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Tandem Catalysis versus One-Pot Catalysis: Ensuring Process Orthogonality in the Transformation of Essential-Oil Phenylpropenoids into High-Value Products via Olefin Isomerization-Metathesis

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Conversion of essential-oil allylbenzenes (phenylpropenoids) to high-value fine chemicals via isomerization-metathesis is reported. The target reaction sequence involves isomerization of $ArCH_2CH=CH_2$ **1** into the corresponding conjugated olefins **2**, and ensuing cross-metathesis with acrylates to generate $ArCH=CHCO_2R$ **3**. The second-generation Hoveyda catalyst **HII** was chosen for the metathesis step. A range of lead candidates was assessed for the isomerization step, of which most active was the Grotjahn catalyst [CpRu(PN)(MeCN)]PF_6 ([**4**]PF_6; PN = 2-P^{i}Pr$_2$-4-^{t}Bu-1-Me-imidazole). The following order of isomerization activity was determined, using the isomerization of estragole **1a** to anethole **2a** (Ar = *p*-$MeOC_6H_4$) as a probe reaction: [CpRu(PN)(MeCN)]PF_6 > $RuHCl(CO)(PPh_3)_3$ > $Ru(Me\text{-}allyl)_2(COD)$ > $Pd_2Br_2(P^tBu_3)_2$ > $RuHCl(PPh_3)_3$ > $RuCl_3(\mu_2\text{-}C)(\kappa^1\text{-}C,\mu_2,\eta^6\text{-}Mes\text{-}H_2IMes)Ru(H)(H_2IMes)$ (the "Grubbs hydride") > $RuHCl(CO)(H_2IMes)(PCy_3)$ > $RuHCl(CO)(IMes)(PCy_3)$ > $RuHCl(CO)(PCy_3)_2$. To maximize process efficiency, a systematic comparison of orthogonal tandem catalysis versus sequential catalyst addition was undertaken, using catalysts [**4**]PF_6 and **HII**. The impact of each process type on product selectivity and catalyst compatibility was assessed. Selectivity was undermined in tandem isomerization-metathesis by competing metathesis of **1**. Sequential catalyst addition eliminated this problem. The isomerization catalyst [**4**]PF_6 adversely affected metathesis yields when equimolar with **HII**, an effect traced to the imidazole functionality in [**4**]PF_6. However, at the low catalyst loadings required for efficient isomerization (0.1 mol% [**4**]PF_6), negligible impact on metathesis yields was evident. The target cinnamates and ferrulates were obtained in quantitative yields by coupling these steps in a one-pot isomerization-metathesis protocol.

Introduction

Notwithstanding recent advances in the discovery and exploitation of fossil-fuel reserves,[1] the long-term prospect is one of dwindling supplies at increasing cost. Development of synthetic methodologies based on renewable resources thus remains an imperative.[2,3] Among such resources, essential oils stand out for the high proportion of functionalized, readily modified aromatic compounds more typically available from petrochemicals.[4] Of particular note for their abundance are functionalized allylbenzenes **1** (Fig. 1a), which serve as important precursors to the conjugated phenylpropenoids **2**. We recently described the metathetical transformation of **2** into high-value antioxidants for the personal-care market (see, e.g., **3a'**; Fig 1b).[5] More generally, conjugated arylpropenes of type **2** are of interest as renewable feedstocks that can be elaborated into polyfunctional aromatic targets via olefin metathesis.[4-10] This approach can be seen as complementary to strategies focused on metathetical degradation of biomass into simple building-blocks for commodity chemicals manufacturing.[11-13]

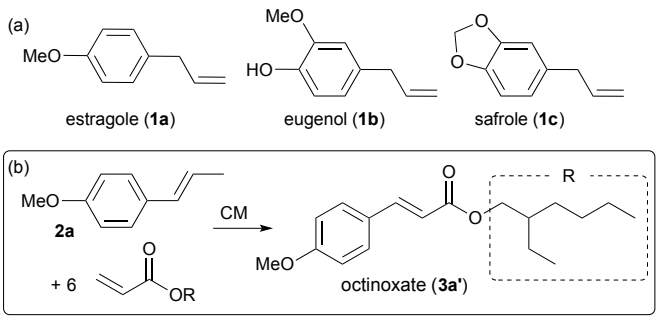

Fig. 1. (a) Functionalized allylbenzenes (phenylpropenoids; 2-propenylbenzenes). (b) Transformation of conjugated phenylpropenoids (1-propenylbenzenes) to high-value cinnamates and ferulates.

In the present study, we sought to expand the scope of this chemistry by coupling the metathesis step with a prior

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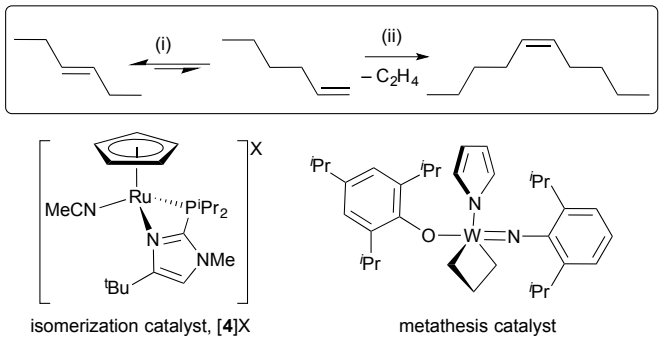
isomerization reaction, in order to harness the more abundant 1-arylpropene feedstocks. Industrially, isomerization of estragole **1a** to its conjugated isomer anethole **2a** is reportedly effected by treatment with excess KOH at 200 °C.[14,15] Much interest has focused on the development of alternative, catalytic routes, and a wide range of catalysts has now been reported.[16]

In considering routes from **1** to **3**, we were particularly interested in one-pot processes, which eliminate the inefficiency and materials waste associated with the intervening workup to isolate **2**. Tandem catalysis, as a specific embodiment of this approach, is of added interest in moving beyond stoichiometric methodologies.[17] Tandem metathesis-isomerization is now well established, and has recently been reviewed.[18,19] Such processes typically rely on "assisted tandem catalysis",[17c] involving the induced decomposition of a ruthenium metathesis catalyst into isomerization-active species. Isomerization can be highly efficient, ambiguities in the identity of the active catalyst notwithstanding.[20]

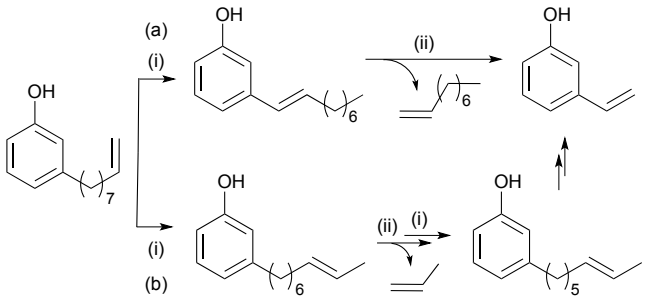
Required here is the opposite sequence: that is, tandem isomerization-metathesis. Early examples of success in such methodologies were largely substrate-specific, in that ring strain or steric constraints precluded metathesis prior to the isomerization step.[21-23] In the absence of such constraints, tandem isomerization-metathesis is commonly hampered by poor process orthogonality. Product selectivity is limited by both premature metathesis, and isomerization of the product. In an elegant example of orthogonal tandem catalysis[17c] applied to olefin homologation, Grotjahn and Schrock resolved this issue by deploying a metathesis catalyst that is unreactive toward internal olefins, and an isomerization catalyst that was found to be remarkably selective for reaction with trans-olefinic linkages (see Scheme 1).[24]



Scheme 1. Selective homologation of C_n (*E*)-olefins into C_{2n-2} (*Z*)-olefins via orthogonal tandem catalysis, involving concurrent processes of (i) isomerization; (ii) metathesis.

In related work, Consorti, Dupont, and co-workers achieved selectivity by immobilizing the metathesis catalyst in an ionic liquid phase, with an isomerization catalyst in the organic phase. The preferential solubility of the olefinic substrates in the organic layer accelerated isomerization relative to metathesis.[25] Finally, Mauduit and Carreaux employed a system in which isomerization is promoted by choosing a Ru-IPr metathesis catalyst, for which the onset of decomposition to isomerization-active species is rapid (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[26]

Gooβen's synthesis of functionalized styrenes via "isomerizing metathesis" embodies an alternative strategy, again based on orthogonal tandem catalysis.[27,28] Here the terminal olefin in the phenolic precursor is isomerized toward the more thermodynamically stable, conjugated site, following which the styrenyl target is generated by cross-metathesis with ethylene ("ethenolysis"; Scheme 2, top). Any incidence of metathesis prior to complete isomerization is immaterial, as this simply results in stepwise shortening of the side-chain by ethenolysis, prior to another isomerization step (Scheme 2, bottom). Gooβen and Cole-Hamilton recently applied this strategy to the synthesis of tsetse fly attractants,[27] while Nolan and co-workers utilized the same approach to convert **1** into the corresponding styrenes.[29]



Scheme 2. Example of selectivity in isomerization-metathesis, achieved by metathetical excision of the extraneous alkyl chain. Shown are two extremes: (a) Multi-site isomerization to the conjugated position, followed by ethenolysis. (b) Stepwise isomerization-CM (CM = cross-metathesis). (i) $Pd_2Br(PtBu_3)_2$ **7**; (ii) C_2H_4 + Ru metathesis catalyst.

More generally, however, poor orthogonality between the two processes can limit selectivity, and sequential catalyst addition is used to control the process. Sequential addition has been extensively deployed for the assembly of heterocyclic compounds, including indoles and other benzo-fused heterocycles.[30,31] In a modified approach, the Hulea group recently demonstrated the utility of serially linked, differentially packed catalyst beds to effect the transformation of ethylene to propylene via dimerization-isomerization-metathesis.[32]

Anticipated as a challenge in the present work is the higher metathesis reactivity of the terminal olefin, relative to the internal olefin generated in the isomerization step. Nevertheless, selectivity can be envisaged if the isomerization catalyst is sufficiently reactive to promote initial isomerization relative to metathesis. We therefore explored both tandem and one-pot transformations in developing a methodology for the transformation of essential-oil allylbenzenes into high-value cinnamate and ferulate targets.

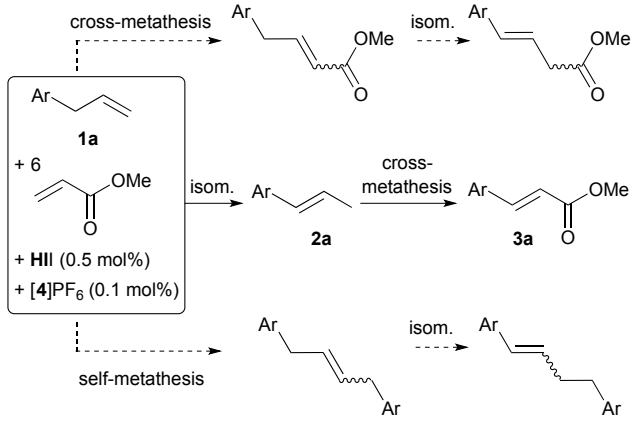
Results and discussion

Initial experiments focused on the isomerization of estragole **1a**, as a representative, abundant allylbenzene. In developing methodologies for the transformation of **1a** into cinnamate **3a**,

we considered a range of candidates for the isomerization step, as discussed below. For the metathesis step, however, we selected the second-generation Hoveyda catalyst **HII**, on the basis of prior work.[5,11,33,34] The dominant Grubbs-class catalysts (that is, phosphine-stabilized pre-catalysts, of which **GII** is the exemplar) were rejected on the basis of their incompatibility with acrylates.[35] The incompatibility arises from Michael reactions between the electron-deficient olefin and the PCy_3 ligand liberated from **GII** during catalyst initiation. Such reactions yield reactive enolates[36] that were shown to trigger rapid catalyst decomposition.[34]

Attempted tandem catalysis

The first question explored was that of process efficiency: specifically, the viability of orthogonal tandem catalysis. Prior work aimed at the self-metathesis of estragole **1a** using **HII** demonstrated that unintended isomerization of **1a** can compete with metathesis,[7] as indeed noted more broadly elsewhere.[37] We therefore considered it possible that deliberate use of a highly reactive isomerization catalyst (e.g. the Grotjahn catalyst [**4**]PF_6),[38,39] in conjunction with **HII**, could promote initial isomerization relative to metathesis, and enable selectivity for the target cinnamates. This proved unsuccessful. As shown in Scheme 3, very poor selectivities were observed under conditions previously established as optimal for the CM reaction, when estragole and methyl acrylate were present simultaneously with **HII** and [**4**]PF_6. Competing metathesis of **1a** afforded homocoupled and cross-products, among a multiplicity of other products (see ESI), and yields of the target **3a** were limited to 55%.



Scheme 3. Target tandem isomerization-metathesis reaction (solid arrows; Ar = *p*-$MeOC_6H_4$). Dashed arrows show representative, competing metathesis and metathesis-isomerization processes. Conditions: C_7H_8, 70 °C, 6 h. Catalyst loadings are based on literature precedents for both **HII**[5] and [**4**]PF_6,[38,39] and validated below.

While competing metathesis of **1** could potentially be overcome by using higher loadings of [**4**]PF_6, or a less reactive metathesis catalyst, either comes at a price: that is, the requirement for excess catalyst (with attendant issues of cost and Ru removal), or slow throughput. We therefore accepted the necessity of sequential catalytic processes, in which the metathesis catalyst and acrylate coupling partner are added only once isomerization is complete.

Isomerization of estragole

In the next phase of the study, we screened a range of known isomerization catalysts (Fig. 2) for maximum activity in the transformation of **1a** to anethole **2a.** Leading reviews have described the isomerization activity of a large number of potential catalysts, with a particular focus on the impact of substrate functional groups on activity.[40-42] Additional candidates were identified from the recent literature.[16,42] As well as the Grotjahn catalyst [**4**]PF_6,[39] which has previously shown exceptional activity for isomerization of estragole and eugenol to the (*E*)-olefins,[38] we examined $RuHCl(CO)(PPh_3)_3$ **5** and $RuHCl(PPh_3)_3$ **6**, the highest-performing isomerization catalysts among several comparators recently examined.[20] Other candidates emerge from the tandem catalysis studies described in the Introduction, including dimeric $Pd_2Br(PtBu_3)_2$ **7**,[27,28] and Ru(COD)(methallyl)$_2$ **8**.[43]

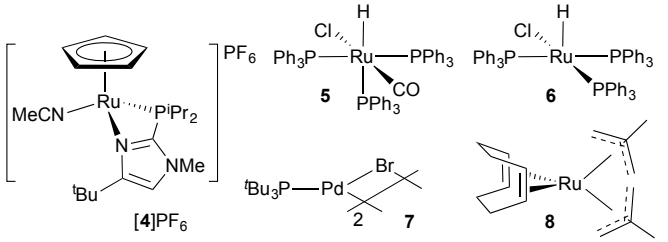
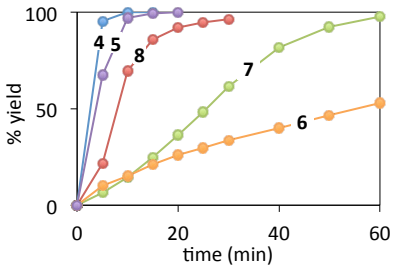


Fig. 2. Candidate complexes screened for isomerization activity in this work.

Isomerization experiments were carried out at 40 °C in toluene, at a catalyst loading of 1 mol% (Fig. 3). Under these conditions, the Grotjahn catalyst [**4**]PF_6 exhibited highest activity, delivering quantitative yields of **2a** within 5 min. Hydridochlorocarbonyl complex **5** and bis-allyl catalyst **8** were also highly active, while dimeric **7** (0.5 mol%, i.e. 1 mol% Pd) required 1 h for complete reaction. In comparison, $RuHCl(PPh_3)_3$ **6** reached only ca. 50% conversion at 1 h. All catalysts showed >95% selectivity for (*E*)-anethole **2a** by 1 h, with the sole exception of **5**, for which 10% of (*Z*)-**2a** was present at 100% yield. However, the proportion of (*E*)-**2a** increases if reaction is continued after conversion to **2a** is complete.



Catalyst	%*E* at 0.5 h*	%*E* at 1 h
[**4**]PF_6	99	ND
5	90	96
6	96	96
7	94	97
8	97	97

* %*E* at 100% yield for [**4**]PF_6 and **5** (ca. 15 min).

Fig. 3. Assessing the activity of the candidate catalysts in isomerization of estragole. Conditions: 1 mol% Ru or Pd, 40 °C, C_7H_8.

The relatively low isomerization activity of **6** is particularly striking, given that in related work,[20] this catalyst significantly

out-performed others that have been regarded as potentially potent isomerization catalysts, including RuHCl(CO)(L)(PCy_3) (L = PCy_3 **12**, H_2IMes **10**),[44] and the "Grubbs hydride" **9**.[45] All were tested under the conditions shown in Fig. 3,[20] permitting extraction of the order of isomerization activity depicted in Fig. 4.

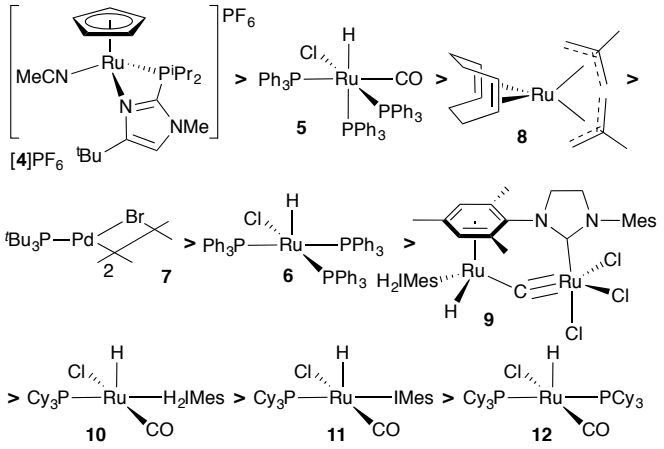


Fig. 4. Order of isomerization activity for catalysts surveyed in the reaction of Fig. 3.

Solvent compatibility

Isomerization using cationic [**4**]PF_6 is normally carried out in acetone.[46] While a range of solvents is feasible for metathesis, toluene and dichloromethane are generally most favourable.[37] Acetone and other polar solvents have been reported to limit catalyst productivity.[47] Moreover, a relatively high-boiling solvent is required for efficiency in the targeted metathesis step, in which formation of cinnamate **3a** is retarded by the intermediate formation of stilbenes, which are slowly consumed even at 70 °C.[5] To identify a reaction medium that balances the requirements for each reaction type, we examined the solvent dependence for isomerization of **1a** and metathesis of **2a**, in THF, toluene, and dichloroethane (DCE; Fig. 5). Given the high activity of [**4**]PF_6, isomerization was undertaken at RT, with the metathesis step being carried out at a bath temperature of 70 °C. As noted previously,[5] efficient volatilization of the propylene and ethylene byproducts from metathesis is essential to promote selectivity for the desired CM reaction. Metathesis reactions were therefore carried out with efficient stirring in open vessels in a well-purged glovebox.

While isomerization was marginally faster in the polar solvent THF (declining in the order THF > DCE > toluene; Fig. 5a), reaction was complete in all cases within 0.5 h at RT. In comparison, metathesis of **2a** was considerably slower in THF (Fig. 5b). Given the equivalent performance of DCE and toluene, the latter was adopted as the less toxic, environmentally less undesirable[48] alternative, and used as a good compromise solvent for both reactions.[49]

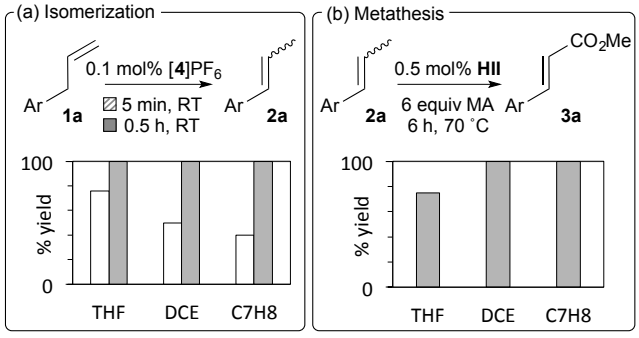
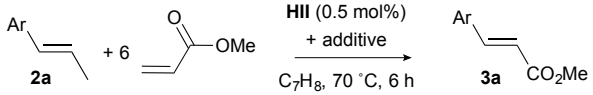


Fig. 5 Evaluating the impact of solvent on the isomerization and cross-metathesis steps.

Compatibility of metathesis and isomerization catalysts

A final question in developing the one-pot / dual catalyst methodology lay in the potential sensitivity of the metathesis step to the isomerization catalyst [**4**]PF_6. To dissect out this effect, we focused on metathesis of anethole **2a**, the intended product of estragole isomerization, and examined the impact of added [**4**]PF_6 on yields of **3a**. Metathesis yields suffered when [**4**]PF_6 is present in amounts equimolar with **HII** (Table 1, entries 1 vs. 2). The detrimental effect was traced to the imidazole moiety by experiments in which free MeCN or imidazole were added to the metathesis reaction, in molar amounts equivalent to **HII**, in the absence of [**4**]PF_6. Added MeCN had essentially no effect, while added imidazole strongly depressed CM yields (entry 3, 4). This behaviour is consistent with the proposed hemilability of the phosphine-imidazole ligand.[50]

Table 1. Evaluating the robustness of anethole–acrylate CM toward isomerization catalyst [**4**]PF_6 and its constituent ligands.



Entry	Additive	mol% additive	% conv	% yield
1	none	---	100	100
2	[**4**]PF_6	0.5	100	73[a]
3	MeCN	0.5	100	100
4	imidazole	0.5	81	48[a]
5	[**4**]PF_6	0.1	100	100

GC-FID analysis. [a]Stilbenes resulting from self-metathesis constitute the balance of material.

The negative impact of free imidazole is unsurprising. Not only do imidazole[51] and methyl imidazole[52] function as effective quenching agents in metathesis, but the metallacyclobutane intermediate that carries metathesis was recently shown to be highly sensitive to deprotonation by Bronsted base.[53] Importantly, however, the relative rates of metathesis and deactivation can be tuned by adjusting the ratio of **HII** to [**4**]PF_6. Thus, quantitative metathesis could be achieved by

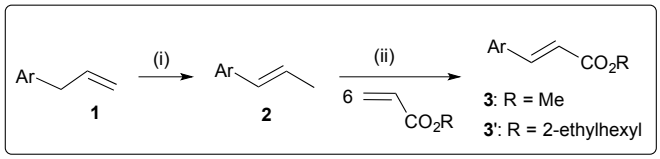
reducing the proportion of [**4**]PF_6 fivefold (to 0.1 mol%; Entry 5). The impact on isomerization rates is minor, as the transformation of **1a** to **2a** was shown above to be complete within 30 min at this catalyst loading, even at RT.

One-pot isomerization-metathesis.

Sequential isomerization-metathesis was carried out using the optimized conditions identified above. Accordingly, a toluene solution of estragole **1a** and catalyst [**4**]PF_6 (0.1 mol%) was stirred for 0.5 h at RT under N_2, following which methyl acrylate and the metathesis catalyst **HII** (0.5 mol%) were added, and the reaction was heated at 70 °C for 6 h. ^{1}H NMR analysis indicated quantitative yields of the desired cinnamate **3a** (Table 2, entry 1).

This sequential isomerization-metathesis methodology shows excellent tolerance for the unprotected phenolic functionality in eugenol **1b**, affording the ferulate target **3b** in quantitative yields (entry 2). Similar performance was also found for safrole **1c** (entry 3). Likewise successful was the transformation of estragole by isomerization and cross-metathesis with 2-ethylhexyl acrylate (entry 4). This reaction is of particular interest, given the high value of the octinoxate product **3a'**, an important sunscreen agent. CM of eugenol **1b** and safrole **1c** proceeded correspondingly well (entries 5, 6). In all cases, quantitative yields were achieved, irrespective of the phenylpropenoid / acrylate combination.

Table 2. One-pot isomerization-cross-metathesis of phenylpropenes with acrylates to yield high-value cinnamates and ferulates.[a]



entry	substrate	product	% conv	% yield
methyl acrylate				
1	**1a**	**3a**	100	100
2	**1b**	**3b**	100	>99
3	**1c**	**3c**	100	>99
2-ethylhexyl acrylate				
4	**1a**	**3a'**	100	>99
5	**1b**	**3b'**	100	>99
6	**1c**	**3c'**	100	>99

Conditions. (i) Isomerization: [**4**]PF_6 (0.1 mol%), C_7H_8, RT, 0.5 h. Quantitative formation of **2** confirmed prior to adding reagents for next step. (ii) Metathesis: Addition of **HII** (0.5 mol%), acrylate (6 equiv); 70 °C, 6 h. Conversions of **2** assessed by GC-FID, yields of **3** by GC-FID or ^{1}H NMR analysis; see Experimental. *Note:* While no other products were evident, NMR yields are indicated merely as >99%, given limits on the accuracy of NMR integration.

Conclusions

The foregoing highlights the potential of olefin metathesis to elaborate the conjugated phenolic structures that represent key chemical motifs in naturally-occurring essential oils, and expands the available pool of such resources by coupling isomerization with metathesis catalysis. Thus, the renewable phenylpropenoids estragole, eugenol, and safrole are converted into cinnamate and ferulate products relevant to fine-chemicals markets, via sequential processes of isomerization and acrylate cross-metathesis.

The high propensity of the terminal olefins toward metathesis, in competition with isomerization, hampered development of orthogonal tandem catalysis methodologies. Such processes are attractive for their operational simplicity; specifically, "walk-away" operation, but are frequently constrained by such imperfect orthogonality. Process efficiency was nevertheless achieved by identifying conditions suitable for performing the two reactions in a single vessel. Addition of the metathesis catalyst following isomerization reduces waste by eliminating the need for intervening workup and purification. Key to overcoming the incomplete tolerance of the metathesis process for the isomerization catalyst is the high activity of the latter, which permits use of catalyst loadings sufficiently low that metathesis proceeds unimpeded.

Experimental

Materials and methods

All reactions were carried out in an N_2-filled glove-box. Dry, oxygen-free C_7H_8 and THF were obtained using a Glass Contour solvent purification system and stored in the glovebox in amber bottles over 4 Å molecular sieves. Dichloroethane was dried over $CaSO_4$ for 12 h under N_2, then refluxed over P_2O_5 for 6 h prior to distillation, and stored as above, over 5 Å molecular sieves. Anhydrous *n*-decane (internal standard for gas chromatography) was purchased from Sigma-Aldrich.

Substrates **1a** (98%), **1b** (99%), **1c** (>97%), and **2a** (99%) were purchased from Sigma-Aldrich, and passed over neutral alumina prior to use. Acrylates (Sigma-Aldrich; 99% (methyl) or 98% (2-ethylhexyl)) were used without removing the phenolic stabilizers. Acrylates and phenylpropenes were degassed by five freeze-pump-thaw cycles, and stored protected from light under N_2 in the glovebox freezer (–35 °C). Catalysts [**4**]PF_6, **7**, and **8** were purchased from Strem and used as received. Catalysts **HII**,[54] **5**,[55] and **6**[56] were synthesized by literature methods. Potassium hydrotris(1-pyrazolyl)borate (KTp; >97%) was purchased from TCI and used as received to quench the metathesis catalyst[52] prior to workup and analysis.

NMR spectra were recorded on a Bruker Avance 300 or 500 MHz spectrometer at 298 K, and referenced to the residual proton or carbon signals of the deuterated solvent (^{1}H, ^{13}C(^{1}H) NMR). Signals are reported in ppm, relative to TMS (^{1}H, ^{13}C) at 0 ppm. GC quantification was performed on samples diluted with CH_2Cl_2 (ACS reagent grade) on an Agilent 7890A Series GC equipped with a flame ionization detector (FID), an Agilent 7683B Series autosampler and an Agilent HP-5 polysiloxane column (30 m length, 320 µm diameter), using an inlet split ratio of 10:1, an inlet temperature of 250 °C, and helium (UHP grade) as the carrier gas to maintain column pressure at 11.512 psi. The FID response was maintained between 50-2000 ρA, using analyte concentrations of ca. 5 mM. Calibration curves (peak areas vs. concentration) were constructed in the relevant concentration regime, to account for the dependence on detector response for substrates, products and decane (internal standard in catalytic runs). Conversions and yields in catalytic runs were determined from the integrated peak areas, referenced against decane, and compared to the initial substrate : decane integration ratio. Conversions of **1** and **2**, and yields of products **2** and **3a**, were assessed by GC-FID. Other product yields (**3b**, **3c**, **3a'**, **3b'**, **3c'**) were assessed by ^{1}H NMR analysis, as poor peak shapes hampered GC quantification. The NMR data for these compounds are provided in the ESI.

Representative Procedure for Isomerization.

A 20 mL vial was loaded with estragole **1a** (59 mg, 0.40 mmol), decane (GC internal standard; 57 mg, 0.40 mmol) and toluene (1.9 mL). An aliquot was removed for GC-FID analysis to establish the starting ratio of substrate to decane. Catalyst was added from a stock solution of [**4**]PF_6 (11 µL, 0.40 µmol, 0.1 mol%); stock solution 11 mg in 0.50 mL toluene; 40 mM). Aliquots were taken from the stirred reaction at specific time intervals, quenched with air, diluted with CH_2Cl_2 on the bench, and analyzed by GC-FID.

Representative Procedure for Cross-Metathesis.

Reaction carried out as above, with the following changes: anethole (59 mg, 0.40 mmol), in 1.6 mL toluene, with the addition of methyl acrylate (207 mg, 2.40 mmol, 6 equiv), and **HII** as catalyst (63 µL, 2.0 µmol, 0.5 mol%); stock solution 10 mg in 0.50 mL toluene (36 mM). The reaction was heated in a thermostatted oil bath open to the glovebox atmosphere, and analyzed as above after quenching with KTp (glovebox; solution in THF, 10 mg/1 mL, 10 equiv vs. **HII**).

Attempted Tandem Isomerization / Cross-Metathesis.

Reaction carried out as for estragole **1a** above, with methyl acrylate (207 mg, 2.40 mmol, 6 equiv) in 1.6 mL toluene, and addition of both [**4**]PF_6 (0.40 µmol, 0.1 mol%) and **HII** (2.0 µmol, 0.5 mol%) from stock solutions. The reaction was heated in a thermostatted oil bath at 70 °C, open to the glovebox atmosphere, and analyzed as above after quenching with KTp then air.

Representative Procedure for One-Pot Isomerization / Cross-Metathesis.

Reaction carried out as above, using 20 mg estragole (0.20 mmol), decane (29 mg, 0.20 mmol) and toluene (0.80 mL). An aliquot taken after 30 min confirmed complete conversion to anethole **2a**. Methyl acrylate (103 mg, 1.20 mmol, 6 equiv) and **HII** (1.0 µmol from stock solution, 0.5 mol%) were then added. The reaction was heated as above for 6 h, after which an aliquot was quenched with KTp, then air, and analyzed.

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TOC text and graphic

One-pot and tandem catalysis methodologies are explored in developing efficient isomerization-metathesis routes to high-value cinnamates and ferulates from essential-oil allylbenzenes.