-CH_2), 3.74 (d, $^3J_{H,H}$ = 21.5 Hz, 2H, N-CH_2), 2.65 (S, 1H, BH), 2.57 (d, $^3J_{H,H}$ = 14.9 Hz, 6H, $PhCH_3$), 2.44 (s, 3H, $PhCH_3$), 2.33 (S, 1H, BH), 2.22 (S, 2H, BH), 2.17 (d, $^3J_{H,H}$ = 5.8 Hz, 6H, $PhCH_3$), 2.03 (S, 1H, BH), 1.80 (S, 1H, BH), 1.68 (d, $^3J_{H,H}$ = 6.7 Hz, 3H, $CH_3(CHCH_3)$), 1.64 (s, 3H, $PhCH_3$), 1.58 (S, 2H, BH), 1.44 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, $CH_3(CHCH_3)$), 1.42 (S, 1H, BH), 1.34 (S, 1H, BH) ppm. IR (KBr): *v* 3446, 3051, 2981, 2919, 2606 (B-H), 2578 (B-H), 2559 (B-H), 1608, 1588, 1575, 1478, 1452, 1427, 1388, 1374, 1308, 1282, 1266, 1185, 1111, 1033, 917, 848, 755, 731, 576, 419 cm^{-1}. HRMS [M]$^+$ calcd for $C_{33}H_{48}B_{10}N_2ORuS_2$: 762.3255; found: 762.3226.

***Z*-Selective ROMP Reaction**

An oven-dried 10 mL vial equipped with a magnetic stir bar is charged with 0.1 mL CH_2Cl_2 solution which contain complex **9** (0.8 mg, 0.001 mmol), then a solution of norbornene (94.2 mg, 1.0 mmol) in 1.5 mL CH_2Cl_2 is added. The solution is stir for 1 h at room temperature and the solution becomes very viscous. Then MeOH (5 mL) is added, the white poly-norbornene settles out with vigorous stirring. The polymer washed with MeOH (4 mL x 3) and dried under vacuum for 1 h to provide a white solid **11** (87.5 mg, yield 93%) in 98:2 ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 5.11 (m, 2H), 2.81 (dd, *J* = 12.3, 9.6 Hz, 2H), 1.97 – 1.86 (m, 1H), 1.86 – 1.72 (m, 2H), 1.46 – 1.25 (m, 2H), 1.02 (dd, *J* = 22.7, 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.87, 42.71, 38.61, 33.21.

An oven-dried 50 mL vial equipped with a magnetic stir bar is charged with 0.1 mL CH_2Cl_2 solution which contain complex 9 (0.8 mg, 0.001 mmol), then a solution of norbornene (2.0 g, 21.2 mmol) in 10 mL CH_2Cl_2 is added. The solution is stir for 1 h at room temperature and the solution becomes gelatinous form. Then MeOH (10 mL) is added, the white poly-norbornene settles out with vigorous stirring. The polymer washed with MeOH (10 mL x 3) and dried under vacuum for 8 h to provide a white solid **11** (0.5555 g, yield 28%, TON 5900) in 98:2 ratio. 1H NMR (400 MHz, CDCl3) δ 5.32 – 5.11 (m, 2H), 2.81 (dd, J = 12.3, 9.6 Hz, 2H), 1.97 – 1.86 (m, 1H), 1.86 – 1.72 (m, 2H), 1.46 – 1.25 (m, 2H), 1.02 (dd, J = 22.7, 10.4 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 133.87, 42.71, 38.61, 33.21.

***Z*-Selective ROCM Reactions**

General Procedure: An oven-dried 10 mL vial equipped with a magnetic stir bar is charged with alkene substrate (1.0 equiv.) and terminal olefin (20 equiv.) in a fume hood. The vial is then sealed, evacuated and purged with N_2. To this vessel, a solution of complex **9** (1.0-3.0 mol%) in THF is added. The resulting solution is allowed to stir for 6 hours at 40 °C, after which the reaction is concentrated in vacuum. Purification is performed through silica gel chromatography.

((*Z*)-2-((1*S*,3*R*)-3-Vinylcyclopentyl)vinyl)benzene **(12a)**: Complex **9** (3.0 mol%) dissolve in 0.2 mL THF was used. The product was purified by column chromatography with hexane to provide a colorless oil (22.9 mg, yield 73%) in 98:2 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 2H), 7.29 – 7.17 (m, 3H), 6.36 (d, *J* = 11.5 Hz, 1H), 5.82 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.58 (dd, *J* = 11.5, 10.1 Hz, 1H), 4.94 (dddd, *J* = 34.5, 10.2, 1.9, 1.1 Hz, 2H), 3.16 – 2.93 (m, 1H), 2.64 – 2.43 (m, 1H), 2.09 – 1.97 (m, 1H), 1.97 – 1.76 (m, 2H), 1.54 – 1.43 (m, 2H), 1.27 – 1.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.07, 137.90, 128.63, 128.16, 127.63, 126.51, 112.58, 44.58, 41.48, 38.72, 33.06, 31.96.

(*Z*)-1-Fluoro-4-(2-((1S,3R)3-vinylcyclopentyl)vinyl)benzene **(12b)**: Complex **9** (3.0 mol%) dissolve in 0.2 mL THF was added. The product was purified by column chromatography with hexane to provide a colorless oil (26.4 mg, yield 77%) in 98:2

Z/E ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 2H), 7.11 – 6.91 (m, 2H), 6.32 (d, *J* = 11.5 Hz, 1H), 5.83 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.58 (dd, *J* = 11.3, 10.2 Hz, 1H), 4.96 (dddd, *J* = 33.9, 10.2, 1.8, 1.1 Hz, 2H), 3.10 – 2.90 (m, 1H), 2.64 – 2.45 (m, 1H), 2.12 – 1.96 (m, 1H), 1.96 – 1.78 (m, 2H), 1.58 – 1.44 (m, 2H), 1.23 (dt, *J* = 12.4, 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.75, 160.31, 142.95, 137.89, 133.79, 130.11, 126.52, 115.12, 114.91, 112.65, 44.56, 41.39, 38.58, 32.99, 31.93.

3-((*Z*)-Styryl)-5-vinylcyclopentane-1, 2-diyl)dimethanol **(14a)**: Complex **9** (3.0 mol%) dissolve in 0.2 mL THF was added. The product was purified by column chromatography with hexane/ether (3/7) to provide a colorless oil (22.0 mg, yield 88%) in 98:2 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 6.47 (d, *J* = 11.5 Hz, 1H), 5.74 (ddd, *J* = 17.8, 10.1, 7.8 Hz, 1H), 5.52 (dd, *J* = 11.5, 10.2 Hz, 1H), 5.09 – 4.91 (m, 2H), 3.64 (d, *J* = 18.3 Hz, 2H), 3.60 – 3.40 (m, 3H), 3.28 (s, 1H), 2.73 (ddd, *J* = 16.7, 10.4, 6.4 Hz, 1H), 2.24 – 2.15 (m, 1H), 2.15 – 2.06 (m, 2H), 2.06 – 1.95 (m, 1H), 1.36 (dd, *J* = 23.3, 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.40, 137.44, 135.81, 129.80, 128.41, 126.75, 114.54, 61.92, 50.45, 48.48, 46.32, 40.14, 39.77.

3-((*Z*)-4-Fluorostyryl)-5-vinylcyclopentane-1,2-diyl)dimethanol **(14b)**: Complex **9** (3.0 mol%) dissolve in 0.2 mL THF was added. The product was purified by column chromatography with hexane/ether (3/7) to provide a colorless oil (21.5 mg, yield 80%) in 98:2 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.73 (ddd, *J* = 17.8, 10.1, 7.8 Hz, 1H), 5.50 (dd, *J* = 11.3, 10.3 Hz, 1H), 5.08 – 4.93 (m, 2H), 3.62 (d, *J* = 3.3 Hz, 2H), 3.62 – 3.44 (m, 4H), 2.79 – 2.57 (m, 1H), 2.25 – 2.15 (m, 1H), 2.11 (dd, *J* = 9.3, 5.8 Hz, 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 162.83, 160.38, 141.27, 135.83, 133.41, 130.06, 128.68, 115.29, 115.08, 114.63, 61.85, 50.40, 48.42, 46.31, 40.06, 39.71.

***Z*-Selective CM Reactions**

General Procedure: An oven-dried 10 mL vial equipped with a magnetic stir bar is charged with alkene substrate (1.0 equiv.) and *Z*-2-butene-1,4-diol (2.0 equiv.) in a fume hood. The vial is then sealed, evacuated and purged with N_2. To this vessel, a solution of Ru-based complex (5.0 mol %) in tetrahydrofuran (0.5 mL) is added. The resulting solution is allowed to stir for 8 hours at 60 °C, after which the reaction is concentrated in vacuo (percent conversion determined by 400 MHz ^{1}H NMR analysis). Purification is performed through silica gel chromatography.

(*Z*)-5-(4-nitrophenoxy)pent-2-en-1-ol (**15**)[15]: This was purified by column chromatography to provide brown oil (yield 38%) in 95:5 *Z/E* ratio. ^{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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.77, 131.72, 127.48, 125.93, 114.44, 67.90, 58.47, 27.38.

(*Z*)-2-((4-Hydroxybut-2-en-1-yl)thio)phenol **(16)**: This was purified by column chromatography to provide yellow oil (yield 31%) in 87:13 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 5.83 – 5.47 (m, 2H), 4.24 – 3.93 (m, 2H), 3.72 (d, *J* = 5.6 Hz, 2H), 3.36 (d, *J* = 7.0 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.02, 136.76, 132.11, 131.62, 126.62, 120.35, 117.96, 115.27, 57.68, 32.93 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{10}H_{12}O_2S$: 196.2640, found: 219.0448. Analytical Data. Found (calcd) for: $C_{10}H_{12}O_2S$ C, 61.20 (61.15); H, 6.16 (6.22).

(*Z*)-2-((5-Hydroxypent-3-en-1-yl)oxy)benzaldehyde **(17)**: This was purified by column chromatography to provide colorless oil (yield 34%) in 90:10 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H, PhCHO), 7.82 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.91 – 5.74 (m, 1H), 5.66 (dd, *J* = 17.7, 7.9 Hz, 1H), 4.27 (d, *J* = 6.2 Hz, 2H), 4.12 (t, *J* = 6.3 Hz, 2H), 2.67 (dd, *J* = 13.3, 6.6 Hz, 2H), 1.86 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.01, 161.05, 136.02, 131.53, 128.96, 127.63, 124.89, 120.84, 112.54, 67.71, 58.51, 27.53 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).

(*Z*)-1-(4-hydroxy-3-(4-hydroxybut-2-en-1-yl)phenyl)ethan-1-one (**18**)[15]: This was purified by column chromatography to provide off-white solid (yield 32%) in 93:7 *Z/E* ratio. ^{1}H NMR (600 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). ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.68, 159.87, 131.86, 131.25, 129.67, 129.36, 127.57, 125.87, 115.84, 68.00, 58.37, 29.71, 26.30, 25.60.

(*Z*)-2-(7-hydroxyhept-5-en-1-yl)isoindoline-1,3-dione (**19**)[15]: This was purified by column chromatography to provide yellow oil (yield 41%) in 95:5 *Z/E* ratio. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.69 – 5.57 (m, 1H), 5.54 – 5.42 (m, 1H), 4.20 (d, *J* = 6.8 Hz, 2H), 3.80 – 3.45 (m, 2H), 2.20 – 1.99 (m, 2H), 1.75 (s, 1H), 1.73 – 1.59 (m, 2H), 1.51 – 1.37 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.51, 133.96, 132.09, 129.22, 123.24, 58.48, 37.58, 27.76, 26.56, 26.39.

(*Z*)-4-hydroxybut-2-en-1-yl benzoate (**20**)[45]: This was purified by column chromatography to provide yellow oil (yield 28%) in 96:4 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.95 (dt, *J* = 13.0, 7.7 Hz, 1H), 5.84 – 5.62 (m, 1H), 4.96 (d, *J* = 7.0 Hz, 2H), 4.36 (d, *J* = 6.5 Hz, 2H), 2.16 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.69, 133.58, 133.15, 130.01, 129.66, 128.43, 125.62, 60.61, 58.54.

(*Z*)-12-Hydroxydodec-10-en-1-yl benzoate **(21)**: This was purified by column chromatography to provide pale yellow oil (yield 49%) in 97:3 Z/E ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H),

5.66 – 5.56 (m, 1H), 5.56 – 5.44 (m, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 4.19 (t, *J* = 5.1 Hz, 2H), 2.06 (dd, *J* = 13.7 Hz, 6.8, 2H), 1.81 – 1.72 (m, 2H), 1.54 (s, 1H), 1.49 – 1.40 (m, 2H), 1.35(m, 4H), 1.29 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ166.76, 133.23, 132.84, 130.50, 129.55, 128.34, 65.15, 58.63, 29.72, 29.59, 29.46, 29.39, 29.25, 29.18, 28.71, 27.43, 26.02 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{19}H_{28}O_3$: 304.4220, found: 327.1937. Analytical Data Found (calcd) for: $C_{19}H_{28}O_3$ C, 74.96 (74.83); H, 9.27 (9.21).

(Z)-7-Hydroxyhept-5-en-1-yl benzoate **(22)**: This was purified by column chromatography to provide pale yellow oil (yield 45%) in 96:4 *Z/E* ratio. ^1H 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 – 5.51 (m, 1H), 4.33 (t, *J* = 6.6 Hz, 1H), 4.21 (d, *J* = 6.6 Hz, 1H), 2.17 (q, *J* = 7.3 Hz, 1H), 1.81 – 1.76 (m, 1H), 1.67 (s, 1H), 1.54 (dt, *J* = 15.0, 7.5 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.72, 132.93, 132.32, 130.36, 129.56, 129.06, 128.38, 64.76, 58.57, 28.21, 26.95, 25.93 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{14}H_{18}O_3$: 234.2950, found: 257.1154. Analytical Data. Found (calcd) for: $C_{14}H_{18}O_3$ C, 71.77 (71.62); H, 7.74 (7.88).

(*Z*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (**23**)[15]: This was purified by column chromatography to provide pale yellow oil (yield 28%) in 97:3 *Z/E* ratio. ^1H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 11.8 Hz, 1H), 6.08 – 5.93 (m, 1H), 4.42 (d, *J* = 6.4 Hz, 2H), 1.66 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.99, 133.19, 129.82, 129.34, 128.99, 126.50, 125.23, 123.33, 59.48.

(*Z*)-3-phenylprop-2-en-1-ol (**24**)[46]: This was purified by column chromatography to provide pale yellow oil (yield 24%) in 91:9 *Z/E* ratio. ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.24 (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). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.51, 131.11, 128.80, 128.29, 127.30, 59.75.

(*Z*)-7-(2-nitrophenoxy)hept-2-en-1-ol (**25**): This was purified by column chromatography to provide pale yellow oil (yield 41%) in 97:3 *Z/E* ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.49 (ddd, *J* = 9.0, 7.5, 1.7 Hz, 1H), 7.07 – 7.02 (m, 1H), 7.02 – 6.95 (m, 1H), 5.67 – 5.57 (m, 1H), 5.57 – 5.48 (m, 1H), 4.18 (d, *J* = 6.4 Hz, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.61 (s, 1H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.38, 134.04, 132.25, 129.08, 125.51, 120.15, 114.47, 69.34, 58.52, 28.45, 26.95, 25.87. ESI-MS $[M+H]^+$ calcd for $C_{13}H_{17}NO_4$: 251.1158, found: 252.1236. Analytical Data. Found (calcd) for: $C_{13}H_{17}NO_4$ C, 62.14 (62.12); H, 6.82 (6.79); N, 5.57 (5.55).

(*Z*)-4-((7-hydroxyhept-5-en-1-yl)oxy)benzaldehyde (**26**): This was purified by column chromatography to provide pale yellow oil (yield 40%) in 85:15 *Z/E* ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.88 – 7.72 (m, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.71 – 5.60 (m, 1H), 5.55 (dt, *J* = 11.0, 7.3 Hz, 1H), 4.20 (d, *J* = 6.5 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 2.16 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.67 (s, 1H), 1.60 – 1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.85, 164.16, 132.27, 132.01, 129.83, 129.08, 114.75, 68.13, 58.54, 28.56, 27.05, 25.98. ESI-MS [M+H]+ calcd for $C_{14}H_{18}O_3$: 234.1256, found: 235.1329. Analytical Data. Found (calcd) for: $C_{14}H_{18}O_3$ C, 71.77 (71.76); H, 7.74 (7.72).

(*Z*)-dec-5-ene-1,10-diyl dibenzoate **(27)**: This was purified by column chromatography to provide pale yellow oil (yield 27%) in 76:24 Z/E ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 5.41 (t, *J* = 4.6 Hz, 2H), 4.32 (t, *J* = 6.5 Hz, 4H), 2.12 (dd, *J* = 12.6, 7.0 Hz, 4H), 1.82 – 1.70 (m, 4H), 1.52 (dt, *J* = 14.9, 7.5 Hz, 4H). ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 166.70, 132.87, 130.45, 130.33, 129.81, 129.55, 128.35, 64.99, 64.94, 32.16, 28.35, 28.21, 26.85, 26.13, 25.96 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 (75.75); H, 7.42 (7.39).

(*Z*)-2,2'-(dec-5-ene-1,10-diyl)bis(isoindoline-1,3-dione) **(28)**: This was purified by column chromatography to provide brown oil (yield 28%) in 71:29 Z/E ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.4, 3.0 Hz, 4H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 4H), 5.37 (dt, *J* = 9.4, 4.2 Hz, 2H), 3.69 (td, *J* = 7.3, 2.7 Hz, 4H), 2.08 (dd, *J* = 12.7, 7.2 Hz, 4H), 1.69 (dd, *J* = 15.1, 7.5 Hz, 4H), 1.41 (dt, *J* = 15.1, 7.5 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.48, 133.86, 132.16, 130.21, 129.66, 123.18, 37.91, 32.07, 28.18, 28.08, 26.86, 26.71 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 (72.56); H, 6.09 (6.11); N, 6.51 (6.48).

(*Z*)-1,6-bis(4-nitrophenoxy)hex-3-ene **(29)**: This was purified by column chromatography to provide brown oil (yield 31%) in 84:16 Z/E ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.2 Hz, 4H), 6.96 (d, *J* = 9.2 Hz, 4H), 5.69 (t, *J* = 4.8 Hz, 2H), 4.12 (t, *J* = 6.5 Hz, 4H), 2.67 (dd, *J* = 12.0 Hz, 6.3 Hz, 4H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.86, 141.59, 127.55, 125.94, 114.41, 68.00, 27.37 ppm. ESI-MS $[M+Na]^+$ calcd for $C_{18}H_{18}N_2O_6$: 358.3500, found: 381.1056. Analytical Data. Found (calcd) for: $C_{18}H_{18}N_2O_6$ C, 60.33 (60.30); H, 5.06 (5.04); N, 7.82 (7.81).

(*Z*)-1,10-bis(4-nitrophenoxy)dec-5-ene (**30**): This was puri-fied by column chromatography to provide white solid (yield 35%) in 75:25 *Z/E* ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.2 Hz, 1H), 7.01 – 6.82 (m, 1H), 5.56 – 5.32 (m, 1H), 4.05 (t, *J* = 6.4 Hz, 1H), 2.17 – 2.11 (m, 1H), 2.08 (dd, *J* = 11.6, 6.7 Hz, 1H), 2.08 (dd, *J* = 11.6, 6.7 Hz, 1H), 1.82 (dt, *J* = 12.8, 5.7 Hz, 1H), 1.61 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.18, 141.37, 130.31, 129.76, 125.90, 114.39, 68.71, 32.13, 28.43, 25.80 ppm. 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 (63.74); H, 6.32 (6.30); N, 6.76 (7.73).

(*Z*)-1,10-bis(2-nitrophenoxy)dec-5-ene (**31**): This was purified by column chromatography to provide white solid (yield 32%) in 78:22 *Z/E* ratio. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.02 – 6.95 (m, 2H), 5.52 – 5.34 (m, 2H), 4.10 (td, *J* = 6.3, 2.4 Hz, 4H), 2.17 – 1.97 (m, 4H), 1.82 (dd, *J* = 8.6, 6.6 Hz, 4H), 1.56 (dd, *J* = 15.0, 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.48, 140.01,

133.96, 130.34, 129.82, 125.48, 120.00, 114.47, 69.49, 32.02, 28.34, 25.66. 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).

(*Z*)-4,4'-(dec-5-ene-1,10-diylbis(oxy))dibenzaldehyde (**32**): This was purified by column chromatography to provide white solid (yield 26%) in 65:35 Z/E ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 2H), 7.84 (d, *J* = 8.7 Hz, 4H), 7.00 (d, *J* = 8.7 Hz, 4H), 5.53 – 5.36 (m, 2H), 4.06 (t, J = 6.4 Hz, 4H), 2.10 (dd, *J* = 11.6, 6.8 Hz, 4H), 1.91 – 1.77 (m, 4H), 1.62 – 1.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.77, 164.21, 131.98, 130.32, 129.79, 114.74, 68.25, 32.16, 28.58, 26.87, 25.94. ESI-MS $[M+H]^+$ calcd for $C_{24}H_{28}O_4$: 380.1988, found: 381.2057. Analytical Data. Found (calcd) for: $C_{24}H_{28}O_4$ C, 75.76 (75.74); H, 7.42 (7.38).

(*Z*)-4,4'-(dec-5-ene-1,10-diylbis(oxy))dibenzonitrile (**33**): This was purified by column chromatography to provide white solid (yield 20%) in 84:16 *Z/E* ratio. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 4H), 5.43 (t, *J* = 4.7 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 4H), 2.14 (dd, *J* = 12.7, 7.2 Hz, 4H), 1.89 – 1.77 (m, 4H), 1.55 (dd, *J* = 15.1, 7.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.38, 133.97, 129.76, 119.25, 115.16, 110.85 – 110.65, 103.80, 68.23, 28.59, 26.85, 25.99. ESI-MS $[M+H]^+$ calcd for $C_{24}H_{26}N_2O_2$: 374.1994, found: 375.2064. Analytical Data. Found (calcd) for: $C_{24}H_{26}N_2O_2$ C, 76.98 (76.99); H, 7.00 (7.68); N, 7.48 (7.47).

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