A Synthesis of Trisubstituted Alkenes by a Ru-Catalyzed Addition

Barry M. Trost,* Hong C. Shen, and Anthony B. Pinkerton[a]

Abstract: Catalyzed by ruthenium trisacetonitrile hexafluorophosphate **4**, the Alder-ene type reaction of alkenes and internal alkynes provides an effective way to synthesize trisubstituted alkenes. Unlike most typical olefination protocols, this reaction is atom economical, and affords trisubstituted alkenes with defined olefin geometry. The regioselectivity can be explained invoking a steric argument based on the proposed mechanism. The first C–C bond formation generally involves sterically less hindered carbons of the alkenes and alkynes. Modest to very high regioselectivity can be achieved depending on the steric difference of the two substituents of alkynes.

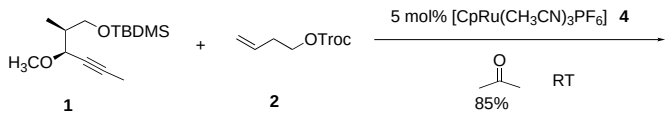
Keywords: alkenes · C–C coupling · homogeneous catalysis · olefination · ruthenium

Introduction

The synthesis of trisubstitued alkenes of defined geometry remains a challenge. Olefination protocols frequently lack control of alkene geometry.[1] Carbametallation of internal alkynes normally occurs with good control of alkene geometry involving a *cis* addition, but issues of regioselectivity of addition to internal alkynes normally make the reaction useless.[2] The ruthenium catalyzed addition of alkenes and alkynes, while a carbametallation protocol, is believed to proceed through a metallation as depicted in Scheme 1.[3, 4]

The work to date suggests that the cyclopentadienyl ruthenium catalyst has high steric demands and thus shows great sensitivity to steric effects. Thus, it was postulated that such an observation might lead to enhanced regioselectivity in contrast to typical carbametallation protocols. In conjunction with our efforts towards the total synthesis of callipeltoside A,[5] we observed that the internal alkyne **1** and alkene **2** underwent addition to generate a single trisubstituted alkene **3** in high yield under very mild conditions [Eq. (1), Troc = 2,2,2-trichloroethoxycarbonyl]. This observation stimulated the exploration of its generality.

Based on the proposed mechanism as depicted in Scheme 1,[3] an alkyne and an alkene can coordinate to ruthenium in two modes prior to the formation of ruthenacyclopentene. This coordination is assumed to be fast and reversible. Examining the two possible metallacycles formed in the oxidative cyclization (step 2), steric interaction with respect to the C–C bond formation favors the formation of C (if $R > R'$); steric factors concerning the interaction with the Cp favors the formation of C′ (if $R > R'$). If R and R′ have similar electronic properties, it is envisioned that steric factors will control the regioselectivity of the Alder-ene type reaction. The β-hydride elimination (step 3) followed by the subsequent reductive elimination (step 4) gives rise to the diene and regenerates the catalyst presumably in a non-reversible manner. This study not only helps to understand whether one of the two steric factors described above dictates the regioselectivity, but provides an atom economical strategy to afford trisubstituted alkenes as well. A set of conditions that proved effective for good regioselectivity in ruthenium catalyzed addition to terminal alkynes was adopted here (5–10 mol% **4**, DMF, RT).

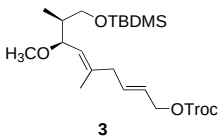


1 2

[a] Prof. B. M. Trost, H. C. Shen, A. B. Pinkerton
Department of Chemistry, Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-725-0259
E-mail: bmtrost@leland.stanford.edu

Results

In Table 1, a wide range of alkyne and alkene substrates have been studied to probe the scope of this reaction and the alkyne substituent effect on the regioselectivity. It was found that the steric interaction of alkyne and alkene subsitutuents adjacent to the newly formed C–C bond is more important than that of the alkyne substituent with the Cp group. As a result, excellent regioselectivity has been obtained in cases where the size of R and R′ are quite different. In the substrates where R is quaternary and R′ is secondary, the initial C–C bond formation occurs exclusively



3 (1)

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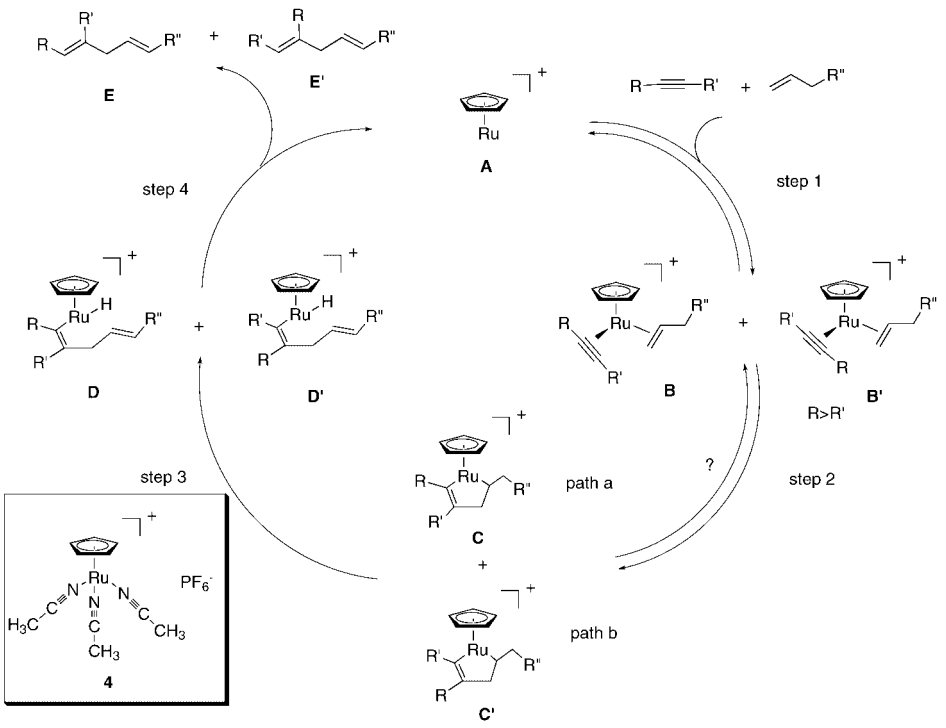


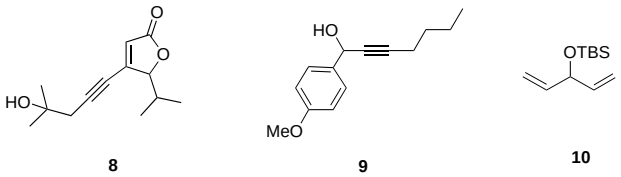
Scheme 1.

between the terminal carbon of the olefin and the less hindered carbon of the alkyne (path a), as shown in entries 1–4. In the first three cases, coordination of the free hydroxyl group to ruthenium may have been thought to influence the regioselectivity. To check this point, the hydroxyl group was placed on the less sterically demanding substituent, but again only the product involving new C–C bond formation to the less sterically encumbered terminus of the alkyne was formed (entry 4). Moving the quaternary center one carbon away from the alkyne still maintains the excellent regioselectivity (entry 5). On the other hand, making it a tertiary center as in entry 9 does lead to erosion of the regioselectivity, but, nevertheless, still quite high. A tertiary center, as in entries 6 and 7 also gave an excellent regioselectivity with only one regioisomer being detected. A hydroxymethyl substituent did have a profound effect on the regioselectivity if the other alkyne substituent is not sterically demanding (entries 8, 11, and 12). Placing the hydroxyl group on a secondary carbon can enhance the regioselectivity (entry 10), but in another case slightly reduced it (entries 15 and 18). The example of entry 8 is also somewhat surprising in the high selectivity observed and may involve some electronic effect of the cyclopropyl ring. A phenyl group appears to favor attack distal to the aromatic ring (entry 19) but the results are somewhat inconsistent (entries 20, 22, and 24).

A homopropargylic alcohol (entries 13 and 16) and even a bis-homopropargylic alcohol (entry 14) also impact the regioselectivity in a similar way to the propargylic alcohol. The role of the hydroxyl group in the latter case is not overwhelming as even 1-dodecyne shows nearly 3:1 regioselectivity (entry 21). Indeed, the level of selectivity in such an unbiased substrate is surprising. In this case, a comparison of acetone to DMF as solvent was made. As observed in the case of terminal alkynes, use of DMF gave a better regioselectivity than use of acetone.

A few alkynes, **8** and **9**, were not successful. The latter presumably derives from the acid lability of the benzylic alcohol since replacing the methoxy group by trifluoromethyl allows reaction to proceed in good yield (entry 15). The one case of an alkene that failed, **10**, derives from difficulties of inserting into the tertiary C–H bond.

Mechanistic considerations suggest that the alkene geometry derives from a *cis* addition as depicted. This assumption has been supported by NOE studies for a select group of products. For example, in the case of **7d** (entry 4), a 5.7% NOE was observed between the vinyl hydrogen at $\delta = 5.36$ and the doubly allylic methylene hydrogen at $\delta = 2.75$ but no NOE with the methylene group hydrogen next to the OH. Similar observations were made for the products of entries 5–7 and 9.



8 **9** **10**

Discussion and Conclusions

The mechanism of the reaction as outlined in Scheme 1 is consistent with our observations. The major question that is not resolved is the degree of reversibility in the formation of the metallacycles **C** and **C′** compared with the β-hydride elimination to **D** and **D′**. The combination of these two events appear to explain the results. The high selectivity with the more sterically bulky substrates is consistent with the product determining step being metallacycle formation. On the other hand, the odd cases such as entries 12–18 and the unusually high selectivity of cases involving 2-tridecyne may result from the β-hydride elimination step becoming product determining.

Regardless of mechanism, it is clear that a mild way to generate trisubstituted alkenes by a carbametallation approach has evolved. Regioselectivities are reasonable in most cases and can indeed be exceptional. As anticipated, geometrical selectivity is exquisite. The mild reaction conditions translate into excellent chemoselectivity as well.

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Table 1. Trisubstituted alkene synthesis.[a]

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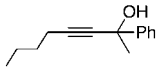
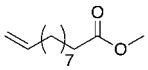
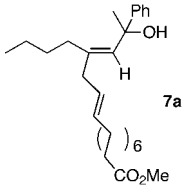
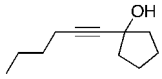
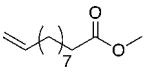
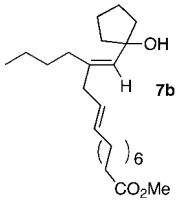
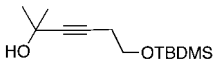
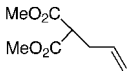
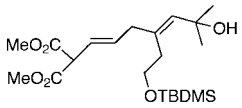
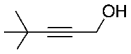
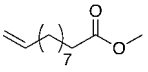
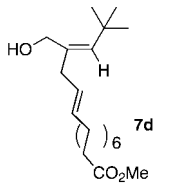
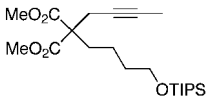
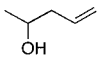
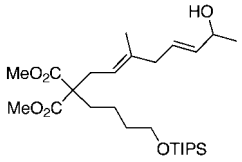
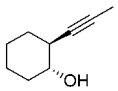
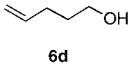
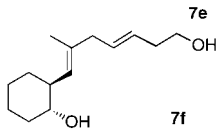
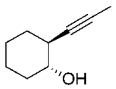
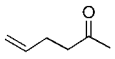
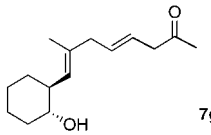
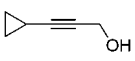
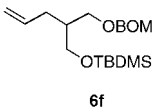
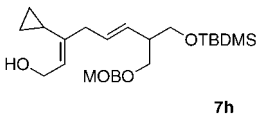
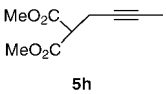
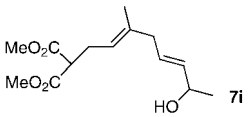
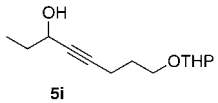
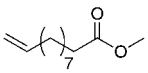
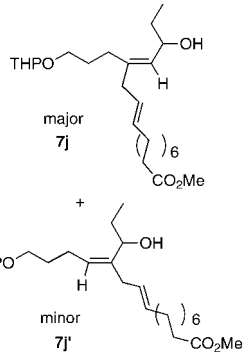
1	 **5a**	 **6a**	 **7a**	84	> 20:1
2	 **5b**	 **6a**	 **7b**	71	> 20:1
3	 **5c**	 **6b**	 **7c**	58	> 20:1
4	 **5d**	 **6a**	 **7d**	76	> 20:1
5	 **5e**	 **6c**		54	> 20:1
6	 **5f**	 **6d**	 **7e** **7f**	88	> 15:1
7	 **5f**	 **6e**	 **7g**	91	> 15:1
8	 **5g**	 **6f**	 **7h**	67	13:1
9	 **5h**	 **6c**	 **7i**	60	13:1
10	 **5i**	 **6a**	 major **7j** + minor **7j'**	89	7:1

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Table 1. (Continued).

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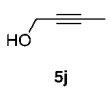
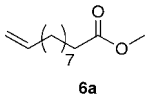
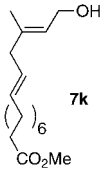
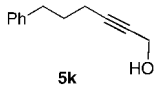
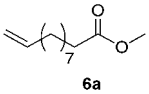
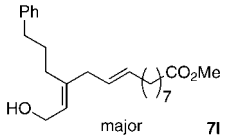
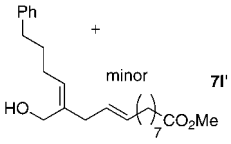
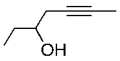
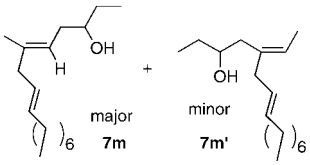
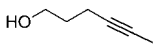
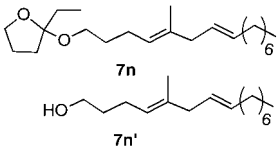
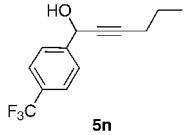
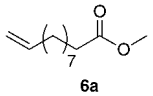
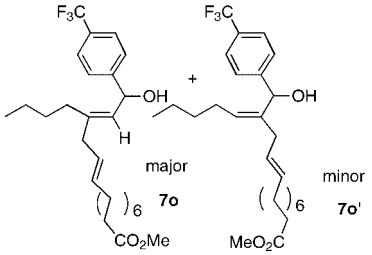
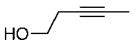
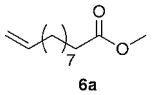
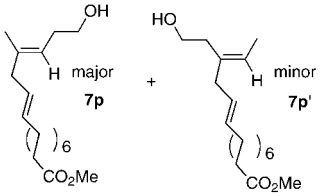
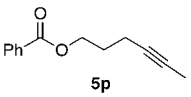
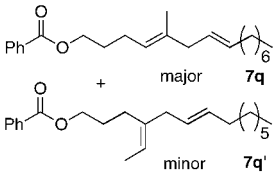
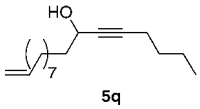
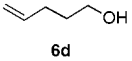
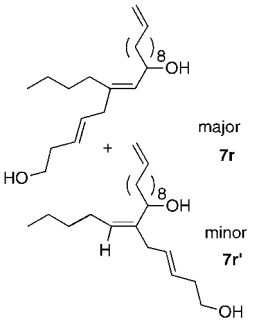
11	 **5j**	 **6a**	 **7k**	71	6:1
12	 **5k**	 **6a**	 major **7l** +  minor **7l'**	58	4.7:1
13	 **5l**	 **6g**	 major **7m** + minor **7m'**	71	4.1:1
14	 **5m**	 **6g**	 **7n** + **7n'**	72	4.1:1[d]
15	 **5n**	 **6a**	 major **7o** + minor **7o'**	64	3.7:1
16	 **5o**	 **6a**	 major **7p** + minor **7p'**	74	3.6:1
17	 **5p**	 **6g**	 major **7q** + minor **7q'**	80	3.1:1
18[c]	 **5q**	 **6d**	 major **7r** + minor **7r'**	52	3:1

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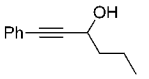
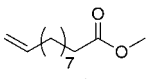
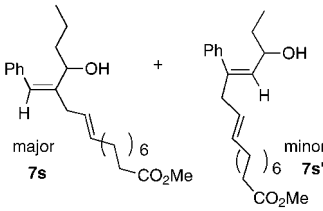
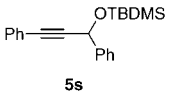
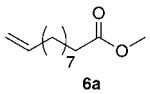
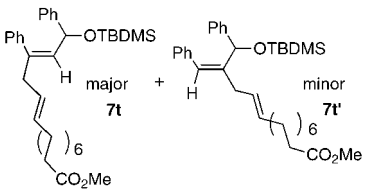
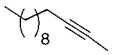
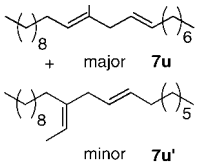
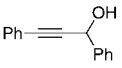
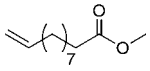
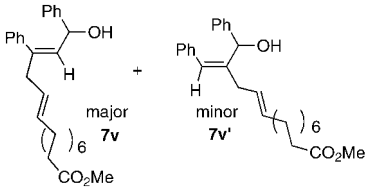
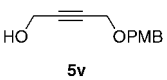
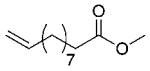
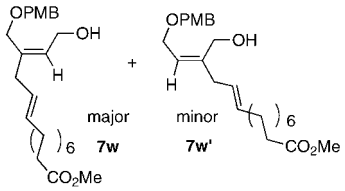
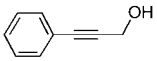
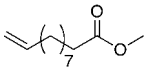
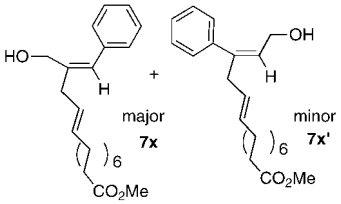
Table 1. (Continued).

	Alkyne	Alkene	Product	Yield [%]	Ratio[b]
19	 **5r**	 **6a**	 major **7s** + minor **7s'**	61	3:1
20	 **5s**	 **6a**	 major **7t** + minor **7t'**	76	3:1
21	 **5t**	 **6g**	 major **7u** + minor **7u'**	88 86	2.9:1 1.6:1[e]
22	 **5u**	 **6a**	 major **7v** + minor **7v'**	64	1.8:1
23	 **5v**	 **6a**	 major **7w** + minor **7w'**	78	1.8:1
24	 **5w**	 **6a**	 major **7x** + minor **7x'**	78	1.3:1

[a] All reactions were performed using a 1:1 ratio of alkyne:alkene in the presence of 10% catalyst **4** in dry DMF, at ambient temperature and under inert atmosphere (argon or nitrogen) for 4 h or less followed by flash chromatography without further work-up. [b] Ratio is referred to the ratio of major regioisomer to minor regioisomer as determined by ^{1}H NMR spectroscopy. [c] In this case, 5 equiv alkene were used. [d] Ratio is referred to **7n**:**7n′**. [e] Acetone was used as the solvent.

Experimental Section

General remarks: All reactions were carried out in a flame-dried flask under dry nitrogen or argon. All solvents were HPLC grade or analytical pure. Flash chromatography employed ICN silica gel (Kieselgel 60, 230–400 mesh), analytical TLC was performed with 0.2 mm silica-coated glass plates (E. Merck, DC-Platten Kieselgel 60 F_{254}). IR spectra were recorded using the Perkin–Elmer FT-IR spectrometer PARAGON 500. NMR spectra were recorded at room temperature, using either the Varian Gemini 300 MHz or Varian Gemini 500 MHz spectrometer. Elemental analyses were performed by M-H-W Laboratories (USA). HRMS (EI) m/z spectra were recorded by the Mass Spectrometer Facility of the School of Pharmacy, University of California, San Francisco (USA).

General procedure for the preparation of the 1,4-dienes: Alkene and alkyne was added to a flame-dried flask under nitrogen or argon followed by the addition of DMF (HPLC grade) at RT. To the mixture was then added ruthenium trisacetonitrile hexafluorophosphate. The resulting brown solution was stirred at RT for additional 1–4 h. The mixture was directly purified with a silica gel column chromatography eluting with petroleum ether/diethyl ether to yield 1,4-dienes.

Methyl 12-butyl-14-hydroxy-14-phenylpentadeca-9,12-dienoate (7a): This compound was prepared according to the general procedure: Methyl undec-10-enoate (40 mg, 0.20 mmol), 2-phenyl-oct-3-yn-2-ol (40 mg, 0.20 mmol), cyclopentadienyl ruthenium tris(acetonitrile) hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7a** as a pale yellow oil (67 mg, 0.17 mmol, 84%). IR (film): $\tilde{\nu}$ = 3515b, 2928s, 2856s, 1741s, 1446m, 1366m, 1199m, 1172m, 1089m, 1028w, 970m, 920w, 903w, 756m, 701s cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (dd, J = 1.0, 8.5 Hz, 2H), 7.33 (m, 2H), 7.22 (t, J = 7.0 Hz, 1H), 5.74 (s, 1H), 5.41 (m, 2H), 3.68 (s, 3H), 2.69 (d, J = 6.5 Hz, 2H), 2.32 (t, J = 9.0 Hz, 2H), 2.03 (q, J = 6.5 Hz, 2H), 1.97 (s, 1H), 1.90 (m, 2H), 1.63 (m, 5H), 1.28 (m, 8H), 1.18 (m, 1H),

0.98 (m, 3H), 0.73 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 174.3, 149.3, 144.1, 132.9, 132.4, 128.1, 127.9, 127.8, 126.2, 125.1, 124.5, 73.8, 51.4, 40.1, 34.1, 34.0, 33.5, 32.4, 30.6, 29.5, 29.3, 29.0, 28.8, 24.9, 22.9, 13.8$; elemental analysis calcd (%) for $C_{26}H_{40}O_3$: C 77.95, H 10.06; found: C 77.82, H 9.88.

Methyl 12-butyl-13-(1-hydroxycyclopentyl)-trideca-9,12-dienoate (7b): This compound was prepared according to the general procedure: Methyl undec-10-enoate (20 mg, 0.10 mmol), 1-hex-1-ynyl-cyclopentanol (17 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.25 mL) provided **7b** (26 mg, 0.071 mmol, 71%). IR (film): $\tilde{\nu} = 3527$b, 2928s, 2856s, 1742s, 1458m, 1436m, 1198m, 1172m, 994w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.47$ (s, 1H), 5.43 (m, 2H), 3.68 (s, 3H), 2.67 (d, $J = 7.0$ Hz, 2H), 2.31 (q, $J = 7.5$ Hz, 4H), 2.01 (q, $J = 7.0$ Hz, 2H), 1.91 (m, 2H), 1.88 (m, 2H), 1.67 (m, 8H), 1.39 (m, 10H), 0.93 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 174.3, 143.2, 132.2, 131.3, 128.2, 81.3, 51.4, 42.5, 42.0, 40.3, 34.1, 32.5, 30.9, 30.7, 29.4, 29.1, 28.9, 24.9, 23.45, 23.35, 14.1$; HRMS: calcd for $C_{23}H_{40}O_3$: 364.2977; found: 364.2977.

Dimethyl 2-{4-[2-(*tert*-butyldimethylsilanyloxy)-ethyl]-6-hydroxy-6-methylhepta-1,4-dienyl}-malonate (7c): This compound was prepared according to the general procedure: Dimethyl 2-allyl-malonoate (17 mg, 0.10 mmol), 6-(*tert*-butyldimethylsilanyloxy)-2-methyl-hex-3-yn-2-ol (24 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.40 mL) provided **7c** (24 mg, 0.058 mmol, 58%). IR (film): $\tilde{\nu} = 3452$b, 2956s, 2930s, 2858m, 1741s, 1463w, 1436m, 1360w, 1257s, 1149m, 1083m, 1031w, 972w, 924w, 836s, 779m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.68$ (m, 2H), 5.50 (s, 1H), 4.13 (s, 1H), 4.07 (d, $J = 8.5$ Hz, 1H), 3.775 (s, 3H), 3.774 (s, 3H), 3.71 (t, $J = 5.5$ Hz, 2H), 2.75 (d, $J = 6.5$ Hz, 2H), 2.62 (t, $J = 5.5$ Hz, 2H), 1.30 (s, 6H), 0.923 (s, 9H), 0.096 (s, 3H), 0.095 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 168.6, 137.5, 135.0, 132.3, 123.0, 70.6, 60.6, 55.2, 52.7, 40.4, 32.0, 31.9, 26.0, 18.5, -5.5$; elemental analysis calcd (%) for $C_{21}H_{38}O_6Si$: C 60.24, H 9.24; found: C 60.59, H 9.12; HRMS: calcd for $C_{17}H_{29}O_6Si$: 357.1733 $[M - C_4H_9]^+$; found: 357.1737.

Methyl 12-hydroxymethyl-14,14-dimethylpentadeca-9,12-dienoate (7d): This compound was prepared according to the general procedure: Methyl undec-10-enoate (20 mg, 0.10 mmol), 4,4-dimethyl-pent-2-en-1-ol (11 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (2.2 mg, 0.005 mmol), and DMF (0.25 mL) provided **7d** (24 mg, 0.076 mmol, 76%). IR (film): $\tilde{\nu} = 3444$b, 2928s, 2856s, 1742s, 1460w, 1436m, 1363m, 1243w, 1199m, 1172m, 971w cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.43$ (m, 2H), 5.36 (s, 1H), 4.23 (s, 2H), 3.66 (s, 3H), 2.75 (d, $J = 6.3$ Hz, 2H), 2.29 (t, $J = 7.5$ Hz, 2H), 1.98 (q, $J = 6.6$ Hz, 2H), 1.61 (m, 3H), 1.29 (m, 7H), 1.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 174.3, 139.9, 136.2, 132.3, 128.7, 60.2, 51.4, 48.0, 40.1, 34.1, 32.5, 31.7, 29.4, 29.1, 28.9, 24.9$; HRMS: calcd for $C_{19}H_{34}O_3$: 310.2508; found: 310.2498.

Dimethyl 2-(7-hydroxy-3-methylocta-2,5-dienyl)-2-{4-[tris(isopropyl)-silanyloxy]-butyl}-malonate (7e): This compound was prepared according to the general procedure: Dimethyl 2-but-2-ynyl-2-{4-[tris(isopropyl)-silanyloxy]-butyl}-malonoate (41 mg, 0.10 mmol), 4-penten-2-ol (10 mg, 0.12 mmol), ruthenium trisacetonitrile hexafluorophosphate (5.0 mg, 0.015 mmol), and DMF (0.5 mL) provided **7e** (27 mg, 0.054 mmol, 54%). IR (film): $\tilde{\nu} = 3457$b, 2943s, 2866s, 1737s, 1462m, 1384w, 1248m, 1229m, 1193w, 1109s, 1062m, 1012w, 971w, 882m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.56$ (m, 2H), 5.02 (t, $J = 7.5$ Hz, 1H), 4.30 (m, 1H), 3.72 (s, 6H), 3.69 (t, $J = 6.5$ Hz, 2H), 2.68 (d, $J = 5.5$ Hz, 2H), 2.65 (d, $J = 7.5$ Hz, 2H), 1.90 (m, 2H), 1.61 (d, $J = 3.0$ Hz, 3H), 1.55 (m, 2H), 1.46 (s, 3H), 1.27 (m, 2H), 1.07 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 172.0, 137.5, 135.8, 128.5, 125.5, 118.9, 68.7, 62.9, 57.7, 52.3, 42.4, 33.3, 32.3, 32.2, 31.0, 30.3, 23.4, 20.6, 18.0, 11.9$; HRMS: calcd for $C_{24}H_{43}O_6Si$: 456.2829 $[M - C_3H_7]^+$; found: 456.2834.

***trans*-2-(7-Hydroxyl-2-methylhepta-1,4-dienyl)-cyclohexanol (7f)**: This compound was prepared according to the general procedure: Pent-4-en-1-ol (22 mg, 0.25 mmol), *trans*-2-prop-1-ynyl-cyclohexanol (35 mg, 0.25 mmol), ruthenium trisacetonitrile hexafluorophosphate (11 mg, 0.025 mmol), and DMF (0.5 mL) provided **7f** (49 mg, 0.22 mmol, 88%). IR (film): $\tilde{\nu} = 3374$b, 2928s, 2855s, 1448m, 1381w, 1355w, 1263w, 1233w, 1044s, 970m, 867w, 797w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.45$ (m, 2H), 4.95 (dd, $J = 1.0, 10.0$ Hz, 1H), 3.60 (t, $J = 6.5$ Hz, 2H), 3.17 (m, 1H), 2.68 (d, $J = 6.5$ Hz, 2H), 2.28–2.08 (m, 4H), 1.98 (m, 1H), 1.73 (m, 1H), 1.63 (d, $J = 1.5$ Hz, 3H), 1.60 (m, 3H), 1.23 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 137.3, 131.1, 127.8, 127.3, 61.9, 45.4, 42.9, 36.4, 35.8, 33.5, 31.3, 25.2, 24.7, 16.6$; HRMS: calcd for $C_{14}H_{24}O_2$: 224.1776; found: 224.1772.

8-(*trans*-2-Hydroxycyclohexyl)-7-methylocta-4,7-dien-2-one (7g): This compound was prepared according to the general procedure: Hex-5-en-2-one (29 mg, 0.30 mmol), *trans*-2-prop-1-ynyl-cyclohexanol (41 mg, 0.30 mmol), ruthenium trisacetonitrile hexafluorophosphate (13 mg, 0.030 mmol), and DMF (0.5 mL) provided **7g** (64 mg, 0.270 mmol, 91%). IR (film): $\tilde{\nu} = 3460$b, 2927s, 2856s, 1715s, 1448s, 1358s, 1267w, 1231m, 1158m, 1061s, 1040s, 971s, 936w, 869w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.56$ (m, 2H), 5.00 (dd, $J = 1.0, 10.0$ Hz, 1H), 3.22 (m, 1H), 3.16 (d, $J = 6.5$ Hz, 2H), 2.77 (d, $J = 5.5$ Hz, 2H), 2.17 (s, 3H), 2.15 (m, 2H), 2.03 (m, 1H), 1.77 (m, 3H), 1.68 (d, $J = 1.0$ Hz, 3H), 1.28 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 207.2, 137.0, 132.8, 127.7, 123.5, 74.2, 47.4, 45.5, 42.9, 33.6, 31.4, 29.3, 25.2, 24.8, 16.7$; HRMS: calcd for $C_{15}H_{24}O_2$: 236.1776; found: 236.1776.

7-Benzyloxymethoxymethyl-8-(*tert*-butyldimethylsilanyloxy)-3-cyclopropylocta-2,5-dien-1-ol (7h): This compound was prepared according to the general procedure: 3-Cyclopropyl-prop-2-yn-1-ol (28 mg, 0.29 mmol), (2-benzyloxymethylpent-4-enyloxy)-*tert*-butyldimethylsilane (102 mg, 0.29 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7h** (87 mg, 0.195 mmol, 67%). IR (film): $\tilde{\nu} = 3452$b, 3083w, 3005w, 2954s, 2929s, 2858s, 1471m, 1382w, 1253m, 1169m, 1105s, 1046s, 972m, 837s, 777s, 737m, 698m, 665w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.37$ (m, 4H), 7.32 (m, 1H), 5.82 (m, 1H), 5.57 (m, 2H), 4.77 (s, 2H), 4.61 (s, 2H), 4.12 (d, $J = 7.0$ Hz, 2H), 3.66 (m, 4H), 2.76 (d, $J = 6.0$ Hz, 2H), 2.49 (m, 1H), 1.72 (br s, 1H), 1.40 (m, 1H), 0.91 (s, 9H), 0.63 (m, 2H), 0.48 (m, 2H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 142.7, 137.9, 130.6, 129.6, 128.4, 127.8, 127.6, 122.5, 94.7, 69.2, 68.5, 63.6, 58.9, 45.2, 33.1, 25.9, 18.3, 17.2, 5.41, -5.44, -5.47$; HRMS: calcd for $C_{26}H_{42}O_4Si$: 446.2852; found: 446.2858.

Dimethyl 2-(7-hydroxy-3-methylocta-2,5-dienyl)-malonate (7i): This compound was prepared according to the general procedure: Dimethyl 2-but-2-ynyl-malonoate (37 mg, 0.20 mmol), 4-penten-2-ol (17 mg, 0.20 mmol), ruthenium trisacetonitrile hexafluorophosphate (8.6 mg, 0.02 mmol), and DMF (1.0 mL) provided **7i** (27 mg, 0.12 mmol, 60%). IR (film): $\tilde{\nu} = 3538$b, 2957m, 1737s, 1438s, 1342m, 1275s, 1241s, 1207m, 1151s, 1059w, 1030w, 972w cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.57$ (m, 2H), 5.13 (tm, $J = 7.0$ Hz, 1H), 4.28 (p, $J = 6.5$ Hz, 1H), 3.75 (s, 6H), 3.40 (t, $J = 7.5$ Hz, 1H), 2.68 (d, $J = 6.0$ Hz, 2H), 2.63 (t, $J = 7.5$ Hz, 2H), 1.63 (t, $J = 1.0$ Hz, 3H), 1.26 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.5, 137.2, 135.8, 128.3, 120.5, 68.7, 52.5, 51.7, 42.2, 30.3, 27.5, 23.4, 16.1$; HRMS: calcd for $C_{14}H_{20}O_4$: 252.1350 $[M - H_2O]^+$; found: 252.1362.

Methyl 14-hydroxy-12-[3-(tetrahydropyran-2-yloxyl)-propyl]-hexadeca-9,12-dienoate, methyl 12-(1-hydroxy-propyl)-16-(tetrahydropyran-2-yloxy)-hexadeca-9,12-dienoate (7j, j′): These compounds were prepared according to the general procedure: Methyl undec-10-enoate (20 mg, 0.10 mmol), 8-(tetrahydropyran-2-yloxy)-oct-4-yn-3-ol (23 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (13 mg, 0.030 mmol), and DMF (0.5 mL) provided **7j** and **7j′** (38 mg, 0.089 mmol, 89%) as a mixture of two regioisomers. IR (film): $\tilde{\nu} = 3460$b, 2928s, 2855s, 1741s, 1438w, 1354w, 1200m, 1168m, 1137s, 1120s, 1076s, 1033s, 969w, 868w, 814w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7j**: $\delta = 5.44$ (m, 1H), 5.39 (m, 1H), 4.59 (m, 1H), 4.52 (m, 1H), 3.90 (m, 2H), 3.69 (s, 3H), 3.51 (m, 2H), 2.69 (m, 2H), 2.31 (t, $J = 8.0$ Hz, 3H), 2.01 (m, 2H), 1.62 (m, 12H), 1.30 (m, 9H), 0.91 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7j**: $\delta = 174.3, 141.4, 132.4, 130.4, 121.8, 99.6, 68.7, 66.8, 62.5, 51.4, 39.7, 39.5, 34.0, 30.6, 30.4, 30.3, 29.0, 28.9, 26.9, 25.3, 24.9, 19.7, 9.93$; ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7j′**: $\delta = 5.24$ (m, 2H), 4.32 (m, 2H), 3.75 (m, 2H), 3.68 (s, 3H), 3.41 (m, 2H), 2.69 (m, 2H), 2.29 (t, $J = 8.0$ Hz, 3H), 2.06 (m, 1H), 2.01 (m, 1H), 1.62 (m, 12H), 1.30 (m, 9H), 0.89 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7j′**: $\delta = 174.3, 139.6, 132.5, 129.2, 121.6, 98.9, 69.3, 65.9, 63.7, 51.4, 39.5, 34.0, 32.4, 30.9, 30.3, 30.1, 29.7, 29.3, 29.0, 28.1, 26.0, 25.4, 24.9, 20.5, 9,91$. For a mixture of **7j** and **7j′**: HRMS: calcd for $C_{25}H_{43}O_4$: 407.3161 $[M - OH]^+$; found: 407.3150.

Methyl 14-hydroxy-12-methyltetradeca-9,12-dienoate (7k): This compound was prepared according to the general procedure: But-2-yn-12-ol (7 mg, 0.10 mmol), methyl undec-10-enoate (20 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7k** (19 mg, 0.071 mmol, 71%). IR (film): $\tilde{\nu} = 3429$b, 2927s, 2855s, 1741s, 1436m, 1362w, 1239w, 1198m, 1172m, 1008w, 967w cm^{-1};

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^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.44$ (m, 3H), 4.17 (d, $J = 7.0$ Hz, 2H), 3.68 (s, 3H), 2.70 (d, $J = 6.5$ Hz, 2H), 2.32 (m, 2H), 2.01 (q, $J = 6.5$ Hz, 2H), 1.68 (s, 3H), 1.64 (m, 2H), 1.32 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 174.4$, 139.1, 132.7, 127.2, 123.6, 59.4, 51.4, 42.7, 37.2, 34.0, 32.4, 29.3, 29.0, 28.8, 24.9, 16.3; HRMS: calcd for $C_{16}H_{28}O_3$: 268.2038; found: 268.2031.

Methyl 14-hydroxy-12-(3-phenylpropyl)-tetradeca-9,12-dienoate, **methyl 12-hydroxymethyl-16-phenylhexadeca-9,12-dienoate (7l, l′)**: These compounds were prepared according to the general procedure: 6-Phenyl-hex-2-yn-1-ol (29 mg, 0.17 mmol), methyl undec-10-enoate (33 mg, 0.17 mmol), ruthenium trisacetonitrile hexafluorophosphate (7.2 mg, 0.017 mmol), and DMF (0.5 mL) provided **7l** and **7l′** (36 mg, 0.097 mmol, 58%) as a mixture of two regioisomers. For a mixture of **7l** and **7l′**: IR (film): $\tilde{\nu} = 3429$b, 2926s, 2854s, 1739s, 1434m, 1365w, 1243m, 1198m, 1172m, 1012w, 970w, 745w, 699m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7l**: $\delta = 7.28$ (m, 2H), 7.20 (m, 3H), 5.43 (m, 3H), 4.13 (d, $J = 7.0$ Hz, 2H), 3.69 (s, 3H), 2.72 (d, $J = 6.5$ Hz, 2H), 2.63 (m, 2H), 2.32 (m, 3H), 2.12 (m, 2H), 2.02 (m, 2H), 1.70 (m, 2H), 1.62 (m, 4H), 1.25 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7l**: $\delta = 174.4$, 142.8, 132.7, 128.3, 127.4, 125.8, 125.3, 124.4, 124.3, 59.2, 51.5, 40.1, 35.7, 34.1, 32.4, 30.3, 29.9, 29.7, 29.3, 29.1, 28.9, 25.0; ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7l′**: $\delta = 7.28$ (m, 2H), 7.20 (m, 3H), 5.43 (m, 3H), 4.19 (d, $J = 7.0$ Hz, 2H), 3.69 (s, 3H), 2.77 (d, $J = 6.5$ Hz, 2H), 2.63 (m, 2H), 2.32 (m, 3H), 2.12 (m, 2H), 2.02 (m, 2H), 1.70 (m, 2H), 1.62 (m, 4H), 1.25 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7l′**: $\delta = 174.4$, 142.1, 128.4, 128.3, 127.4, 125.6, 125.5, 124.4, 124.3, 58.8, 51.5, 40.1, 34.2, 34.1, 32.4, 30.1, 29.6, 29.3, 29.1, 28.9, 27.1, 24.5. For a mixture of **7l** and **7l′**: HRMS: calcd for $C_{24}H_{34}O_2$: 354.2559 $[M - H_2O]^+$; found: 354.2546.

6-Methylhexadeca-5,8-dien-3-ol, **5-ethylidenepentadec-7-en-3-ol (7m, m′)**: These compounds were prepared according to the general procedure: 4-Hexyn-2-ol (22 mg, 0.20 mmol), decene (28 mg, 0.20 mmol), ruthenium trisacetonitrile hexafluorophosphate (8.6 mg, 0.02 mmol), and DMF (0.5 mL) provided **7m** and **7m′** (36 mg, 0.143 mmol, 74%). For a mixture of **7m** and **7m′**: IR (film): $\tilde{\nu} = 3356$b, 2959s, 2925s, 2855s, 1362m, 1379w, 1115w, 1021w, 968s cm^{-1}. For major isomer **7m**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.40$ (m, 2H), 5.22 (t, $J = 1.0$ Hz, 1H), 3.56 (m, 1H), 2.70 (d, $J = 6.5$ Hz, 2H), 2.20 (m, 2H), 2.05 (m, 2H), 1.64 (s, 3H), 1.52 (m, 4H), 1.30 (m, 8H), 0.98 (t, $J = 7.5$ Hz, 3H), 0.90 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 138.3$, 132.3, 127.8, 120.3, 73.0, 43.1, 35.7, 32.5, 31.9, 30.0, 29.5, 29.2, 29.1, 22.7, 16.3, 14.1, 10.0. For minor isomer **7m′**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.42$ (m, 3H), 3.64 (m, 1H), 2.72 (d, $J = 7.5$ Hz, 2H), 2.30 (dd, $J = 9.5$, 13.5 Hz, 1H), 2.13 (dd, $J = 4.0$, 13.5 Hz, 1H), 2.01 (q, $J = 7.0$ Hz, 2H), 1.67 (d, $J = 6.5$ Hz, 3H), 1.37 (m, 12H), 1.00 (t, $J = 6.5$ Hz, 3H), 0.90 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 135.9$, 132.5, 128.0, 123.0, 71.1, 40.6, 37.4, 32.5, 31.9, 30.0, 29.5, 29.2, 29.1, 22.7, 14.1, 13.7, 10.1. For a mixture of **7m** and **7m′**: elemental analysis calcd (%) for $C_{17}H_{32}O$: C 80.89, H 12.78; found: C 80.65, H 12.53; HRMS: calcd for $C_{17}H_{32}O$: 252.2453; found: 252.2452.

2-Ethyl-2-(5-methylpentadeca-4,7-dienyloxy) tetrahydrofuran, **5-methylpentadeca-4,7-dien-1-ol (7n, n′)**: These compounds were prepared according to the general procedure: 4-Hexyn-1-ol (49 mg, 0.50 mmol), 1-decene (105 mg, 0.75 mmol), ruthenium trisacetonitrile hexafluorophosphate (22 mg, 0.05 mmol), and DMF (1.0 mL) provided **7n** (50 mg, 0.29 mmol, 58%) and **7n′** (17 mg, 0.07 mmol, 14%). For **7n**: IR (film): $\tilde{\nu} = 3848$b, 2925s, 1943w, 1721m, 1641m, 1550w, 1464s, 1381m, 1343m, 1324m, 1279s, 1230w, 1188s, 1156s, 1075s, 1040s, 968s, 920m, 868m, 724m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.47-5.34$ (m, 2H), 5.17 (t, $J = 6.9$ Hz, 1H), 3.90 (t, $J = 7.2$ Hz, 2H), 3.48–3.43 (m, 1H), 3.36–3.32 (m, 1H), 2.65 (d, $J = 6.4$ Hz, 2H), 2.13–1.81 (m, 7H), 1.74–1.54 (m, 6H), 1.38–1.24 (m, 12H), 0.93 (t, $J = 7.4$ Hz, 3H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 134.7$, 131.9, 128.2, 124.5, 109.9, 67.4, 59.8, 42.9, 35.2, 32.6, 31.9, 30.4, 29.6, 29.2, 29.1, 27.7, 24.8, 24.3, 24.2, 22.7, 14.1, 9.1; HRMS: calcd for $C_{16}H_{30}O$: 238.2297 $[M - C_6H_{10}O]^+$; found: 238.2310. For **7n′**: IR (film): $\tilde{\nu} = 3346$, 2926, 2856, 1461, 1380, 1156, 1058, 968, 918 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.46-5.34$ (m, 2H), 5.18 (t, $J = 6.6$ Hz, 1H), 3.67 (t, $J = 6.5$ Hz, 2H), 2.66 (d, $J = 6.6$ Hz, 2H), 2.10 (q, $J = 7.1$ Hz, 2H), 2.01 (q, $J = 7.1$ Hz, 2H), 1.65 (quint, $J = 7.3$ Hz, 2H), 1.61 (s, 3H), 1.38–1.28 (m, 11H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 135.3$, 132.1, 128.0, 124.0, 62.8, 42.9, 32.7, 32.5, 31.9, 29.5, 29.2, 29.1, 24.3, 22.7, 16.0, 14.1; elemental analysis calcd (%) for $C_{16}H_{30}O$: C 80.61, H 12.68; found: C 80.44, H 12.39; HRMS: calcd for $C_{16}H_{30}O$: 238.2297; found: 238.2295.

Methyl 12-butyl-14-hydroxy-14-(4-trifluoromethylphenyl)-tetradeca-9,12-dienoate, **methyl 12-[hydroxy-(4-trifluoromethylphenyl)-methyl]-heptadeca-9,12-dienoate (7o, o′)**: These compounds were prepared according to the general procedure: 1-(4-Trifluoromethyl-phenyl)-hept-2-yn-1-ol (26 mg, 0.10 mmol), methyl undec-10-enoate (20 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7o** and **7o′** (29 mg, 0.064 mmol, 64%) as a mixture of two regioisomers. For a mixture of **7o** and **7o′**: IR (film): $\tilde{\nu} = 3463$b, 2929s, 2858s, 1740s, 1619m, 1456m, 1437m, 1415m, 1326s, 1163s, 1125s, 1068s, 1017m, 971m, 843m, 728w cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) for the major isomer **7o**: $\delta = 7.37$ (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 5.33 (m, 4H), 3.34 (s, 3H), 2.66 (d, $J = 5.5$ Hz, 2H), 2.08 (m, 4H), 1.95 (m, 3H), 1.53 (m, 3H), 1.28 (m, 10H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7o**: $\delta = 174.4$, 148.0, 143.9, 133.0, 129.2, 126.21, 126.17, 125.31, 125.28, 69.7, 40.0, 36.6, 34.1, 34.0, 32.4, 30.8, 30.5, 29.9, 29.03, 29.01, 28.9, 24.9, 22.9, 14.0; ^{1}H NMR (500 MHz, C_6D_6) for the minor isomer **7o′**: $\delta = 7.40$ (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 5.30 (m, 4H), 3.34 (s, 3H), 2.77 (d, $J = 6.0$ Hz, 2H), 2.08 (m, 4H), 1.94 (m, 3H), 1.54 (m, 3H), 1.28 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7o′**: $\delta = 174.4$, 148.0, 132.2, 130.4, 127.12, 127.07, 126.2, 125.9, 125.2, 51.4, 36.6, 34.1, 34.0, 32.4, 30.8, 30.5, 29.9, 29.3, 28.9, 28.8, 24.9, 22.9, 22.4, 14.0. For a mixture of **7o** and **7o′**: HRMS: calcd for $C_{26}H_{37}F_3O_3$: 454.2695; found: 454.2690.

Methyl 15-hydroxy-12-methylpentadeca-9,12-dienoate, **methyl 12-(2-hydroxyethyl)-tetradeca-9,12-dienoate (7p, p′)**: These compounds were prepared according to the general procedure: 3-Pentyn-1-ol (8.4 mg, 0.10 mmol), methyl undec-10-enoate (20 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7p** and **7p′** (21 mg, 0.074 mmol, 74%). For a mixture of **7p** and **7p′**: IR (film): $\tilde{\nu} = 3423$b, 2927s, 2856s, 1741s, 1438m, 1364w, 1199m, 1172m, 1048m, 970w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7p**: $\delta = 5.38$ (m, 2H), 5.16 (td, $J = 1.0$, 7.5 Hz, 1H), 3.68 (s, 3H), 3.64 (t, $J = 6.5$ Hz, 2H), 2.68 (d, $J = 6.0$ Hz, 2H), 2.32 (m, 4H), 2.00 (q, $J = 6.5$ Hz, 2H), 1.64 (m, 5H), 1.31 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7p**: $\delta = 174.3$, 138.1, 132.1, 127.9, 120.1, 62.4, 51.4, 42.9, 34.1, 32.4, 31.5, 29.4, 29.1, 29.0, 28.9, 24.9, 16.2. ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7p′**: $\delta = 5.38$ (m, 3H), 3.68 (s, 3H), 3.65 (t, $J = 6.5$ Hz, 2H), 2.68 (d, $J = 6.0$ Hz, 2H), 2.32 (m, 4H), 2.00 (q, $J = 6.5$ Hz, 2H), 1.64 (m, 5H), 1.31 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7p′**: $\delta = 174.3$, 135.1, 132.4, 128.1, 122.6, 60.7, 51.4, 40.5, 34.1, 33.0, 32.4, 31.5, 29.4, 29.0, 28.9, 24.9, 16.2. For a mixture of **7p** and **7p′**: HRMS: calcd for $C_{17}H_{30}O_3$: 282.2195; found: 282.2204.

5-Methylpentadeca-4,7-dienyl benzoate, **4-ethylidenetetradec-6-enyl benzoate (7q, q′)**: These compounds were prepared according to the general procedure: Hex-4-ynyl benzoate (51 mg, 0.25 mmol), 1-decene (53 mg, 0.375 mmol) and ruthenium trisacetonitrile hexafluorophosphate (10.9 mg, 0.025 mmol), and DMF (0.5 mL) provided **7q** and **7q′** (69 mg, 0.20 mmol, 80%). IR (film): $\tilde{\nu} = 2957$, 2925, 2855, 2361, 2342, 1723, 1452, 1315, 1273, 1115, 1070, 1028 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7q**: $\delta = 8.08$ (d, $J = 8.5$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.9$ Hz, 2H), 5.48–5.35 (m, 2H), 5.21 (tt, $J = 1.2$, 7.2 Hz, 1H), 4.34 (t, $J = 6.6$ Hz, 2H), 2.67 (d, $J = 6.6$ Hz, 2H), 2.21 (quint, $J = 6.9$ Hz, 2H), 2.02 (q, $J = 7.3$ Hz, 2H), 1.85 (quint, $J = 6.9$, 2H), 1.62 (s, 3H), 1.40–1.29 (m, 10H), 0.90 (t, $J = 6.9$ Hz, 3H). Additional peaks for minor isomer **7q′**: 5.32 (q, $J = 6.8$ Hz, 1H), 2.71 (d, $J = 6.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.6$, 135.7, 132.8, 132.1, 130.5, 129.5, 128.3, 128.0, 123.4, 64.6, 42.9, 32.5, 31.9, 29.5, 29.2, 29.1, 28.8, 24.4, 22.6, 16.0, 14.1. Peaks for minor isomer **7q′**: $\delta = 137.9$, 132.2, 130.4, 128.1, 120.3, 64.7, 40.3; HRMS: calcd for $C_{23}H_{34}O_2$: 342.2559; found: 342.2553.

6-Butyloctadeca-3,16,17-triene-1,8-diol, **6-pentylideneheptadeca-3,16-diene-1,7-diol (7r, r′)**: These compounds were prepared according to the general procedure: Pent-4-en-1-ol (14 mg, 0.16 mmol), heptadec-16-en-5-yn-7-ol (40 mg, 0.16 mmol), ruthenium trisacetonitrile hexafluorophosphate (6.9 mg, 0.016 mmol), and DMF (0.5 mL) provided **7r** and **7r′** (28 mg, 0.083 mmol, 52%) as a mixture of two regioisomers. IR (film): $\tilde{\nu} = 3354$b, 2924s, 2856s, 1688s, 1464s, 1048s, 970s, 909m, 725w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) of major isomer **7r**: $\delta = 5.83$ (m, 1H), 5.55 (m, 1H), 5.47 (m, 1H), 5.16 (dd, $J = 4.0$, 5.5 Hz, 1H), 5.00 (dd, $J = 3.5$, 18.5 Hz, 1H), 4.93 (dd, $J = 2.0$, 10.5 Hz, 1H), 4.36 (m, 1H), 3.69 (m, 2H), 2.74 (d, $J = 6.5$ Hz, 2H), 2.38 (m, 2H), 2.16 (m, 6H), 1.30 (m, 16H), 0.93 (t, $J = 7.0$ Hz, 3H).

Additional peaks for minor isomer **7r′**: $\delta = 5.56$ (m, 1H), 5.47 (m, 1H), 5.37 (m, 1H), 5.25 (m, 1H), 2.70 (d, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) of major isomer **7r**: $\delta = 139.2$, 131.3, 128.8, 127.9, 127.6, 114.1, 68.2, 62.2, 40.0, 37.7, 36.5, 33.8, 31.4, 30.8, 30.3, 29.54, 29.49, 29.38, 29.1, 25.5, 22.8, 14.0. Additional peaks for minor isomer **7r′**: $\delta = 143.4$, 128.5, 36.0, 35.9, 32.5, 28.9; HRMS: calcd for $C_{22}H_{40}O_2$: 336.3029; found: 336.3028.

Methyl 12-(1-hydroxypropyl)-13-phenyltrideca-9,12-dienoate, **methyl 14-hydroxy-12-phenylhexadeca-9,12-dienoate (7s, s′)**: These compounds were prepared according to the general procedure: 1-Phenylpent-1-yn-3-ol (17 mg, 0.10 mmol), methyl undec-10-enoate (20 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.010 mmol), and DMF (0.5 mL) provided **7s** and **7s′** (23 mg, 0.061 mmol, 61%) as a mixture of two regioisomers. For a mixture of **7s** and **7s′**: IR (film): $\tilde{\nu} = 3444$b, 2928s, 2855s, 1741s, 1493w, 1436m, 1361w, 1247m, 1198s, 1172m, 1134m, 1107w, 1076w, 1076w, 1020w, 968w, 765w, 702s cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7s**: $\delta = 7.42 - 7.16$ (m, 5H), 5.46 (d, $J = 8.5$ Hz, 1H), 5.40 (m, 2H), 4.08 (dt, $J = 6.5$, 8.5 Hz, 1H), 3.69 (s, 3H), 3.03 (d, $J = 4.5$ Hz, 2H), 2.32 (t, $J = 7.5$ Hz, 2H), 1.98 (m, 2H), 1.63 (m, 2H), 1.32 (m, 12H), 0.86 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7s**: $\delta =$ 174.3, 143.1, 132.9, 130.0, 128.1, 128.0, 127.1, 126.8, 68.9, 51.5, 42.2, 39.8, 34.1, 33.6, 32.4, 29.2, 29.1, 29.0, 28.8, 24.9, 18.6, 14.0. ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7s′**: $\delta = 7.42 - 7.16$ (m, 5H), 5.78 (d, $J = 9.0$ Hz, 1H), 5.52 (m, 1H), 5.41 (m, 1H), 4.53 (dt, $J = 6.5$, 8.5 Hz, 1H), 3.68 (s, 3H), 3.27 (d, $J = 5.0$ Hz, 2H), 2.31 (t, $J = 7.5$ Hz, 2H), 1.97 (m, 2H), 1.55 (m, 2H), 1.32 (m, 12H), 0.98 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7s′**: $\delta = 174.3$, 140.7, 131.9, 131.8, 128.2, 127.6, 126.8, 126.4, 68.5, 51.5, 42.2, 39.7, 37.8, 33.6, 32.4, 30.3, 29.2, 29.0, 28.8, 24.9, 18.7, 14.1. For a mixture of **7s** and **7s′**: HRMS: calcd for $C_{24}H_{36}O_3$: 372.2664; found: 372.2673.

Methyl 14-(*tert*-butyldimethylsilanyloxy)-12,14-diphenyltetradeca-9,12-dienoate, **methyl 13-(*tert*-butyldimethylsilanyloxy)-13-phenyl-12-benzylidenetrideca-9,12-dienoate(7t, t′)**: These compounds were prepared according to the general procedure: *tert*-Butyl-1,3-diphenyl-prop-2-ynyloxydimethylsilane (40 mg, 0.12 mmol), methyl undec-10-enoate (25 mg, 0.12 mmol), ruthenium trisacetonitrile hexafluorophosphate (5.4 mg, 0.012 mmol), and DMF (0.5 mL) provided **7t** and **7t′** (49 mg, 0.094 mmol, 76%) as a mixture of two regioisomers. For a mixture of **7t** and **7t′**: IR (film): $\tilde{\nu} = 3028$w, 2929s, 2856s, 1742s, 1493w, 1462w, 1442w, 1360w, 1251m, 1196w, 1172w, 1061m, 1027w, 1005w, 969w, 836s, 776s, 699s cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7t**: $\delta = 7.44$ (m, 10H), 5.65 (d, $J = 9.5$ Hz, 1H), 5.40 (m, 2H), 5.16 (d, $J = 9.5$ Hz, 1H), 3.70 (s, 3H), 3.04 (d, $J = 4.0$ Hz, 2H), 2.36 (m, 4H), 1.95 (m, 3H), 1.61 (m, 4H), 1.25 (m, 3H), 0.96 (s, 9H), -0.04 (s, 3H), -0.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7t**: $\delta = 174.3$, 140.6, 140.1, 132.8, 130.7, 128.7, 128.3, 128.1, 128.0, 126.92, 126.88, 126.8, 126.1, 71.7, 51.4, 42.2, 34.1, 33.5, 32.4, 29.3, 29.1, 28.9, 25.9, 24.9, -4.30, -4.85. ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7t′**: $\delta = 7.44$ (m, 10H), 5.91 (d, $J =$ 9.0 Hz, 1H), 5.40 (m, 3H), 3.69 (s, 3H), 3.42 (dd, $J = 6.5$, 16.0 Hz, 1H), 3.36 (dd, $J = 6.5$, 16.0 Hz, 1H), 2.36 (m, 4H), 2.06 (dd, $J = 5.5$, 13.0 Hz, 1H), 1.95 (m, 3H), 1.61 (m, 4H), 1.26 (m, 2H), 0.87 (m, 9H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7t′**: $\delta = 174.3$, 144.9, 144.4, 136.7, 132.8, 132.4, 128.05, 127.9, 127.1, 127.0, 126.7, 126.5, 126.0, 71.3, 51.4, 42.2, 33.8, 32.5, 32.4, 29.2, 29.1, 28.8, 25.8, 18.1, -4.20, -4.66; HRMS: calcd for $C_{33}H_{48}O_3Si$: 520.3373; found: 520.3376.

11-Methyldocosa-8,11-diene, **3-decyltrideca-2,5-diene(7u,u′)**: These compounds were prepared according to the general procedure: Tridec-2-yne (45 mg, 0.25 mmol), 1-decene (53 mg, 0.375 mmol), ruthenium trisacetonitrile hexafluorophosphate (10.9 mg, 0.025 mmol), and DMF (0.5 mL) provided **7u** and **7u′** (70 mg, 0.22 mmol, 88%). IR (film): $\tilde{\nu} = 2957$s, 2923s, 2854s, 2360s, 2342s, 1466m, 1379w, 968m, 721w, 668w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7u**: $\delta = 5.47 - 5.36$ (m, 2H), 5.17 (t, $J =$ 6.9 Hz, 1H), 2.66 (d, $J = 6.1$ Hz, 2H), 2.01 (quint, $J = 7.2$ Hz, 2H), 1.60 (s, 3H), 1.39 – 1.29 (m, 28H), 0.91 (t, $J = 6.7$ Hz, 6H). Additional peaks for minor isomer **7u′**: 5.23 (q, $J = 6.8$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 134.1$, 131.8, 128.3, 125.2, 43.0, 32.5, 31.9, 31.8, 29.9, 29.70, 29.67, 29.60, 29.5 (x2), 29.2, 29.1, 28.0, 22.7, 22.6, 14.1 (×2). Additional peaks for minor isomer **7u′**: 139.8, 128.5, 118.9; HRMS: calcd for $C_{23}H_{44}$: 320.3443; found: 320.3439.

Methyl 14-hydroxy-12,14-diphenyltetradeca-9,12-dienoate, **methyl 12-benzylidene-13-hydroxy-13-phenyltrideca-9,12-dienoate (7v, v′)**: These compounds were prepared according to the general procedure: 1,3-Diphenyl-prop-2-yn-1-ol (21 mg, 0.10 mmol), methyl undec-10-enoate (20 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7v** and **7v′** (26 mg, 0.064 mmol, 64%) as a mixture of two regioisomers. For a mixture of **7v** and **7v′**: IR (film): $\tilde{\nu} = 3418$b, 3058w, 3029w, 2927s, 2854s, 1738s, 1400w, 1492s, 1443s, 1365m, 1248m, 1174s, 1107m, 1080m, 1030s, 967m, 915w, 758s, 700s cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7v**: $\delta = 7.42 - 7.20$ (m, 10H), 5.74 (d, $J = 9.5$ Hz, 1H), 5.72 (d, $J = 5.5$ Hz, 1H), 5.41 (m, 1H), 5.18 (d, $J =$ 9.5 Hz, 1H), 3.69 (s, 3H), 3.07 (d, $J = 3.5$ Hz, 2H), 2.46 (d, $J = 5.5$ Hz, 1H), 2.32 (m, 2H), 1.97 (m, 2H), 1.63 (m, 2H), 1.29 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7v**: $\delta = 174.4$, 143.8, 143.3, 140.6, 140.3, 133.2, 131.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.4, 127.1, 126.7, 126.4, 126.1, 88.7, 71.2, 65.1, 42.2, 34.1, 32.4, 29.2, 29.0, 24.9, 24.6. ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7v′**: $\delta = 7.42 - 7.20$ (m, 10H), 6.03 (d, $J = 9.0$ Hz, 1H), 5.65 (d, $J = 9.0$ Hz, 1H), 5.49 (m, 2H), 3.69 (s, 3H), 3.39 (m, 2H), 2.32 (m, 2H), 2.10 (s, 1H), 1.97 (m, 2H), 1.63 (m, 2H), 1.29 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7v′**: $\delta = 174.4$, 143.5, 141.9, 140.2, 132.2, 130.9, 128.9, 128.6, 128.5, 128.4, 128.2, 127.5, 127.3, 127.1, 126.5, 126.1, 122.4, 86.6, 70.7, 51.4, 42.2, 33.6, 29.2, 29.0, 28.76, 28.73, 24.6. For a mixture of **7v** and **7v′**: HRMS: calcd for $C_{27}H_{34}O_3$: 406.2508; found: 406.2498.

Methyl 14-hydroxy-12-(4-methoxybenzyloxymethyl)-tetradeca-9,12-dienoate, **methyl 12-hydroxymethyl-14-(4-methoxybenzyl-oxy)-tetradeca-9,12-dienoate (7w, w′)**: These compounds were prepared according to the general procedure: 1-But-2-ynyloxymethyl-4-methoxy-benzene (28 mg, 0.136 mmol), methyl undec-10-enoate (27 mg, 0.14 mmol), ruthenium trisacetonitrile hexafluorophosphate (5.9 mg, 0.014 mmol), and DMF (0.5 mL) provided **7w** and **7w′** (43 mg, 0.11 mmol, 79%) as a mixture of two regioisomers. For a mixture of **7w** and **7w′**: IR (film): $\tilde{\nu} = 3452$b, 2928s, 2854s, 1738s, 1612m, 1586w, 1514s, 1463m, 1440m, 1360w, 1302m, 1248s, 1207m, 1173s, 1074m, 1035m, 971m, 821w cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7w**: $\delta = 7.28$ (m, 2H), 6.89 (d, $J = 6.5$ Hz, 2H), 5.69 (t, $J = 6.5$ Hz, 1H), 5.41 (m, 2H), 4.44 (s, 2H), 4.16 (d, $J = 7.0$ Hz, 2H), 4.00 (s, 2H), 3.83 (s, 3H), 3.69 (s, 3H), 2.81 (d, $J = 6.0$ Hz, 2H), 2.33 (m, 2H), 2.01 (m, 2H), 1.62 (m, 2H), 1.31 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7w**: $\delta = 174.4$, 133.2, 133.1, 130.0, 129.6, 129.4, 128.4, 113.81, 113.79, 72.1, 67.2, 58.8, 55.2, 51.5, 38.9, 38.8, 34.1, 29.3, 29.1, 29.0, 28.9, 24.9. ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7w′**: $\delta = 7.28$ (m, 2H), 6.89 (d, $J = 6.5$ Hz, 2H), 5.59 (t, $J = 6.5$ Hz, 1H), 5.41 (m, 2H), 4.48 (s, 2H), 4.09 (d, $J = 6.5$ Hz, 2H), 4.11 (s, 2H), 3.83 (s, 3H), 3.69 (s, 3H), 2.85 (d, $J =$ 6.0 Hz, 2H), 2.33 (m, 2H), 2.01 (m, 2H), 1.62 (m, 2H), 1.31 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7w′**: $\delta = 174.3$, 139.4, 132.2, 129.9, 129.3, 127.0, 124.2, 122.4, 113.7, 72.2, 65.6, 60.8, 55.2, 51.5, 38.9, 38.8, 34.1, 29.3, 29.1, 29.0, 28.9, 24.9. For a mixture of **7w** and **7w′**: HRMS: calcd for $C_{24}H_{36}O_5$: 404.2563; found: 404.2553.

Methyl 12-hydroxymethyl-13-phenyl-trideca-9,12-dienoate, **methyl 14-hydroxy-12-phenyltetradeca-9,12-dienoate (7x, x′)**: These compounds were prepared according to the general procedure: 3-Phenyl-prop-2-yn-1-ol (13 mg, 0.10 mmol), methyl undec-10-enoate (20 mg, 0.10 mmol), ruthenium trisacetonitrile hexafluorophosphate (4.3 mg, 0.01 mmol), and DMF (0.5 mL) provided **7x** and **7x′** (26 mg, 0.078 mmol, 78%) as a mixture of two regioisomers. For a mixture of **7x** and **7x′**: IR (film): $\tilde{\nu} = 3452$b, 2927s, 2855s, 1740s, 1494w, 1437m, 1366w, 1199m, 1173m, 1027w, 970w, 759w, 700m cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) for major isomer **7x**: $\delta = 7.43$ (m, 2H), 7.35 (m, 3H), 6.02 (t, $J = 6.5$ Hz, 1H), 5.45 (m, 2H), 4.36 (d, $J = 6.5$ Hz, 2H), 3.69 (s, 3H), 3.24 (d, $J = 4.5$ Hz, 2H), 2.32 (m, 4H), 1.97 (m, 2H), 1.63 (m, 4H), 1.28 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) for major isomer **7x**: $\delta = 174.4$, 143.6, 140.7, 133.0, 128.6, 128.2, 128.0, 127.2, 127.1, 126.6, 126.2, 60.3, 51.5, 41.8, 32.5, 30.3, 29.3, 29.2, 29.0, 28.7, 24.8. ^{1}H NMR (500 MHz, $CDCl_3$) for minor isomer **7x′**: $\delta = 7.43$ (m, 2H), 7.35 (m, 2H), 7.16 (m, 1H), 5.70 (td, $J = 1.0$, 6.5 Hz, 1H), 5.45 (m, 2H), 4.09 (d, $J = 7.0$ Hz, 2H), 3.69 (s, 3H), 3.07 (d, $J = 5.0$ Hz, 2H), 2.32 (m, 4H), 1.97 (m, 2H), 1.63 (m, 4H), 1.28 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) for minor isomer **7x′**: $\delta = 174.4$, 142.1, 140.2, 131.8, 128.14, 128.11, 127.6, 127.3, 127.0, 126.8, 125.9, 60.8, 59.8, 41.8, 32.4, 32.3, 32.0, 29.7, 29.3, 29.0, 28.8, 24.8. For a mixture of **7x** and **7x′**: HRMS: calcd for $C_{21}H_{30}O_3$: 330.2195; found: 330.2200.

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