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Synthesis and evaluation of Naphthalene-1, 8-dithiolate chelating ruthenium carbene catalyst for *Z*-Stereoretentive olefin metathesis

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ABSTRACT

A highly *Z*-stereoretentive olefin metathesis ruthenium carbene catalyst containing a naphthalene-1,8-dithiol ligand was synthesized, and the structure was determined by single-crystal X-ray diffraction. The new ruthenium carbene catalyst could catalyze cross-metathesis reactions of terminal alkenes with (*Z*)-but-2-ene-1,4-diol to give highly *Z*-stereoretentive products. Like to other ruthenium carbene catalysts, the new complex tolerates many different functional groups.

1. Introduction

Olefin metathesis has become an important method of constructing C—C bonds [1–4] and is widely used to synthesize natural organic compounds, medicines, and polymers [5–10]. In general, the products gained from olefin metathesis catalyzed by traditional ruthenium carbene olefin metathesis catalysts are mixtures of *Z*- and *E*-olefin isomers, in which the *E* isomer is usually the major product because it is thermodynamically preferred. However, *Z*-olefin isomers are widely found in natural open-chain compounds (such as oleic acid and linoleic acid), natural macrocyclic compounds (such as civet ketone), and many pharmaceuticals. To apply olefin metathesis as a tool for synthesizing pharmaceuticals and natural products having *Z*-olefin frameworks [11–14], scholars must redesign traditional ruthenium carbene olefin metathesis catalysts to produce *Z*-olefin products with high selectivity during the catalysis of the olefin metathesis reaction. The design and synthesis of *Z*-selective olefin metathesis catalysts are currently a hot research topic in the olefin metathesis field.

Highly *Z*-selective Mo- or W-based catalysts were first developed by Shrock and Hoveyda in 2008 and 2009. These complexes can catalyze ring-closing metathesis reactions [15], ring-opening metathesis (ROM)/cross metathesis (CM) reactions [16], homocoupling of terminal olefin reactions [17], and ROM polymerization (ROMP) reactions to yield high-*Z*-olefin products [18]. In 2011, Grubbs' group first developed a ruthenium complex **1** (Chart 1, **1**) bearing a carbanion-appended N-heterocyclic carbene (NHC) bidentate ligand. This catalyst can catalyze the CM reaction of terminal olefins to form a high-*Z*-olefin product [5,19]. The successful development of catalyst **1** attracted considerable research attention because it can tolerate many functional groups and extend the application scope of *Z*-selective olefin metathesis reactions. Altering the carboxylate ligand and aryl group of NHC substantially decrease the activity and selectivity of the ruthenium carbene complex, which can catalyze the CM of terminal olefins with high *Z*-selectivity and good functional group adaptability [20,21]. In 2013, Hoveyda's group reported stereogenic Ru complexes **3** and **4** bearing a dithiolate ligand that can be applied in ROMP and ROM/CM processes with high efficiency and exceptional *Z*-selectivity (93:7 to >98:2 *Z*:*E*) [22]. Subsequently, Hoveyda et al. found that the catalytic activity and stability of ruthenium complex **5** can be substantially improved when the benzene dithiolate ligand has two *ortho*-chloro substitutions [23–25]. Unlike bidentate ligands, complex **6** was developed from commercial ruthenium catalyst in a process where one chloride is replaced by a steric

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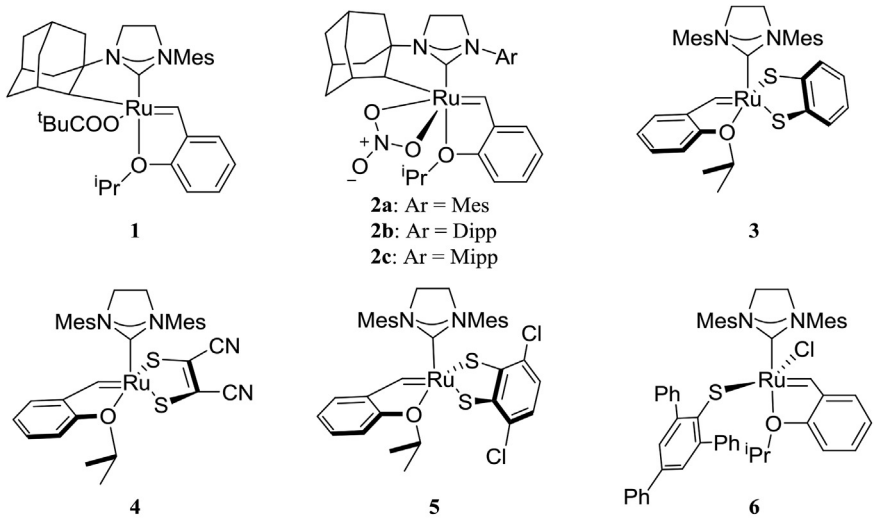


Chart 1. *Z*-selective catalysts for olefin metathesis.

hindrance 2,4,6-triphenylbenzenethiolate ligand. Notably, catalyst **6** displays high catalytic activity and *Z*-selectivity as a catalyst for the homocoupling metathesis of different terminal olefins [26]. Although progress has been attained in developing catalysts for *Z*-selective olefin metathesis reaction, ruthenium carbene complexes with new structures, high catalytic activities, and high *Z*-selectivity remain under great demand.

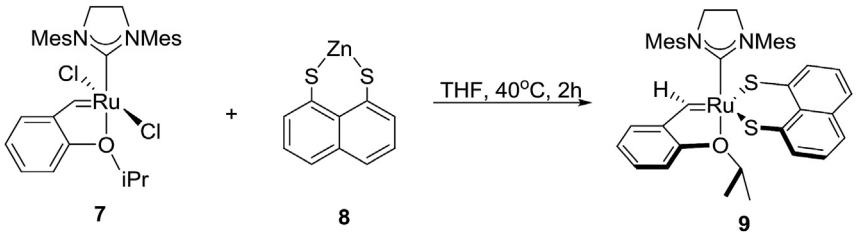
The distance of two sulfur atoms are closer in naphthalene-1, 8-dithiol than in benzene-1, 2-dithiol ligand. When naphthalene-1, 8-dithiolate is used as a bidentate ligand to coordinate with a metal center, this ligand will have a larger geometric coordination angle than benzene-1, 2-dithiol. This larger angle may remarkably influence the catalytic activity and stereoselectivity of the resultant complex. To examine these possible effects, we synthesized the naphthalene-1, 8-dithiolate ligand, prepared its corresponding ruthenium carbene complex, and carefully studied the complex's catalytic activity and *Z*-selectivity. Herein, we report the synthesis and catalytic study of a *Z*-stereoretentive ruthenium carbene catalyst bearing a bidentate naphthalene-1, 8-dithiolate ligand.

2. Results and discussion

Although 1, 8-dimercaptonaphthalene [27a,d] and 1, 8-dimercaptohexachloronaphthalene [27c] have been described in the literature, they have not been investigated extensively as ligands in coordination chemistry [27]. Some complexes bearing such ligands have found their industrial applications, including vulcanization [28], lubricant additives [29], and catalysis [28,30]. As mentioned previously, the distance of the two sulfur atoms of naphthalene-1, 8-dithiol are closer than that of benzene-1, 2-dithiol ligand and will result in a smaller geometric coordination angle when coordinating with the metal center [31–35]. This angle may substantially influence the catalytic activity and stereoselectivity of the resultant complex. Given the reported ruthenium carbene catalyst containing a benzene-1, 2-dithiol developed by Hoveyda and co-workers, we investigated the catalytic activity and stereoselectivity of ruthenium carbene complex bearing a naphthalene-1, 8-dithiolate ligand.

The synthesis route for the naphthalene-1, 8-dithiolate ruthenium carbene complex **9** is shown in Scheme 1. As previously reported, the corresponding zinc naphthalene-1, 8-dithiolate **8** was prepared with a high yield (91%) as a brown-yellow solid by reacting naphthalene-1, 8-dithiol with zinc acetate in the presence of ethylenediamine in isopropanol [36,37]. Subsequently, zinc naphthalene-1, 8-dithiolate (**8**) was reacted with commercially available ruthenium complex **7** to obtain the desired complex **9** as a dark yellow powder at 82% yield after stirring for 3 h in THF at room temperature under a nitrogen atmosphere. The ^{1}H NMR spectra of the complex showed singlet peaks at 15.35 ppm, which corresponded to the benzylidene carbene protons and indicated that the ligand exchange was successful.

A single crystal of complex **9** was grown by slow evaporation from toluene at room temperature under N_2. The structure of **9** as determined by single X-ray diffraction is shown in Fig. 1. Compound **9** exhibited a slightly deformed trigonalbipyramidal structure with an NHC carbene, two sulfides, a phenyl oxide, and a benzylidene carbene ligand seated around the Ru metal center. The bond distances between atoms and the Ru center were as follows: Ru1–S1,



Scheme 1. Synthesis of complex **9** bearing a naphthalene-1, 8-dithiolate ligand.

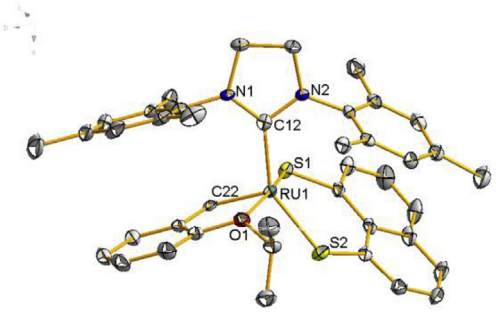


Fig. 1. Perspective view of **9**. Ellipsoids are drawn at 50% probability. For clarity, the hydrogen atoms have been omitted.

2.2719(7) Å; Ru1–S2, 2.2804(7) Å; and Ru1–C12, 2.044(3) Å. These distances were shorter than those in **3** (Ru1–S1, 2.2933(6) Å; Ru1–S2, 2.2830(6) Å; and Ru1–C17 is 2.061(2) Å). The bond distance of Ru1–O1 (2.3260(18) Å) was longer than that in **3** (2.2769(17) Å), and Ru1–C22 (1.831(3) Å) was very close to **3** (Ru1–C1, 1.838(3) Å). The bond angles of S1–Ru1–S2 (93.89(3)°), C12–Ru1–S1 (88.36(7)°) and C12–Ru1–S2 (143.99(8)°) were larger than those in **3** (S2–Ru1–S1 (87.98(2)°), C17–Ru1–S2 87.16(7)°, C17–Ru1–S1 143.40(8)°). S1–Ru1–O1 (168.85(5)°), S2–Ru1–O1 (87.98(5)°), C12–Ru1–O1 (96.59(8)°), and C22–Ru1–S1 (90.95(9)°) were smaller than those of **3** (O1–Ru1–S2, 169.84(5)°; O1–Ru1–S1, 89.77(5)°; C17–Ru1–O1, 100.46(8)°; and C1–Ru1–S2, 93.11(8)°). These results indicated that the introduction of naphthalene-1,8-dithiol changed the steric 3D structure of the catalytic center and altered the catalytic activity, stability, and selectivity of the catalyst.

Complex **9** was stable at room temperature in $CDCl_3$. However, when the temperature was raised to 50 °C, complex **9** was found to convert to complex **7** as displayed by the NMR spectra. In fact, Hoveydas' group has found similar phenomenon in a previous report, this may be because of the high temperature decreased the stability of the Ru–S bond, making complex **9** derived to the dichloride species upon exposure to $CDCl_3$ [38a,b]. To further study the characteristics of complex **9**, we tested the thermal stability in THF-d_8 at 55 °C. The trend of decomposition is presented in Fig. 2. The decomposition of complex **9** was very fast during the first hour and gradually retarded with time until complete decomposition after 23 h. Rapid decomposition may play a competitive role in catalytic reaction and may be disadvantageous to the olefin metathesis reaction.

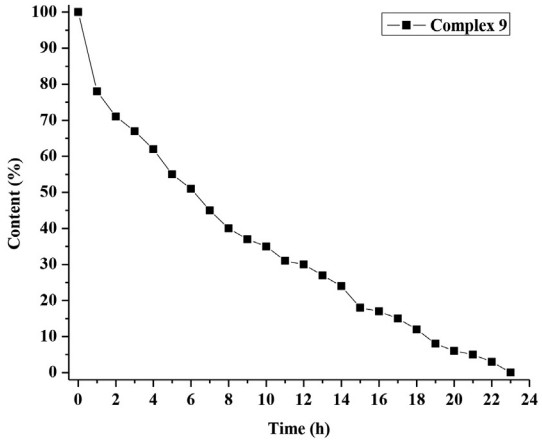


Fig. 2. Stability test of complex **9** in THF-*d*8 at 55 °C under N_2 as monitored by ^1H NMR using benzophenone as the internal standard.

The catalytic activity and *Z*-selectivity of **9** for the CM reactions of terminal olefins and (*Z*)-but-2-ene-1, 4-diol were then tested, and the results are shown in Table 1. The CM reactions in THF at 55 °C in the presence of **9** (5.0 mol%) under N_2 resulted in an array of *Z*-alkenyl alcohol products at a relative low yield. Table 1 reveals that the *Z*-isomers (92:8 to 98:2 of *Z*/*E* ratios) were the major products in all these CM reactions. Similar to other ruthenium based olefin metathesis catalysts, **9** could tolerate many different functional groups. For example, CM occurred between (*Z*)-but-2-ene-1, 4-diol and terminal alkenes with nitro (**10** and **11**), aldehyde (**20**), ketone (**14**), and unprotected amino (**16**) groups. Moreover, the CM reactions were successful for olefins with different chain lengths (**10** and **11**; **14** and **15**), and the olefins with long chains often produced high yields. However, opposite results were observed for **17** and **18**. The yield of **13** (6 carbon chain) was obviously higher than that of **12** (3 carbon chain), but that of **19** (11 carbon chain) did not increase significantly. Therefore, the catalytic efficiency of **9** did not change significantly after the carbon chain length increased to a certain length.

3. Conclusions

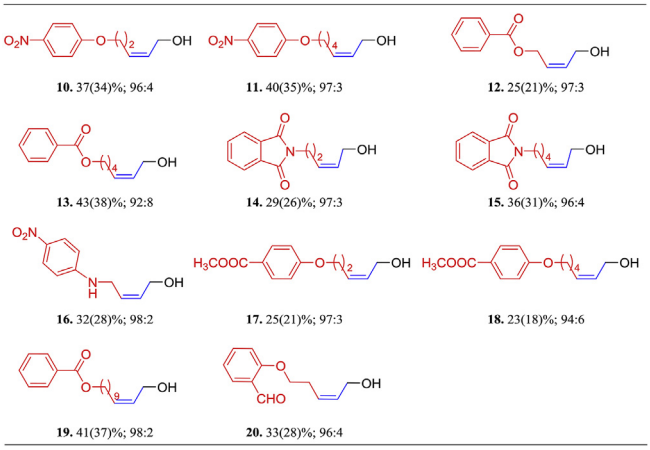
A highly *Z*-retentive ruthenium carbene complex **9** bearing a bidentate naphthalene-1, 8-dithiolate ligand was synthesized, and the complex's catalytic activity and *Z*-retentivity were evaluated for the CM reaction of terminal alkenes and (*Z*)-but-2-ene-1, 4-diol. Catalyst **9** was simple to synthesize, and its structure was determined by single X-ray diffraction. Experiment showed that **9** could catalyze the CM reactions of terminal alkenes with (*Z*)-but-2-ene-1, 4-diol to yield a high-*Z*-olefin product (*Z*/*E* ratios 92:8 to 98:2). Similar to other ruthenium-based catalysts, complex **9** is suitable for many substrates and can tolerate many different functional groups. Further work on improving the activity of this kind of catalyst by modifying the naphthalene-1, 8-dithiolate ligand is currently underway in our laboratory.

4. Experimental

4.1. General procedures

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. The starting products were synthesized according to the literatures (1-(but-3-en-1-yloxy)-4-nitrobenzene [39], 1-(hex-5-en-1-yloxy)-4-nitrobenzene [39], allylben-zoate [40], hex-5-en-1-yl benzoate [40], 10-undecenyl benzoate [40], N-(5-hexenyl)phthalimide [41], 2-(but-3-en-1-yl)isoindoline-1,3-dione [41], 2-(but-3-en-1-yloxy) benzaldehyde [42], N-allyl-4- nitroaniline [43], methyl 4-(but-3-en-1-yloxy)benzoate [39], methyl 4-(hex-5-en-1-yloxy) ben-zoate [39]). All other reagents and solvents were purchased and were used as received from commercial sources. All reactions in non-aqueous solvents were carried out under nitrogen in dried glassware. Solvents were purified and dried as follows: diethyl ether and hexane were distilled from sodium; tetrahydrofuran and toluene were distilled from sodium and benzophenone. TMEDA was distilled from calcium hydride. ^1H and ^{13}C NMR data were recorded on 400 MHz spectrometer with $CDCl_3$ as solvent. The chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta = 7.26$) for ^1H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz for ^1H. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Conversions were obtained by ^1H NMR analysis of the sample. NMR data of known

Table 1
Z-selectivity study of catalyst 9 in cross metathesis[a,b,c].



[a] Reaction duration: 8 h; Solvent: THF (0.5 mL); Temperature: 55 °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* ratios were determined by analysis of ^{1}H NMR spectra of the mixtures.
[c] Yields are based on isolated products.

compounds is in agreement with literature values. Infrared spectra were recorded on FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303 instrument. The yields were determined by isolated products.

4.1.1. General procedure for preparation of compound 8 and 9

4.1.1.1. Preparation of Zinc 1, 8-naphthalenedithiolate ***(8)***. A mixture of 1,8-naphthalenedithiol (150 mg, 0.78 mmol, 1.00equiv), Zn(OAc)$_2$2H$_2$O (684 mg, 3.12 mmol, 4.00 equiv) and ethylenediamine (0.31 mL, 4.68 mmol, 6.00 equiv.) in *i*-PrOH (10 mL) was allowed to stir for 3 h at room temperature. The precipitated solid was filtered, washed with methanol (15.0 mL) and chloroform (15.0 mL), and dried to afford **8** (182 mg, 0.71 mmol, 91% yield) as brown-yellow solid.

4.1.1.2. Preparation of complex ***9***. To a 10 mL oven-dried vial charged with a stir bar and zinc 1,8-naphthalenedithiolate (d) (153.4 mg, 0.60 mmol, 2.00 equiv) under N_2 atmosphere, a solution of complex **7** (188 mg, 0.30 mmol, 1.00 equiv) in tetrahydrofuran (2 mL) was added. The mixture was stirred 3 h at room temperature. Solvent was removed under vacuum, and then the residual tetrahydrofuran was removed through co-evaporation with *n*-hexane (3 × 3 mL). The acquired solid was purified by silica gel column chromatography (CH_2Cl_2) in a glovebox and recrystallized from toluene to afford 183.5 mg of the desired compound (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.35 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 7.12 (d, *J* = 5.1 Hz, 1H), 7.09 (s, 1H), 6.96 (s, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.81 (dt, *J* = 11.9, 7.6 Hz, 2H), 6.74–6.68 (m, 2H), 6.64 (d, *J* = 6.6 Hz, 1H), 6.03 (s, 1H), 5.02 (dt, *J* = 13.1, 6.5 Hz, 1H), 4.04 (s, 1H), 3.88 (dd, *J* = 15.2, 7.7 Hz, 2H), 3.68 (s, 1H), 2.60 (d, *J* = 16.7 Hz, 6H), 2.51 (d, *J* = 3.8 Hz, 3H), 2.16 (s, 6H), 1.59 (d, *J* = 6.6 Hz, 3H), 1.50 (s, 3H), 1.42 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.08, 141.27, 140.87, 138.41, 137.91, 137.68, 136.97, 136.45, 135.57, 130.53, 130.10, 128.35, 126.73, 126.44, 124.61, 123.84, 123.38, 122.92, 121.83, 115.34, 79.16, 52.46, 51.40, 23.94, 21.83, 21.46, 19.33, 19.11, 17.33 ppm. IR (KBr): ν 3442, 3037, 2998, 2971, 2952, 2900, 1606, 1585, 1573, 1538, 1477, 1447, 1428, 1406, 1390, 1368, 1352, 1317, 1282, 1262, 1193, 1183, 1139, 1111, 1065, 1028, 989, 923, 879, 842, 805, 754, 737, 696, 568, 544, 415. ESI-MS $[M]^+$ calcd for $C_{41}H_{45}N_2O_1Ru_1S_2$: 747.0140; found: 747.1944. CCDC: 1580720.

4.1.2. General procedure for experimental procedure for Z-Stereoselective cross- metathesis (CM) reactions

4.1.2.1. General procedure for cross-metathesis (Table 1). In an oven-dried 10 mL vial equipped with a magnetic stir bar were placed the alkene substrate (0.15 mmol, 1.0 equiv) and *Z*-2-butene-1,4-diol (0.30 mmol, 2.0 equiv) under N_2 atmosphere. The mixture was added a solution of **9** (5.0 mol %) in tetrahydrofuran (0.3 mL) and then was vigorously stirred for 8 h at 55 °C to the end of the reaction. Organic solvent was removed in vacuo, and then the residue was purified by silica gel column chromatography (30% Et_2O in hexanes to 50% Et_2O in hexanes) to give the desired product.

4.1.3. The characterization of the olefin matathesis products 10–20 [23].

4.1.3.1. (Z)-5-(4-Nitrophenoxy)-2-pentene-1-ol ***(10)***. Pale yellow oil in 96:4 *Z*/*E* ratio (34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.76 (dt, *J* = 12.3, 6.8 Hz, 1H), 5.58 (q, *J* = 7.9 Hz, 1H), 4.19 (d, *J* = 6.6 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 2.57 (q, *J* = 6.6 Hz, 2H), 1.55 (s, 1H) ppm. ^{13}CNMR (100 MHz, $CDCl_3$) δ 163.7, 131.71, 127.49, 125.97, 114.42, 67.87, 58.45, 27.36 ppm.

4.1.3.2. (Z)-7-(4-Nitrophenoxy)-2-pentene-1-ol ***(11)***. Yellow oil in 97:3 *Z*/*E* ratio (35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.2 Hz, 2H), 6.94 (d, *J* = 9.2 Hz, 2H), 5.66 (dt, *J* = 13.2, 6.6 Hz, 1H), 5.61–5.51 (m, 1H), 4.22 (d, *J* = 6.5 Hz, 2H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.18 (q, *J* = 7.3 Hz, 2H), 1.89–1.79 (m, 2H), 1.57 (p, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.12, 141.38 132.23, 129.10, 125.92, 114.39, 68.59, 58.54, 28.49, 27.02, 25.93 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).

4.1.3.3. (Z)-4-Hydroxyhept-2-en-1-yl benzoate ***(12)***. Yellow oil in 97:3 *Z*/*E* ratio (21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.92 (dt, *J* = 12.1, 6.6 Hz, 1H), 5.76 (dt, *J* = 11.1, 7.0 Hz, 1H), 4.94 (d, *J* = 6.9 Hz, 2H), 4.34 (d, *J* = 6.5 Hz, 2H), 1.71 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.66, 133.55, 133.12, 130.03, 129.64, 128.40, 125.64, 60.60, 58.55 ppm.

4.1.3.4. (Z)-7-Hydroxyhept-5-en-1-yl benzoate ***(13)***. Pale yellow oil

in 92:8 *Z*/*E* ratio (38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.4 Hz, 2H), 5.57 (dt, J = 12.4, 7.1 Hz, 1H), 5.46 (q, J = 8.3, 7.9 Hz, 1H), 4.25 (t, J = 6.5 Hz, 2H), 4.13 (d, J = 6.5 Hz, 2H), 2.08 (q, J = 7.1 Hz, 2H), 1.70 (dt, J = 13.7, 6.4 Hz, 3H), 1.46 (p, J = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.69, 132.91, 132.30, 130.34, 129.55, 129.06, 128.36, 64.76, 58.56, 28.22, 26.96, 25.93 ppm.

4.1.3.5. (Z)-2-(5-Hydroxyhept-3-enyl)-isoindoline-1,3-dione ***(14)***. Yellow oil in 97:3 *Z*/*E* ratio (26% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.4, 3.0 Hz, 2H), 7.72 (dd, J = 5.4, 3.1 Hz, 2H), 5.75–5.67 (m, 1H), 5.60–5.51 (m, 1H), 4.15 (d, J = 6.7 Hz, 2H), 3.76 (t, J = 7.1 Hz, 2H), 2.51 (q, J = 7.0 Hz, 2H), 1.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.39, 133.99, 132.01, 131.69, 127.95, 123.26, 58.29, 37.49, 26.53 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).

4.1.3.6. (Z)-2-(7-Hydroxyhept-5-enyl)-isoindoline-1,3-dione ***(15)***. Yellow oil in 96:4 *Z*/*E* ratio (31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.78 (m, 2H), 7.72 (d, J = 4.5 Hz, 2H), 5.65 (q, J = 7.6, 6.8 Hz, 1H), 5.49 (q, J = 8.1 Hz, 1H), 4.21 (d, J = 6.3 Hz, 2H), 3.69 (t, J = 6.9 Hz, 2H), 2.16 (q, J = 6.9 Hz, 2H), 1.70 (dd, J = 14.9, 7.2 Hz, 3H), 1.51–1.39 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.48, 133.94, 132.09, 132.07, 129.21, 123.22, 58.47, 37.59, 27.76, 26.57, 26.40 ppm.

4.1.3.7. (Z)-4-((4-Nitrophenyl)amino)but-2-en-1-ol ***(16)***. Yellow oil in 98:2 *Z*/*E* ratio (28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 9.3, 2.6 Hz, 2H), 6.73–6.37 (m, 2H), 5.97–5.80 (m, 1H), 5.68 (q, J = 8.7, 8.2 Hz, 1H), 4.66 (s, 1H), 4.32 (d, J = 6.3 Hz, 2H), 3.92 (d, J = 6.4 Hz, 2H), 1.65 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.94, 132.41, 127.77, 126.40, 111.26, 58.58, 40.61, 29.32 ppm. ESI-MS [M+Na]$^+$ calcd for $C_{10}H_{12}N_2O_3$: 208.1270, found: 231.0741. Analytical Data. Found (calcd) for: $C_{10}H_{12}N_2O_3$ C, 57.69 (57.72); H, 5.81 (5.75); N, 13.45 (13.35).

4.1.3.8. Methyl-(Z)-4-((5-hydroxypent-3-en-1-yl)oxy)benzoate ***(17)***. Colorless oil in 97:3 *Z*/*E* ratio (21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.81 (m, 2H), 6.90–6.76 (m, 2H), 5.82–5.68 (m, 1H), 5.66–5.52 (m, 1H), 4.18 (d, J = 6.8 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 2.54 (q, J = 6.4 Hz, 2H), 1.60 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 162.45, 131.62, 131.48, 127.96, 122.77, 114.06, 67.18, 58.40, 51.88, 27.48 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).

4.1.3.9. Methyl-(Z)-4-((7-hydroxyhept-5-en-1-yl)oxy)benzoate ***(18)***. Colorless oil in 94:6 *Z*/*E* ratio (18% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 5.69–5.61 (m, 1H), 5.61–5.51 (m, 1H), 4.21 (dd, J = 6.7, 1.2 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 3.88 (s, 3H), 2.17 (q, J = 7.4 Hz, 2H), 1.86–1.77 (m, 2H), 1.61–1.53 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.83, 132.44, 131.58, 129.28, 128.96, 122.45, 114.05, 67.89, 58.59, 51.84, 28.63, 27.08, 26.03 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).

4.1.3.10. (Z)-12-Hydroxydodec-10-en-1-yl benzoate ***(19)***. Colorless oil in 98:2 Z/E ratio (37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 5.60 (dt, J = 12.6, 6.4 Hz, 1H), 5.54 (dd, J = 12.6, 5.3 Hz, 1H), 4.31 (t, J = 6.7 Hz, 2H), 4.19 (d, J = 6.3 Hz, 2H), 2.06 (q, J = 7.0 Hz, 2H), 1.76 (p, J = 6.7 Hz, 2H), 1.45 (dd, J = 14.3, 6.7 Hz, 4H), 1.35 (s, 4H), 1.29 (s, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.73, 133.13, 132.82, 130.50, 129.53, 128.39, 128.33, 65.14, 58.60, 29.59, 29.45, 29.39, 29.25, 29.18, 28.71, 27.43, 26.02 ppm.

4.1.3.11. (Z)-2-((5-Hydroxypent-3-en-1-yl)oxy)benzaldehyde ***(20)***. Pale yellow oil in 96:4 *Z*/*E* ratio (28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 5.81 (dt, J = 12.4, 6.7 Hz, 1H), 5.71–5.61 (m, 1H), 4.27 (d, J = 6.5 Hz, 2H), 4.12 (t, J = 6.3 Hz, 2H), 2.67 (q, J = 6.4 Hz, 2H), 1.69 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.90, 161.04, 135.92, 131.51, 128.95, 127.64, 124.98, 120.84, 112.57, 67.75, 58.53, 27.54 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).

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Appendix A. Supplementary data

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