Electronic Supplementary Information for:

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

Carolyn S. Higman, Marcio Peres de Araujo,† Deryn E. Fogg*

Center for Catalysis Research & Innovation and Department of Chemistry, University of Ottawa, Ottawa, ON, Canada, K1N 6N5

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S1. Details of ^{1}H NMR quantification of cinnamate and ferulate products.

While conversions of the 1-allylbenzenes **1a**–**c** and 2-allylbenzenes **2a**–**c**, and yields of products **2a**–**c** and **3a**, could be assessed by GC-FID (see Experimental Procedures in main text), the accuracy of GC quantification for **3b**, **3c**, and **3a'**, **3b'**, **3c'** was hampered by poor peak shapes. Yields for these products were instead assessed by ^{1}H NMR analysis. The ^{1}H NMR signal assignments were confirmed by comparison to the literature values summarized in Tables S1 and S2 below. Quantification was established by integration of well-isolated signals for the desired products against those for the styrene intermediates (Table S3) and stilbene byproducts (Table S4). A representative ^{1}H NMR spectrum for the reaction involving transformation of **1b** to **3b** is provided in Figure S1.

Table S1. Literature ^{1}H NMR data for cinnamate and ferulate methyl esters.

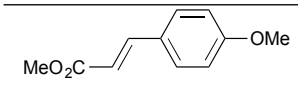
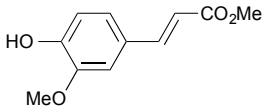
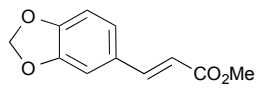
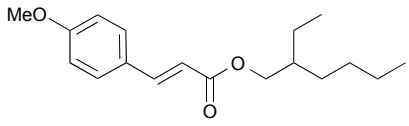
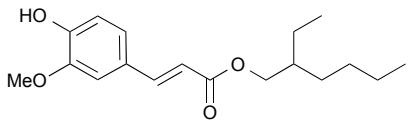
Compound	Reported ^{1}H NMR chemical shifts ($CDCl_3$)	Ref.
 **3a**	7.65 (d, *J* = 16.0 Hz, 1H), 7.47 (m, 2H), 6.93-6.89 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H)	1
 **3b**	7.64 (d, 1H, *J* = 15.9 Hz), 7.09 (dd, 1H, *J* = 1.9 Hz, *J* = 8.2 Hz), 7.04 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 5.89 (s, 1H), 3.95 (s, 3H), 1.61 (s, 1H)	2
 **3c**	7.58 (d, *J* = 15.9 Hz, 1H), 7.02 (s, 1H), 6.99 (dd, *J* = 8.1 Hz, *J* = 1.5 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.00 (s, 2H), 3.79 (s, 3H)	3

Table S2. Literature ^{1}H NMR data for cinnamate and ferulate 2-ethylhexyl esters.

Compound	Reported ^{1}H NMR chemical shifts ($CDCl_3$)	Ref.
 **3a'**	7.64–7.56 (d, *J* = 16.0 Hz, 1H, Ar-C*H*=), 7.48–7.44 (d,*J* = 8.6 Hz, 2H, Ar-*H*), 6.90–6.89 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 6.33–6.25 (d, *J* = 16.0 Hz, 1H, =C*H*-COOR), 4.10–4.07 (d, *J* = 5.7 Hz, 2H, -OCH_2), 3.85 (s, 3H, OCH_3), 1.63–0.85 (m, 15H, -C_7H_{15})	4
 **3b'**	7.60 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 7.08 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 7.04 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 6.92 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 6.29 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 5.88 (s, 1H), 4.11 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 1.7 Hz, 2H), 3.93 (s, 3H), 1.65 (m, 1H), 1.48-1.24 (m, 8H), 0.96-0.86 (m, 6H)	5

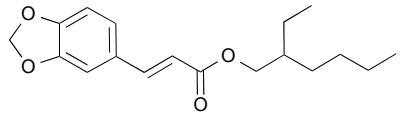
 **3c'**	7.58 (d, $^{2}J_{HH}$ = 15.9 Hz, 1H), 7.04 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H), 7.00 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1H), 6.81 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H), 6.27 (d, $^{2}J_{HH}$ = 15.9 Hz, 1H), 6.00 (s, 2H), 4.10 (dd, $^{3}J_{HH}$ = 5.9 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H), 1.64 (m, 1H), 1.49-1.22 (m, 8H), 0.97-0.84 (m, 6H)	5

Table S3. Literature ^{1}H NMR data for styrene intermediates.

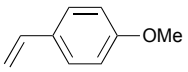
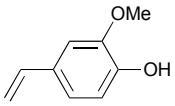
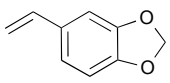
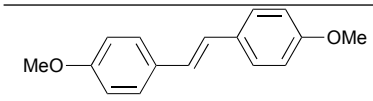
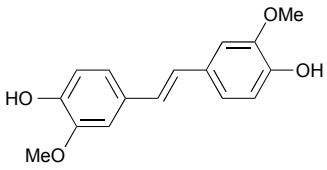
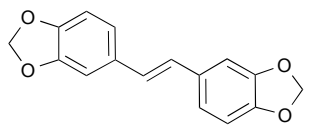
Compound	Reported ^{1}H NMR values ($CDCl_3$)	Ref.
	7.35 (d, *J* = 9.0, 2 H, H3), 6.86 (d, *J* = 8.9, 2 H, H2), 6.66 (dd, *J* = 17.6 Hz, *J* = 10.9, 1 H, Ar-C*H*), 5.62 (dd, *J* = 17.6, *J* = 0.6 Hz, 1 H, Ar-CH=CH_2 trans), 5.12 (dd, *J* = 10.9, *J* = 0.6 Hz, 1 H, Ar-CH=CH_2 cis), 3.81 (s, 3 H, OCH_3)	6
	6.88-6.81 (m, 3H), 6.63-6.54 (m, 1H), 5.68 (s, 1H), 5.71 (d, *J* = 17.56 Hz, 1H), 5.09 (d, *J* = 10.92 Hz, 1H), 3.84 (3H, s)	7
	6.97 (s, 1H), 6.84 (dd, *J* = 8 Hz, *J* = 2 Hz, 1H), 6.77 (d, *J* = 7 Hz, 1H), 6.63 (dd, *J* = 18 Hz, *J* = 10 Hz, 1H), 5.96 (s, 2H), 5.58 (d, *J* = 18 Hz, 1H), 5.13 (d, *J* = 10 Hz, 1H)	8

Table S4. Literature ^{1}H NMR data for stilbene byproducts.

Compound	Reported ^{1}H NMR values ($CDCl_3$)	Ref.
	7.41 (d, $^{3}J_{HH}$ = 8.9 Hz, 4H), 6.92 (s, 2H), 6.87 (d, $^{3}J_{HH}$ = 8.6 Hz, 4H), 3.81 (s, 6H)	9
	7.02 (d, *J* = 2 Hz, 1H, H2), 7.00 (dd, *J* = 8 Hz, *J* = 2 Hz, 1H, H6), 6.90 (d, *J* = 8 Hz, 1H, H5), 6.89 (s, 1H, Ar-C*H*=), 5.61 (s, 1H, O*H*), 3.95 (s, 3H, OCH_3)	10
	7.01 (s, 2H), 6.87 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 6.83 (s, 2H), 6.76 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 5.96 (s, 4H)	11

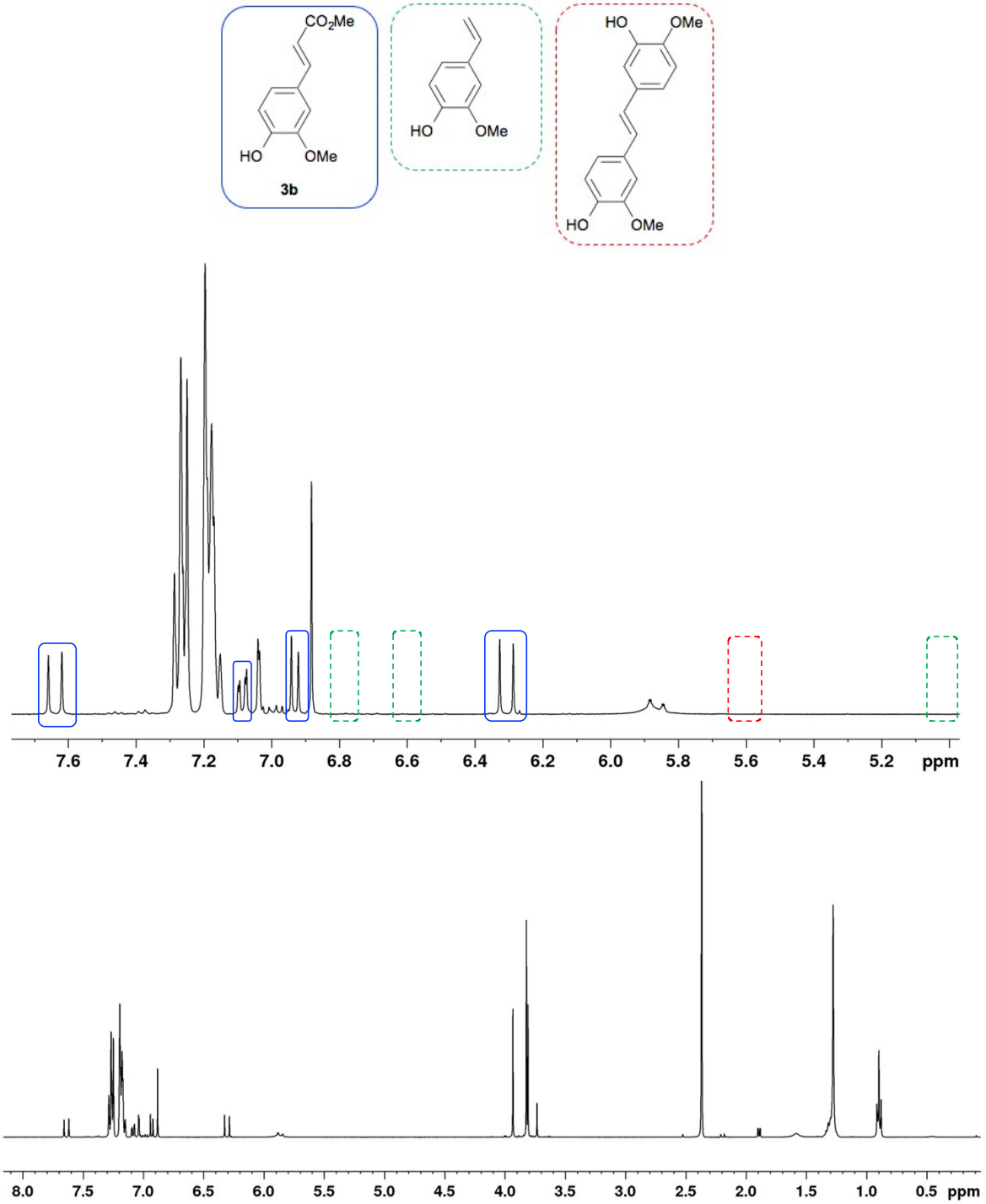


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) for the sequential isomerization-metathesis of anethole **1a** to cinnamate **3a** using the Grotjahn catalyst [**4**]PF_6 and metathesis catalyst **HII**, after a total of 6.5 h reaction (0.5 h isomerization, 6 h cross-metathesis). The upper trace shows the diagnostic olefinic region used for quantification. Peaks for **3b** are indicated with a blue box; locations for the styrene and stilbene intermediates are indicated with green and red boxes, respectively.

S2. Representative GC traces

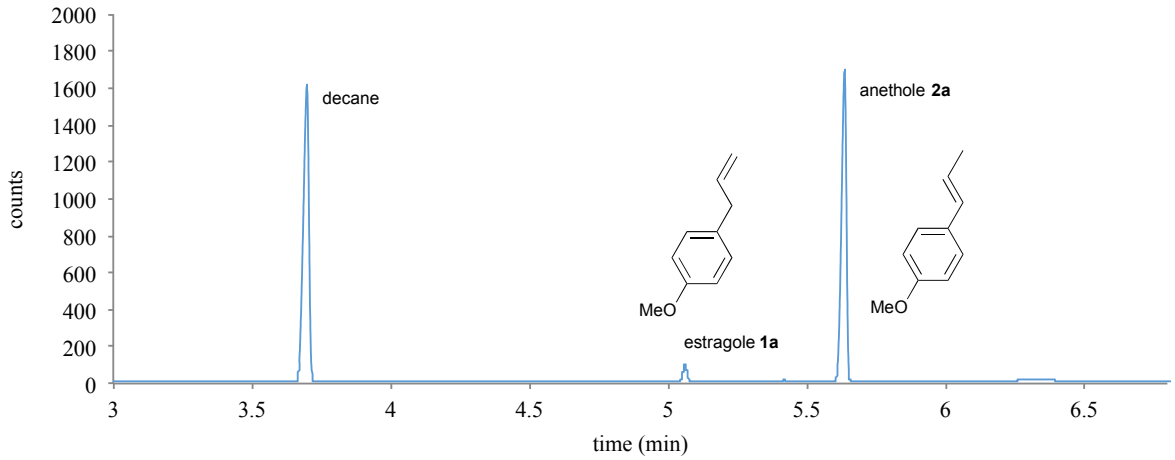


Figure S2. GC-FID trace for isomerization of estragole **1a** to anethole **2a** promoted by the Grotjahn catalyst [**4**]PF_6 at 5 min. Solvent front omitted.

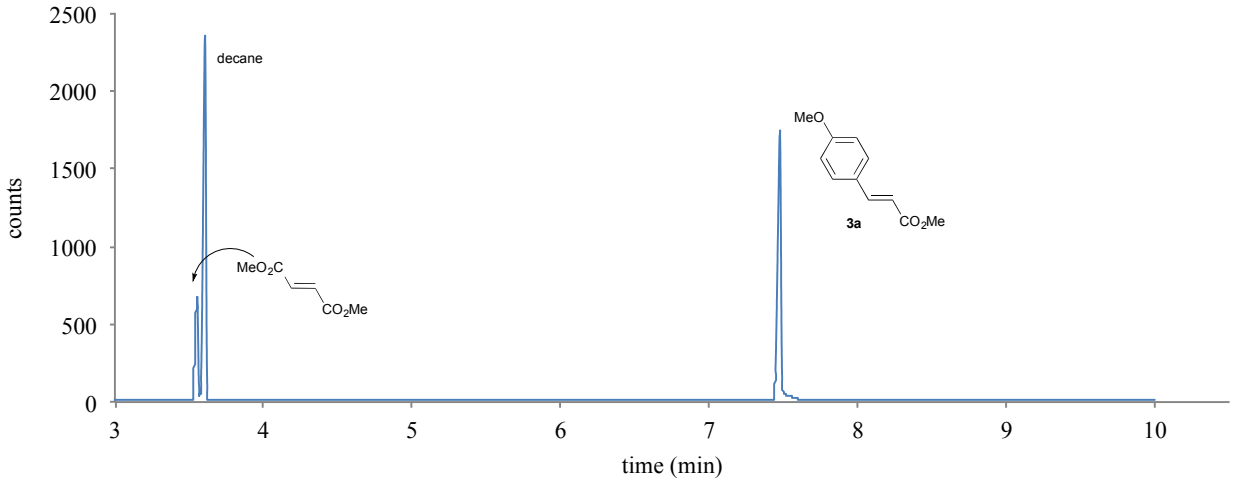


Figure S3. GC-FID trace for sequential isomerization-metathesis of anethole **1a** to cinnamate **3a** using the Grotjahn catalyst [**4**]PF_6 and **HII**, after 6.5 h reaction (0.5 h isomerization, 6 h cross-metathesis). Solvent front omitted.

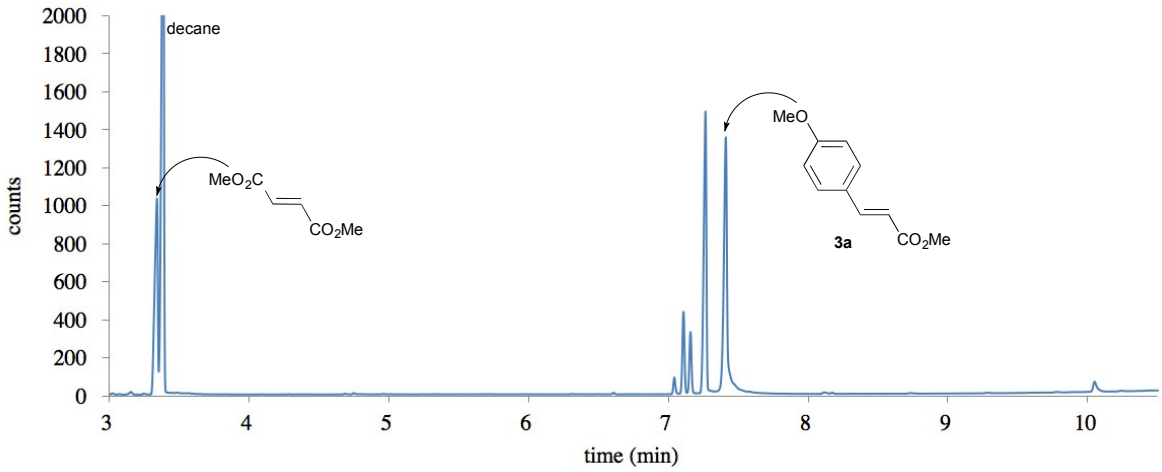


Figure S4. GC-FID trace showing side-products formed during the attempted transformation of **1a** to **3a** by orthogonal tandem catalysis using catalysts [**4**]PF_6 and **HII**. Solvent front omitted.

S3. References

1. Z. Zhang, Z. Zha, C. Gan, C. Pan, Y. Zhou, Z. Wang and M.-M. Zhou, *J. Org. Chem.*, 2006, **71**, 4339–4342.
2. K. S. Putt, V. Nesterenko, R. S. Dothager and P. *J*. Hergenrother, *ChemBioChem*, 2006, **7**, 1916–1922.
3. S. R. Angle, I. Choi and F. S. Tham, *J. Org. Chem.*, 2008, **73**, 6268–6278.
4. T. Monhaphol, B. Albinsson and S. P. Wanichwecharungruang, *J. Pharm. Pharmacol.*, 2007, **59**, 279–288.
5. *J*. A. M. Lummiss, K. C. Oliveira, A. Pranckevicius, A. Santos, E. N. dos Santos and D. E. Fogg, *J. Am. Chem. Soc.*, 2012, **134**, 18889–18891.
6. S. E. Denmark and C. R. Butler, *Org. Lett.*, 2006, **8**, 63–66.
7. A. Sharma, R. Kumar, N. Sharma, V. Kumar and A. K. Sinha, *Adv. Synth. Catal.*, 2008, **350**, 2910–2920.
8. H. Lebel and C. Ladjel, *Organometallics*, 2008, **27**, 2676–2678.
9. A. S. Khartulyari, M. Kapur and M. E. Maier, *Org. Lett.*, 2006, **8**, 5833–5836.
10. L. Li and N. P. Seeram, *J. Agric. Food Chem.*, 2011, **58**, 11673–11679.
11. G. Hua, Y. Li, A. M. Z. Slawin and *J*. D. Woollins, *Dalton Trans.*, 2007, 1477–1480.