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ALICYCLIC PHOSPHOLIPASE A₂ INHIBITORSBACKGROUND

- 10 The invention deals with compounds having activity as phospholipase A₂ (PLA₂) inhibitors. PLA₂ is a calcium-dependent enzyme which cleaves the sn-2 acyl bond of phospholipids to yield arachidonic acid and a lysophospholipid (H. Van den Bosch et al. in *Biochim. Biophys. Acta* 1980, 604, 191). Both products of this reaction
- 15 can serve as starting points for the biosynthesis of inflammatory mediators. Once released, arachidonic acid is rapidly metabolized by enzymes such as cyclooxygenase and lipoxygenases to give prostaglandins and leukotrienes, well-known mediators of inflammation (P. Davies and D.E. MacIntyre in "Inflammation: Basic
- 20 Principles and Clinical Correlates," 2nd Ed., J.I. Gallin, I.M. Goldstein, and R. Snyderman, Eds., Raven Press, Ltd.: New York, 1992; Chapter 7; B.K. Lam and K.F. Austen in "Inflammation: Basic Principles and Clinical Correlates," 2nd Ed., J.I. Gallin, I.M. Goldstein, and R. Snyderman, Eds., Raven Press, Ltd.: New York, 1992; Chapter 8).
- 25 Lysophospholipids can be utilized by certain cell types to produce platelet-activating factor (PAF), another potent inflammatory mediator (G.A. Zimmerman, S.M. Prescott, and T.M. McIntyre in "Inflammation: Basic Principles and Clinical Correlates," 2nd Ed., J.I. Gallin, I.M. Goldstein, and R. Snyderman, Eds., Raven Press, Ltd.: New
- 30 York, 1992; Chapter 9). The role of PLA₂ in inflammatory diseases has been described (P. Vadas and W. Pruzanski in *Laboratory Investigation*, 1986, 55, 391-404; W. Pruzanski, E. Bogoch, M. Wloch, and P. Vadas in *Journal of Rheumatology*, 1991, 18, 117-119; W. Pruzanski, K. Scott, G. Smith, I. Rajkovic, E. Stefanski, and P. Vadas in
- 35 *Inflammation*, 1992, 16, 451-457; W. Pruzanski, D.W. Wilmore, A. Suffredini, G.D. Martich, A.G.D. Hoffman, J.L. Browning, E. Stefanski, B. Sternby, and P. Vadas in *Inflammation*, 1992, 16, 561-570; J.M.

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SUMMARY OF THE INVENTION

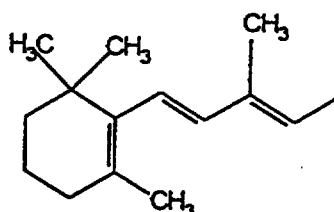
Applicants have discovered novel compounds of Formulas I:



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X = COOH, H, F, Cl, Br, I, COOR'', CONH₂, COR''', CHO, CH₂OH, CH₂OR''', OH, OR''', CF₃, C₁₋₆ alkyl, C₁₋₆ alkenyl, C₁₋₆ haloalkyl, NO₂, P(O)(OH)₂, SO₂H, or SO₃H;

R = substituted or unsubstituted alkyl, aryl, arylalkyl, alkenyl, or arylalkenyl groups, with the proviso that each group ^{must} have 6 or more carbons (preferably 6 to 30 carbons) and R cannot be



R' = H or C₁₋₆ alkyl;

R'' = H, C₁₋₆ alkyl, C(R³)₂OC(O)R⁴, CH₂CH₂NR⁵R⁶, CH₂CH₂CH₂NR⁵R⁶, CH₂C(O)N(R⁶)₂, or other groups yielding physiologically hydrolyzable esters;

R''' = C₁₋₆ alkyl;

R³ = H, CH₃, C₂H₅, CH₃CH₂CH₂ (with R³'s being the same or different);

R⁴ = C₆₋₁₂ aryl, C₁₋₇ linear, branched or cyclic alkyl, or C₁₋₇ linear, branched or cyclic alkoxy;

R⁵ = R⁶, or when linked with R⁶, is a C₃-C₆ cycloalkyl or a -CH₂CH₂OCH₂CH₂- group; and

R⁶ = C₁₋₃ alkyl.

These compounds, their geometric isomers and their pharmaceutical salts, exhibit PLA₂ inhibition with significant anti-inflammatory effects.

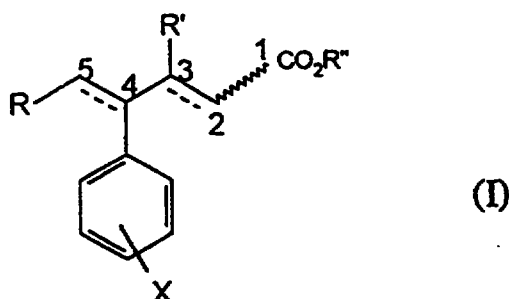
The novel compounds and isomers and derivatives thereof are useful in combination with pharmaceutical carriers and other excipients in formulations to be administered by, preferably, topical or oral routes.

DESCRIPTION OF THE INVENTION

The invention is concerned with novel compounds and the use of those compounds, their isomers or other pharmaceutically acceptable derivatives thereof, in processes and compositions to be used to treat inflammation.

Unless otherwise indicated, all percentages recited herein are weight percents, based upon total composition weight.

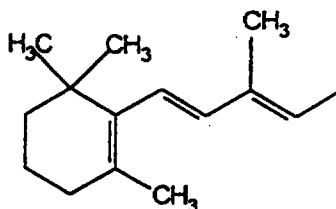
The compounds of the invention generally conform to
5 Formula I:



wherein the bonds between C₂ and C₃ and/or between C₄ and C₅ are unsaturated;

15 X = COOH, H, F, Cl, Br, I, COOR'', CONH₂, COR''', CHO, CH₂OH, CH₂OR''', OH, OR''', CF₃, C₁₋₆ alkyl, C₁₋₆ alkenyl, C₁₋₆ haloalkyl, NO₂, P(O)(OH)₂, SO₂H, or SO₃H;

R = substituted or unsubstituted alkyl, aryl, arylalkyl, alkenyl or arylalkenyl groups, with the proviso that each group must have 6 or
20 more carbons (preferable 6 to 30 carbons) and R cannot be



R' = H or C₁₋₆ alkyl;

R'' = H, C₁₋₆ alkyl, C(R³)₂OC(O)R⁴, CH₂CH₂NR⁵R⁶, CH₂CH₂CH₂NR⁵R⁶, CH₂C(O)N(R⁶)₂, or other groups yielding physiologically hydrolyzable
30 esters;

R''' = C₁₋₆ alkyl;

R³ = H, CH₃, C₂H₅, CH₃CH₂CH₂ (with R³'s being the same or different);

R⁴ = C₆₋₁₂ aryl, C₁₋₇ linear, branched or cyclic alkyl, or C₁₋₇ linear, branched or cyclic alkoxy;

35 R⁵ = R⁶, or, when linked with R⁶, is a C₃-C₆ cycloalkyl or a -CH₂CH₂OCH₂CH₂- group; and

R⁶ = C₁₋₃ alkyl.

X is preferably H, COOH, F, CF₃, COOR'' or CONH₂.

In preferred embodiments, the phenyl ring at C₄ has an X substituent in the meta-position. R may be substituted or unsubstituted groups of the types recited. When the R group is substituted, the substituents may be OH, C₁₋₁₂ alkyloxy, C₁₋₁₂ alkenyloxy, C₁₋₁₂ cycloalkyl, C₁₋₁₂ halophenylalkyloxy, C₁₋₁₂ hydroxyalkyl or adamantyl. R may have from one to six substituents, with "substituents" meaning groups other than hydrogen. Preferred R groups are set out in Tables 1 and 2.

By "6 or more" carbons, applicants mean 6 to 30, and preferably 14 to 30.

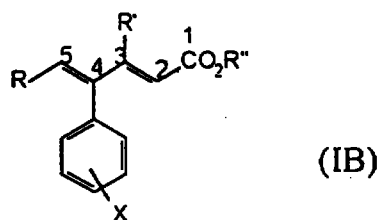
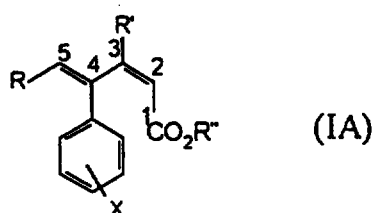
R' may be H or C₁₋₆ alkyl, but is preferably H or CH₃.

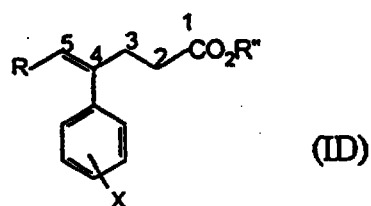
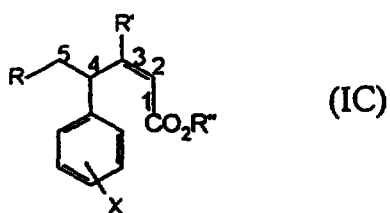
R'' is preferably H.

By "halo" applicants mean Br, Cl, F, or I.

R³, R⁵ and R⁶, when independent moieties (i.e., not linked to each other), may be the same or different.

Compounds of the invention preferably conform to formula types IA, IB, IC or ID, as follows:





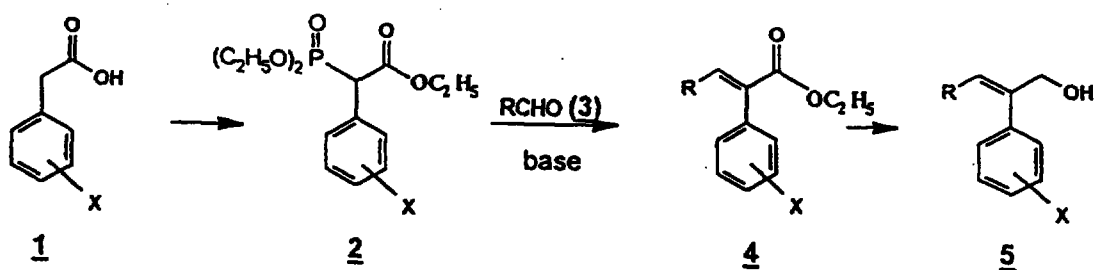
20 wherein the substituents are as defined above.

When $R' = H$, compounds of structure types 11 and 14 conform to IA, types 18 and 20 conform to IB. When $R' = CH_3$, compounds of structure 11k conform to IA.

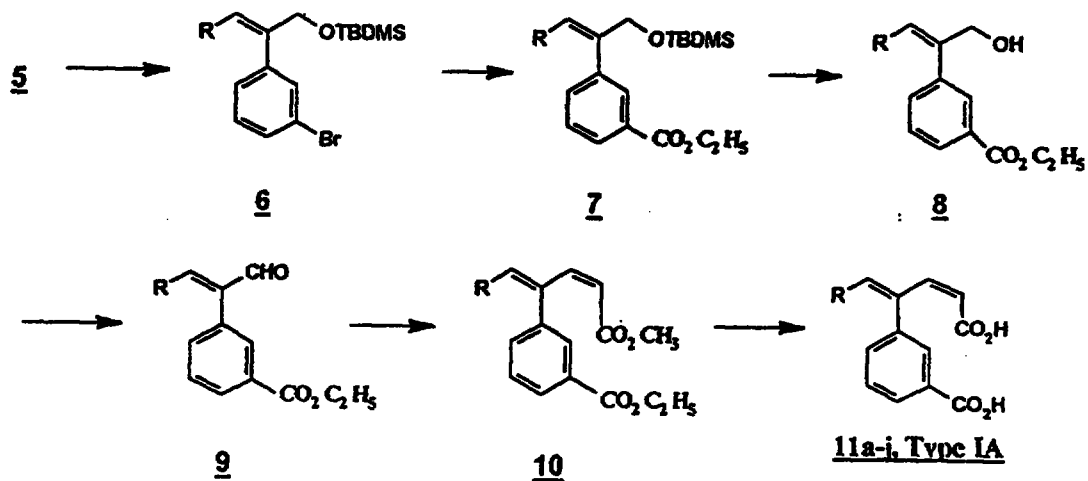
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PREPARATION

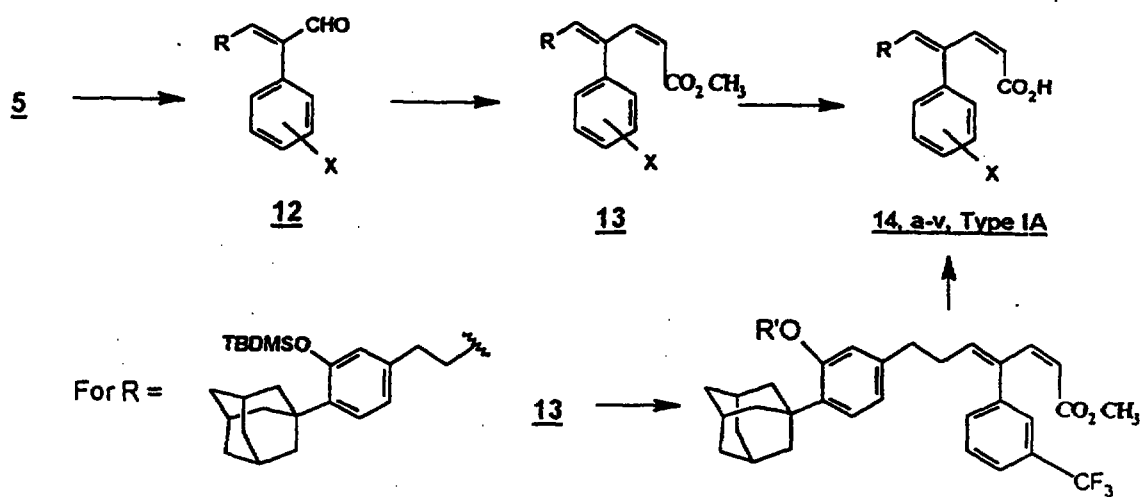
The compounds of the invention are typically prepared using one or more of the steps shown below:

Scheme 1: Synthesis of Analogues of Type IA

X = CO₂H from X = Br:



X = other than CO₂H:



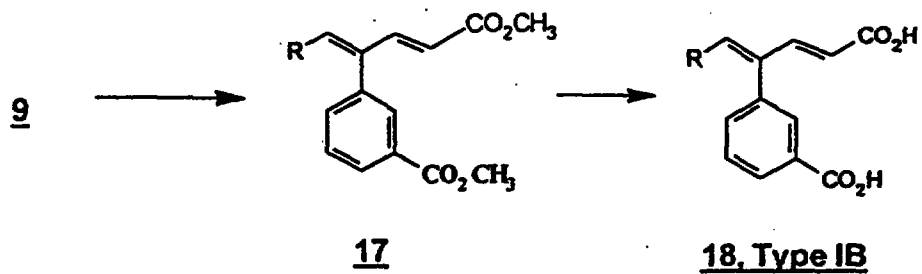
OTBDMS = TBDMSO = tertiary butyl dimethylsiloxy

15 R' = H

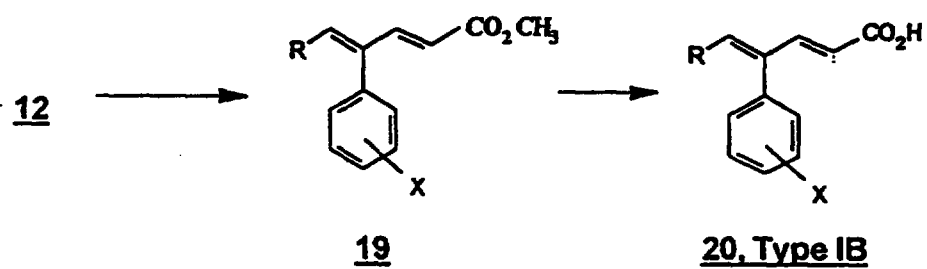
16 R' = alkyl

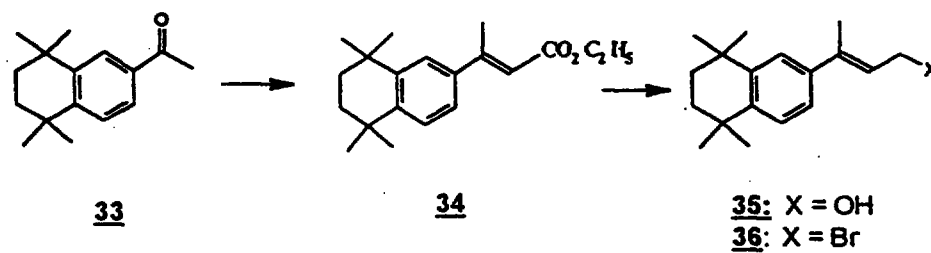
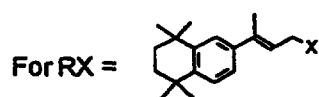
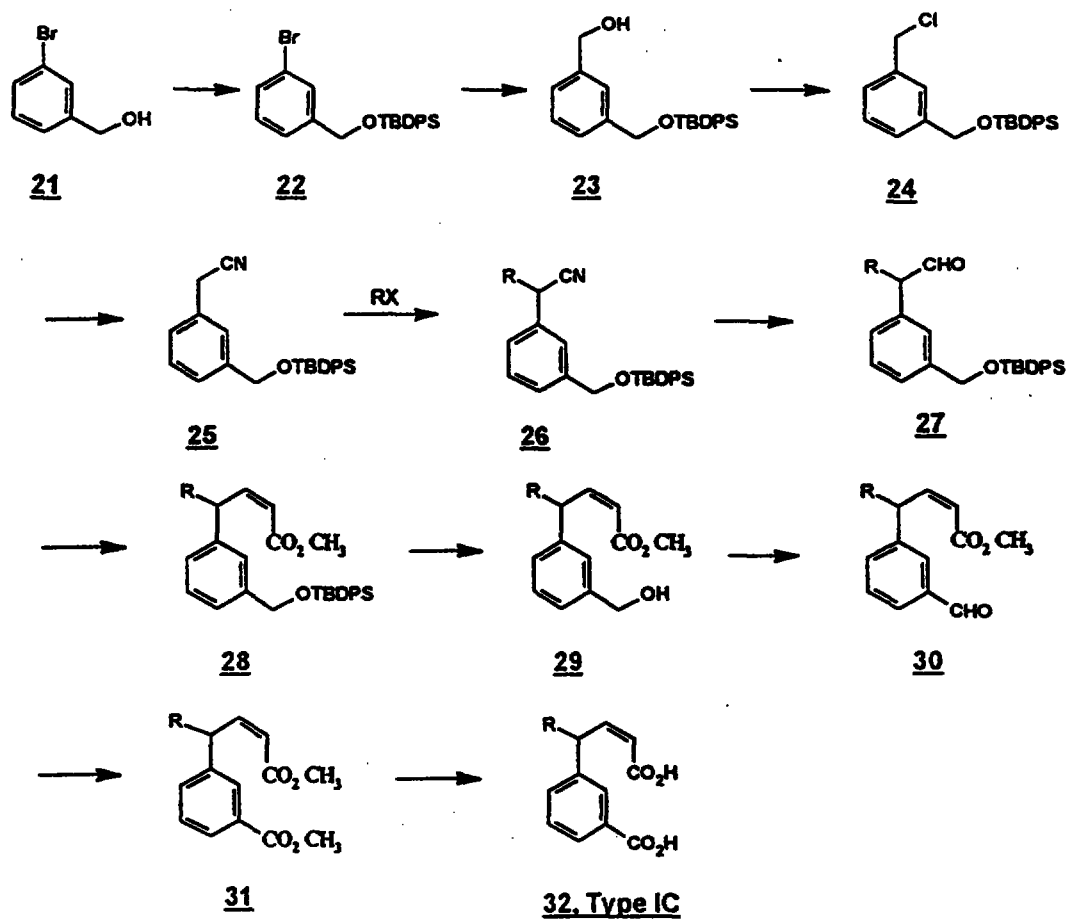
Scheme 2: Synthesis of Analogues of Type IB

$X = \text{CO}_2\text{H}$:

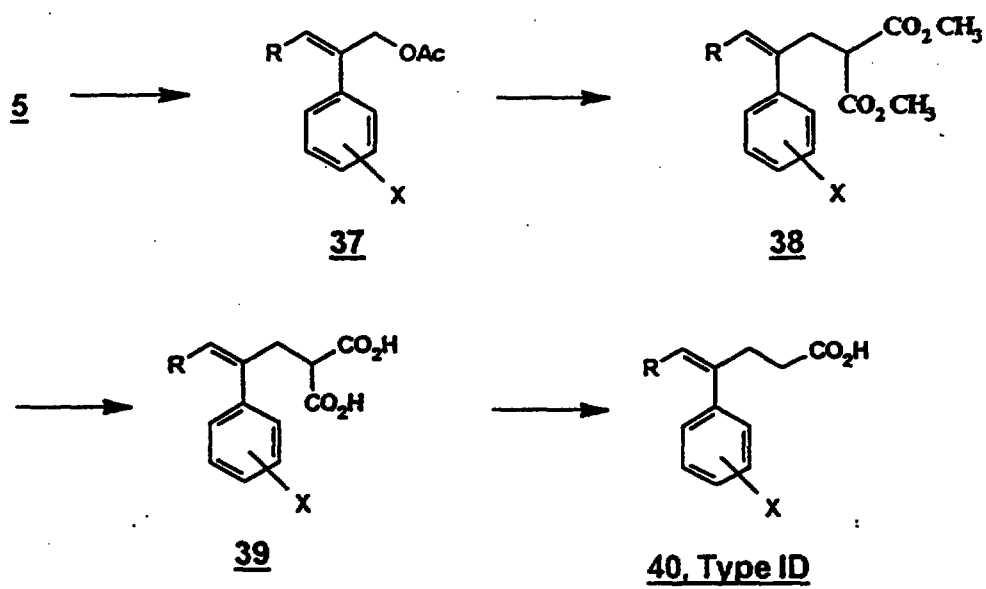


$X = \text{other than } \text{CO}_2\text{H}$:



Scheme 3: Example of Type IC

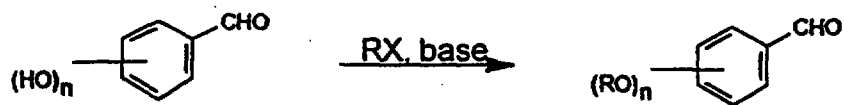
OTBDPS = tertiary butyl diphenylsiloxy

Scheme 4: Synthesis of Analogues of Type ID

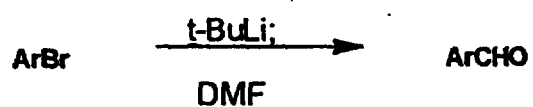
Ac = acetyl

Scheme 5: Synthesis of Aldehydes (3)

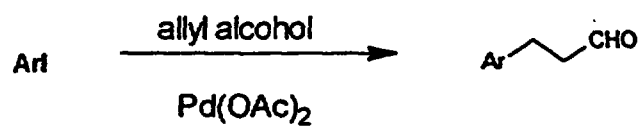
A.



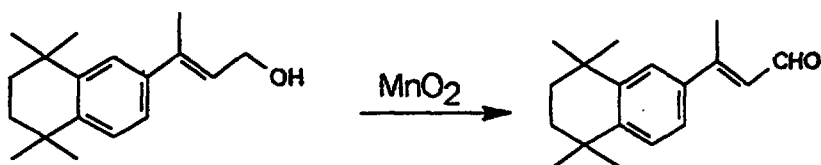
B.

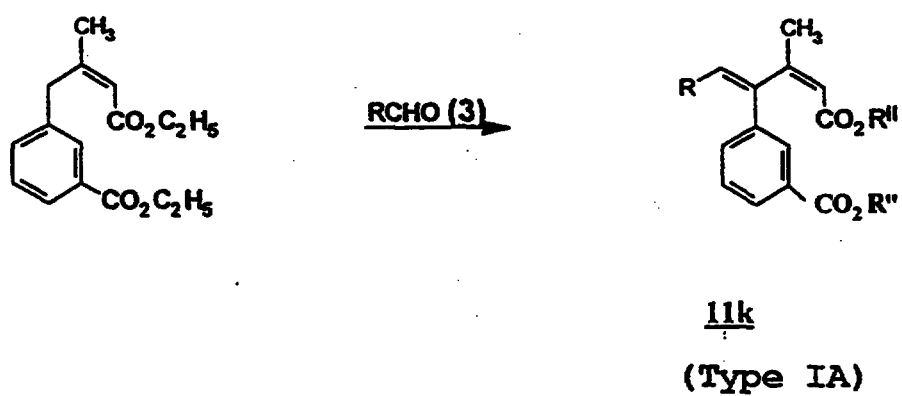


C.



D.

 $n = 1, 2$ Ar = substituted phenyl, naphthyl, or anthracenyl

Scheme 6: Synthesis of 11k

PLA₂ Inhibition Assay

The method used is similar to that reported by Franson, et al. [Jesse, R.L. and Franson R.C., Biochim. Biophys. Acta 575: 467-470 (1979); Franson, R.C., Patriarca, P., and Elsbach, P., J. Lipid Res. 15: 380-388 (1974)]. The enzyme is isolated from human platelets. The substrate used consists of ¹⁴C-oleate labeled *Escherichia coli* membranes. *E. coli* cells are grown in the presence of ¹⁴C-oleic acid and then autoclaved to prepare the membranes.

Various concentrations of test compounds are pre-incubated with PLA₂ (3.6 µg/mL in a buffer consisting of 25 mM HEPES (pH 7)), 150 mM NaCl, 5.0 mM CaCl₂, and 10% DMSO (v/v, test compound solvent) at 37°C for 7 minutes. The *E. coli* membrane substrate is then added (0.1 mM phospholipid, 0.005 µCi ¹⁴C) and the reaction is then incubated at 37°C for 30 minutes. The reaction is then terminated by the addition of 1.9 mL tetrahydrofuran (THF), and the entire solution is applied to a solid-phase extraction column (aminopropyl resin, Analytichem). The column is rinsed with an additional 1 mL of THF. The free fatty acid product of the reaction is then eluted from the column with 1 mL of 2% acetic acid in THF and collected in a scintillation vial. The amount of free fatty acid product is determined by liquid scintillation counting. The amount of inhibition produced by the test compound is calculated by comparing the counts obtained in the presence of the compound to those obtained in its absence (solvent only). Background counts were determined by performing incubations in the absence of enzyme.

Percent inhibition is determined by the equation:

$$\% \text{ Inhibition} = \left(1 - \frac{(\text{CPM with test compound}) - (\text{background})}{(\text{CPM without test compound}) - (\text{background})} \right) \times 100$$

The biological activities of compounds of Types IA through ID are given in Tables 1-6. The compounds are effective inhibitors of PLA₂.

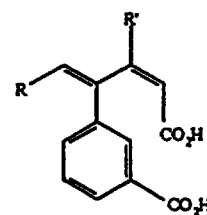
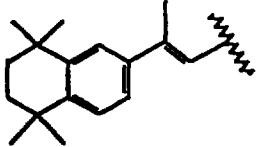
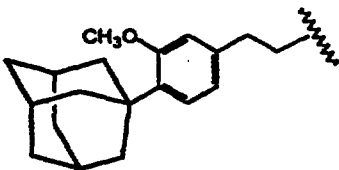
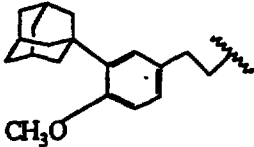
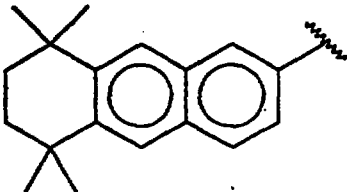


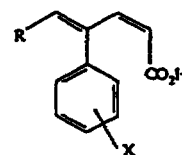
Table 1: Biological Data for Compounds of Structure 11 (Type IA):

R	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	<u>11a</u>	6%
	<u>11b</u>	44%
	<u>11c</u>	97%
	<u>11d</u>	100%
	<u>11e</u>	100%
	<u>11f</u>	15%
	<u>11g</u>	58%

Table 1 (con't) Biological Data for Structural Compounds of Type IA

R	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	<u>11h</u>	97%
	<u>11i</u>	100%
	<u>11j</u>	98%
	<u>11k</u>	98%

R' = H, except for 11k, where R' = CH₃

Table 2: Biological Data for Compounds of Structure 14 (Type IA):

R	X	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	m-CF ₃	<u>14a</u>	100%
	m-CF ₃	<u>14b</u>	100%
	m-CF ₃	<u>14c</u>	92%
	m-CF ₃	<u>14d</u>	98%
	m-CF ₃	<u>14e</u>	99%
	m-CF ₃	<u>14f</u>	71%
	m-CF ₃	<u>14g</u>	96%

Table 2: (cont'd)

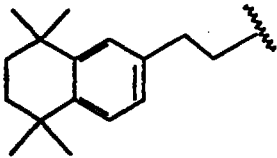
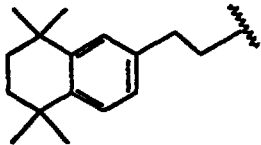
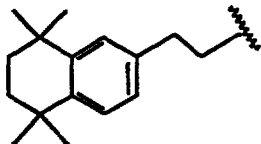
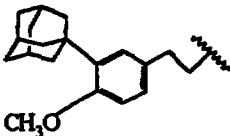
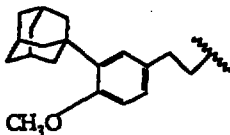
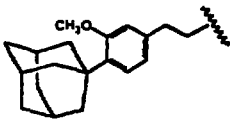
R	X	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	p-F	<u>14h</u>	96%
	m-F	<u>14i</u>	96%
	H	<u>14j</u>	92%
	m-CF ₃	<u>14k</u>	99%
	H	<u>14l</u>	99%
	m-CF ₃	<u>14m</u>	99%

Table 2: (cont'd)

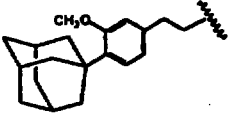
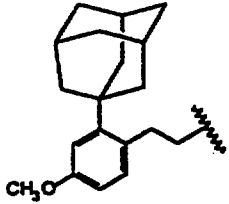
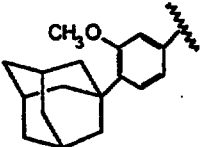
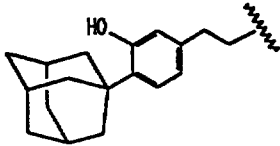
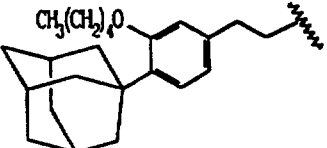
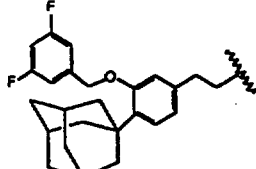
R	X	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	H	<u>14n</u>	100%
	m-CF ₃	<u>14o</u>	99%
	m-CF ₃	<u>14p</u>	93%
	m-CF ₃	<u>14q</u>	100%
	m-CF ₃	<u>14r</u>	95%
	m-CF ₃	<u>14s</u>	100%

Table 2: (cont'd)

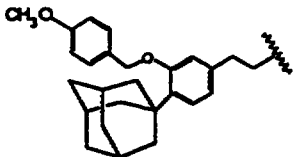
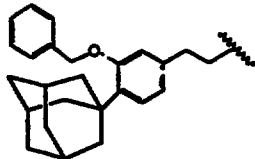
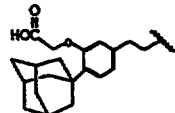
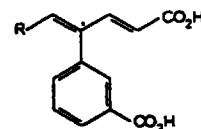
R	X	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	m-CF ₃	<u>14t</u>	100%
	m-CF ₃	<u>14u</u>	100%
	m-CF ₃	<u>14v</u>	100%

Table 3: Biological Data for compounds of Structure 18 (Type IB):

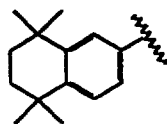
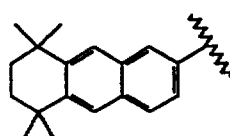
R	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	<u>18a</u>	27%
	<u>18b</u>	100%

Table 3: (cont'd)

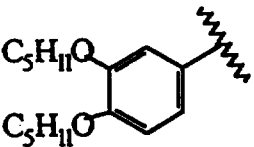
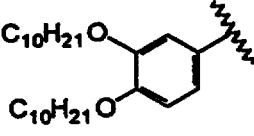
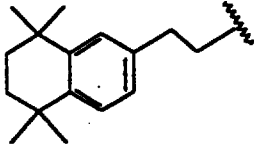
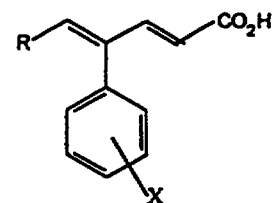
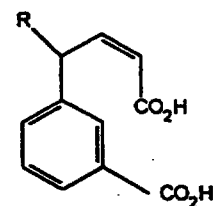
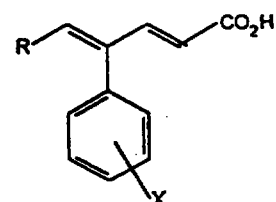
R	X	Structure Number
	<u>18c</u>	70%
	<u>18d</u>	91%
	<u>18e</u>	55%

Table 4: Biological Data for compounds of Structure 20 (Type IB).

R	X	Structure Number	% Inhibition of PLA ₂ at 100 μ M
	m-CF ₃	<u>20a</u>	52%
	p-F	<u>20b</u>	73%
	m-F	<u>20c</u>	67%
	H	<u>20d</u>	62%
	m-CF ₃	<u>20e</u>	81%
	m-CF ₃	<u>20f</u>	90%

Table 5: Biological Data for Compounds of Structure 32 (Type IC):

R	Structure Number	% Inhibition of PLA ₂ at 100 μ m
	<u>32a</u>	1%
	<u>32b</u>	56%
	<u>32c</u>	67%

Table 6: Biological Data for Compounds of Structure 40 (Type ID):

R	X	Structure Number	% Inhibition of PLA ₂ AT 100 μ m
	m-CF ₃	<u>40</u>	79%

Formulations

Compositions or formulations may contain one or more of the compounds themselves. They may also contain isomers and/or pharmaceutically acceptable derivatives or analogs, such as hydrates, salts, e.g., succinates, acetates, hydrochlorides, alkali metal salts, ammonium salts, quaternary alkylammonium salts and the like. Examples of alkali metal salts are potassium and sodium salts. Ammonium and quaternary alkylammonium salts include salts derived from triethanolamine, N-methylglucamine, tris(hydroxymethyl)aminomethane, and L-lysine.

The concentration of active ingredient(s), or compound(s) of the invention, in such formulations will generally be from about 0.005 to about 10.0 wt%, with quantities of about 0.01 to about 5 wt% preferred.

Additives such as carriers, colorants, perfumes, vehicles, stabilizers, flow control agents and other pharmaceutically acceptable excipients can be used. Additionally, one or more other active ingredient(s) may be included.

The concentration of additives, i.e., ingredients other than the compound(s) of the invention, will generally be from about 90 to 99.995 wt%.

Administration

The compounds of the invention, their isomers and pharmaceutically acceptable derivatives or analogs thereof, may be administered to any subjects in need of treatment for inflammatory conditions, e.g., psoriasis, arthritis, and the like. While human subjects are preferred, the subjects may also be mice or other mammalian species.

The formulations discussed above may be adapted for administration via nasal, intravenous, intramuscular, ophthalmic, buccal, oral or topical routes. Transdermal, i.e., topical, and oral administration are the preferred routes.

Suitable dosage forms for administration include pills, tablets, capsules, liquid compositions (administrable by injection, ingestion, or application to the surface of the skin or to other body parts), creams, gels, lotions, ointments and the like.

Examples

The following examples illustrate the preparation of various compounds conforming to Formula I.

In the following examples, all temperatures are given in degrees Centigrade. Melting points were determined on an electrothermal apparatus and are not corrected. Proton and carbon-13 nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded on a Bruker AM-300 or a Varian Gemini 300 spectrometer. All spectra were determined in CDCl_3 , $\text{DMSO}-d_6$, CD_3OD , or D_2O unless otherwise indicated. Chemical shifts are reported in δ units relative to tetramethylsilane (TMS) and interproton coupling constants are reported in Hertz (HZ). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak; dd, doublet of doublets and dt, doublet of triplets. Infrared spectra were determined on a Perkin-Elmer 1800 FT-IR spectrometer from 4000 cm^{-1} to 400 cm^{-1} , calibrated to 1601 cm^{-1} absorption of a polystyrene film, and are reported in reciprocal centimeters (cm^{-1}). Mass spectra were recorded on a Kratos MS-50 or a Finnegan 4500 instrument utilizing direct chemical ionization (DCI, isobutene) or fast atom bombardment (FAB). Ultraviolet spectra were determined on a Hewlett Packard 8452 diode array spectrophotometer in the solvent indicated.

Analytical thin-layer chromatography (TLC) was carried out on precoated silica gel plates (60F-254) and visualized using UV light, iodine vapors, and/or staining by heating with methanolic phosphomolybdic acid. Column chromatography, also referred to as flash chromatography, was performed in a glass column using finely divided silica gel at pressures somewhat above atmospheric pressure with the indicated solvents. Reversed-phase analytical thin-layer chromatography was carried out on precoated reverse phase plates and visualized using UV light or iodine vapors. Reversed-phase plates and visualized using UV light or iodine vapors. Reversed-phase column chromatography was performed in a glass column using Baker Octadecyl (C_{18}), $40\text{ }\mu\text{m}$.

All evaporations of solvent were performed under reduced pressure. Celite is a registered trademark of the Johns-Manville Products Corporation for diatomaceous earth.

5 **Example 1: General Procedure for Synthesis of 2**

The route used to prepare phosphonates **2** was based on the following reference: Berry, J.P.; Isbell, A.F.; Hunt, G.E. *J. Org. Chem.* 1972, 37, 4396. The final product was purified by column
10 chromatography on silica gel (10:1 ratio silica gel/crude compound, elution with 40 % ethyl acetate/hexane) or by distillation at 0.1 mm Hg.

For Ethyl 2-(3-bromophenyl)diethylphosphonoacetate: scale =
15 68.0 mmol, purified by chromatography, yield = 79%; scale = 120 mmol, purified by distillation (bp 135-140 °C, 0.1 mm Hg), yield = 75%; ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 2 Hz, 1 H, ArH), 7.44-7.48 (m, 2 H, ArH), 7.22 (t, *J* = 8 Hz, 1 H, ArH), 4.00-4.31 (m, 7 H, CO₂CH₂, 2 x POCH₂, and CH), 1.21-1.36 (m, 9 H, CO₂CH₂CH₃ and 2 x POCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.50 (d, *J*_{c,p} = 4 Hz, C=O), 133.23, 132.55 (d, *J*_{c,p} = 7 Hz, ArC), 131.10 (d, *J*_{c,p} = 3 Hz, ArC), 129.96, 128.33 (d, *J*_{c,p} = 6 Hz, ArC), 122.36, 63.56 (d, *J*_{c,p} = 7 Hz, POC), 63.29 (d, *J*_{c,p} = 7 Hz, POC), 62.06 (CO₂CH₂), 51.76 (d, *J*_{c,p} = 135 Hz, CHP(O)), 16.27 (d, *J*_{c,p} = 5 Hz, POCH₂CH₃), and 14.04 (CO₂CH₂CH₃); IR (film) 2985, 2935, 2910, 1735 (C=O),
20 1595, 1570, 1475, 1370, 1320, 1300, 1260, 1210, 1150, 1095, 1050, 1025, and 690 cm⁻¹; MS (DCI) *m/e* 379 (MH⁺).

For Ethyl 2-(3-trifluoromethylphenyl)diethylphosphonoacetate:
scale = 34.3 mmol, purified by chromatography, yield = 55%; scale =
30 98.0 mmol, purified by distillation (bp 135-140 °C, 0.1 mm Hg), yield = 69%; ¹H NMR (300 MHz, CDCl₃) δ 7.71-7.75 (m, 2 H, ArH), 7.55 (d, *J* = 8 Hz, 1 H, ArH), 7.45 (t, *J* = 8 Hz, 1 H, ArH), 3.97-4.42 (m, 7 H, CO₂CH₂, 2 x POCH₂, and CH), 1.03-1.33 (m, 9 H, CO₂CH₂CH₃ and 2 x POCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.07 (d, *J*_{c,p} = 4 Hz, C=O), 133.08 (d, *J*_{c,p} = 6 Hz, ArC), 132.17 (d, *J*_{c,f} = 8 Hz), 128.94, 126.52 (overlapping s and d, *J*_{c,p} = 6 Hz, 2 x ArC), 124.76 (d, *J*_{c,f} = 3 Hz, ArC), 123.91 (d, *J*_{c,f} = 272 Hz, CF₃), 63.54 (d, *J*_{c,p} = 7 Hz, POC), 63.27 (d, *J*_{c,p} = 7 Hz, POC), 62.10

(CO₂CH₂), 51.98 (d, $J_{\text{C,P}}^1 = 135$ Hz, CHP(O)), 16.23 (d, $J_{\text{C,P}}^3 = 5$ Hz, POCH₂CH₃), 16.16 (d, $J_{\text{C,P}}^3 = 5$ Hz, POCH₂CH₃), and 13.99 (CO₂CH₂CH₃); IR (film) 2985, 2935, 2910, 1740 (C=O), 1450, 1395, 1370, 1330, 1260, 1210, 1165, 1125, 1100, 1080, 1030, 970, 925, 805, and 700 cm⁻¹; MS (DCI) m/e 369 (MH⁺).

For Ethyl 2-(3-fluorophenyl)diethylphosphonoacetate: scale = 31.4 mmol, purified by chromatography, yield = 69%; ¹H NMR (300 MHz, CDCl₃) δ 7.21-7.32 (m, 3 H, ArH), 6.95-7.01 (m, 1 H, ArH), 3.93-4.29 (m, 7 H, CO₂CH₂, 2 $\times$ POCH₂, and CH), 0.98-1.33 (m, 9 H, CO₂CH₂CH₃ and 2 $\times$ POCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.50 (d, $J_{\text{C,P}}^2 = 4$ Hz, C=O), 162.58 (d, $J_{\text{C,F}}^1 = 245$ Hz, ArC), 133.20 (dd, $J_{\text{C,P}}^3 = 8$ Hz, $J_{\text{C,F}}^3 = 8$ Hz, ArC), 129.83 (d, $J_{\text{C,F}}^3 = 8$ Hz), 125.42 (d, $J_{\text{C,P}}^3 = 4$ Hz, ArC), 116.69 (dd, $J_{\text{C,F}}^2 = 23$ Hz, $J_{\text{C,P}}^3 = 6$ Hz, ArC), 114.94 (d, $J_{\text{C,F}}^2 = 21$ Hz, ArC), 63.50 (d, $J_{\text{C,P}}^2 = 7$ Hz, POC), 63.20 (d, $J_{\text{C,P}}^2 = 7$ Hz, POC), 61.99 (CO₂CH₂), 51.91 (d, $J_{\text{C,P}}^1 = 135$ Hz, CHP(O)), 16.30 (d, $J_{\text{C,P}}^3 = 5$ Hz, POCH₂CH₃), 16.23 (d, $J_{\text{C,P}}^3 = 5$ Hz, POCH₂CH₃), and 14.02 (CO₂CH₂CH₃); IR (film) 2985, 2935, 2910, 1735 (C=O), 1615, 1590, 1490, 1450, 1370, 1320, 1255, 1155, 1100, 1050, 1030, 970, 690, and 620 cm⁻¹; MS (DCI) m/e 319 (MH⁺).

20

For Ethyl 2-(4-fluorophenyl)diethylphosphonoacetate: scale = 32.0 mmol, purified by chromatography, yield = 85%; ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.50 (m, 2 H, ArH), 7.01 (apparent t, $J_{\text{H,F}} = 8.5$ Hz, $J_{\text{H,H}} = 8.5$ Hz, 2 H, ArH), 3.88-4.25 (m, 7 H, CO₂CH₂, 2 $\times$ POCH₂, and CH), 0.99-1.45 (m, 9 H, CO₂CH₂CH₃ and 2 $\times$ POCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.50 (d, $J_{\text{C,P}}^2 = 4$ Hz, C=O), 162.55 (d, $J_{\text{C,F}}^1 = 245$ Hz, ArC), 131.31 (dd, $J_{\text{C,P}}^3 = 8$ Hz, $J_{\text{C,F}}^3 = 8$ Hz, ArC), 126.74 (d, $J_{\text{C,P}}^2 = 6$ Hz), 115.43 (d, $J_{\text{C,F}}^2 = 20$ Hz, ArC), 63.40 (d, $J_{\text{C,P}}^2 = 7$ Hz, POC), 63.12 (d, $J_{\text{C,P}}^2 = 7$ Hz, POC), 61.91 (CO₂CH₂), 51.36 (d, $J_{\text{C,P}}^1 = 135$ Hz, CHP(O)), 16.30 (d, $J_{\text{C,P}}^3 = 5$ Hz, POCH₂CH₃), 16.23 (d, $J_{\text{C,P}}^3 = 5$ Hz, POCH₂CH₃), and 14.02 (CO₂CH₂CH₃); IR (film) 2985, 2935, 2910, 1735 (C=O), 1605, 1510, 1475, 1445, 1390, 1370, 1325, 1300, 1260, 1225, 1150, 1100, 1050, 1030, 970, 900, 850, 815, 795, and 740 cm⁻¹; MS (DCI) m/e 319 (MH⁺).

30

For Ethyl 2-(phenyl)diethylphosphonoacetate: scale = 46.5 mmol, purified by chromatography, yield = 85%; ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.51 (m, 2 H, ArH), 7.25-7.35 (m, 3 H, ArH), 3.88-4.25 (m, 7

35

H, CO₂CH₂, 2 × POCH₂, and CH), 1.14-1.26 (m, 9 H, CO₂CH₂CH₃ and 2 × POCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.63 (d, *J*_{c,p} = 4 Hz, C=O), 130.95 (d, *J*_{c,p} = 8 Hz, ArC), 129.61 (d, *J*_{c,p} = 6 Hz), 128.48, 127.91 (d, *J*_{c,p} = 3 Hz, ArC), 63.38 (d, *J*_{c,p} = 7 Hz, POC), 63.05 (d, *J*_{c,p} = 7 Hz, POC), 5
61.79 (CO₂CH₂), 52.26 (d, *J*_{c,p} = 135 Hz, CHP(O)), 16.29 (d, *J*_{c,p} = 5 Hz, POCH₂CH₃), 16.23 (d, *J*_{c,p} = 5 Hz, POCH₂CH₃), and 14.03 (CO₂CH₂CH₃); IR (film) 2985, 2935, 2910, 1735 (C=O), 1500, 1455, 1390, 1370, 1300, 1260, 1210, 1150, 1095, 1025, 970, 805, 730, and 700 cm⁻¹; MS (DCI) *m/e* 301 (MH⁺).

10

Example 2: Preparation of Aldehydes 3

Procedure A: Aryl aldehydes via transmetallation of aryl halides

15 A solution of the aryl halide (1 equivalent) in anhydrous THF (0.15 - 0.20 M solution) was cooled to -78 °C under argon and treated with *t*-butyllithium solution (ca. 1.6 M in pentane, 2.0 - 2.1
equivalents). The reaction mixture was stirred at -78 °C for 0.5-1 h and then treated with anhydrous *N,N*-dimethylformamide (2.0 - 3.0
20 equivalents). The reaction mixture was allowed to warm to room temperature, and then was poured into a separatory funnel containing diethyl ether and saturated ammonium chloride solution. The layers were agitated and separated, and the organic layer was washed with
saturated sodium chloride solution, dried over anhydrous magnesium
25 sulfate, filtered, and concentrated. The crude product was used without purification or was purified by column chromatography (20:1 ratio silica gel/crude product; elution with 1-10% ethyl acetate in hexanes).

30 For 5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-naphthaldehyde (3a): scale = 10.2 mmol, yield = 95%. The precursor aryl halide, 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-iodonaphthalene, was obtained from 5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalene (Maybridge
Chemicals) via the method of W.W. Sy et al. *Synth. Commun.* 1990,
35 20, 877. For 3a: ¹H NMR (300 MHz, CDCl₃) δ 9.92 (s, 1 H, CHO), 7.80 (d, *J* = 2 Hz, 1 H, ArH), 7.60 (dd, *J* = 2, 8 Hz, 1 H, ArH), 7.44 (d, *J* = 8 Hz, 1 H, ArH), 1.69 (br s, 4 H, CH₂CH₂), 1.30 (s, 6 H, 2 × CH₃), and 1.29 (s, 6 H, 2 ×

- CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 192.38 (C=O), 152.43, 145.92, 134.16, 128.61, 127.41, 126.60, 34.93, 34.73, 34.68, 34.41, 31.75 (CH₃), and 31.59 (CH₃); IR (film) 2960, 2930, 2860, 1695 (C=O), 1600, 1560, 1460, 1390, 1365, 1220, 1210, 1185, 1170, 1065, and 830 cm⁻¹; MS (DCI) *m/e* 217 (MH⁺).
- 5 Anal. Calcd. for C₁₅H₂₀O: C, 83.29; H, 9.32. Found: C, 83.21; H, 9.35.

- For 5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-anthracenaldehyde (3b): scale = 6.60 mmol, yield = 77%. The precursor aryl halide, 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-bromoanthracene, was obtained via
- 10 the method of M. Dawson et al. *J. Labelled Compounds and Radiopharmaceuticals* 1990, 28, 89. For 3b: ¹H NMR (300 MHz, CDCl₃) δ 10.09 (s, 1 H, CHO), 8.23 (s, 1 H, ArH), 7.93 (s, 1 H, ArH), 7.78-7.84 (m, 3 H, ArH), 1.77 (br s, 4 H, CH₂CH₂), and 1.39 (s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 192.38 (C=O), 148.33, 145.83, 134.75, 134.57, 133.56,
- 15 130.97, 128.29, 126.83, 125.26, 121.67, 34.95, 34.85, 34.68, 32.47 (CH₃), and 32.40 (CH₃); IR (film) 2955, 2920, 2860, 1680 (C=O), 1630, 1470, 1460, 1385, 1365, 1310, 1165, 1125, 1110, 910, 895, and 810 cm⁻¹; MS (DCI) *m/e* 267 (MH⁺). Anal. Calcd for C₁₉H₂₂O: C, 84.96; H, 8.27. Found: C, 84.82; H, 8.37.

20

- For 4-(1-Adamantyl)-3-methoxybenzaldehyde (3c): scale = 3.51 mmol, yield = 43%. The precursor aryl halide, 2-adamantyl-5-iodoanisole, was obtained in two steps from 3-iodophenol via the following procedure. 3-Iodophenol was treated with 1-adamantanol
- 25 and sulfuric acid in methylene chloride following the general procedure of Shreet et al. U.S. Patent 4,717,720, 1/1988. This gave, without recrystallization, pure 2-adamantyl-5-iodophenol: scale = 114 mmol, yield = 91%; mp 142-44 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.08 (d, *J* = 2 Hz, 1 H, ArH), 7.04 (dd, *J* = 2, 8 Hz, 1 H, ArH), 6.80 (d, *J* = 8
- 30 Hz, 1 H, ArH), 3.36 (s, 1 H, OH), 1.99 (s, 9 H, adamantyl), and 1.68 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 157.26, 135.66, 128.32, 127.54, 124.50, 91.23, 39.61, 36.56, 36.12, and 28.32; IR (KBr) 3480 (OH), 2900, 2845, 1490, 1395, 1210, and 875 cm⁻¹; MS (DCI) *m/e* 355 (MH⁺), 354 (M⁺), 353 (M-H)⁺, 135 (C₁₀H₁₅)⁺. Anal. Calcd for C₁₆H₁₉OI: C, 54.25; H,
- 35 5.41. Found: C, 54.32; H, 5.37. A solution of 2-adamantyl-5-iodophenol (7.70 g, 21.7 mmol) in acetone (100 mL) was treated with dimethylsulfate (4.11 g, 32.6 mmol) and potassium carbonate (4.50 g,

32.6 mmol). The reaction mixture was stirred at reflux for 24 h, cooled, and concentrated in vacuo. The crude product was partitioned between methylene chloride and water. The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated to provide 6.5 g (81 %) of 2-adamantyl-5-iodoanisole; ¹H NMR (300 MHz, CDCl₃) δ 7.22 (dd, *J* = 2, 8 Hz, 1 H, ArH), 7.10 (d, *J* = 2 Hz, 1 H, ArH), 6.89 (d, *J* = 8 Hz, 1 H, ArH), 3.79 (s, 3 H, OCH₃), 2.02 (s, 9 H, adamantyl), and 1.73 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 159.35, 138.43, 129.63, 128.25, 120.75, 91.20, 55.22 (OCH₃), 40.35, 37.02, 36.92, and 28.97; MS (DCI) *m/e* 369 (MH⁺), 368 (M⁺), 367 (M-H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₁₇H₂₁OI: C, 55.45; H, 5.75. Found: C, 55.51; H, 5.81.

Reaction of 2-adamantyl-5-iodoanisole according to general procedure A gave **3c**: ¹H NMR (300 MHz, CDCl₃) δ 9.92 (s, 1 H, CHO), 7.35-7.41 (m, 3 H, ArH), 3.88 (s, 3 H, OCH₃), 2.08 (s, 9 H, adamantyl), and 1.76 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 192.04 (C=O), 159.38, 146.00, 135.36, 127.06, 124.45, 109.54, 55.09 (OCH₃), 40.15, 37.79, 36.95, and 28.90; IR (KBr) 2965, 2900, 2850, 1690 (C=O), 1250, 1160, 1135, 1035, and 1025 cm⁻¹; MS (DCI) *m/e* 271 (MH⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₁₈H₂₂O₂ • 0.02 H₂O: C, 79.86; H, 8.21. Found: C, 79.48; H, 8.34.

Procedure B: Alkoxyarylaldehydes via alkylation of hydroxybenzaldehydes with alkyl halides

Procedure B-1: Sodium hydride (1.1 - 2.1 equivalents, 80% dispersion in oil) was washed with pentane (3 x) and suspended in anhydrous dimethyl sulfoxide (0.3 - 0.4 M solution) at room temperature under argon. A solution of the hydroxybenzaldehyde (1 equivalent) in DMSO (0.2 - 0.25 M final volume) was added via cannula and the solution was stirred at room temperature for 1 h. The alkyl halide (1.2 - 2.0 equivalents) was added next and the mixture was stirred for 12-20 h further. The mixture was then poured into a separatory funnel containing ethyl acetate and saturated ammonium chloride solution. The layers were agitated and separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic phases were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was

purified by column chromatography on silica gel (10:1 to 20:1, elution with hexanes to 5% to 10% ethyl acetate in hexanes).

Procedure B-2: A solution of the hydroxybenzaldehyde (1 equivalent) in acetone (0.5 M) was treated with the alkyl halide (2-4 equivalents) and potassium carbonate (2 - 4 equivalents) at room temperature under argon. The resulting slurry was heated at reflux for 14-20 h, and then allowed to cool to room temperature. The mixture was partitioned between diethyl ether and water. The aqueous layer was extracted twice with diethyl ether, and the combined organic layers were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification of the residue was achieved by column chromatography on silica gel (10:1 to 20:1, elution with hexanes to 5% to 10% ethyl acetate in hexanes).

4-Decyloxybenzaldehyde (3d): commercially available from Lancaster Chemicals.

For 3-decyloxybenzaldehyde (3e): from 3-hydroxybenzaldehyde (Aldrich Chemicals) via procedure B-1, scale = 7.50 mmol, yield = 72%; ^1H NMR (300 MHz, CDCl_3) δ 9.95 (s, 1 H, CHO), 7.35-7.44 (m, 3 H, ArH), 7.11-7.18 (m, 1 H, ArH), 3.99 (t, J = 7 Hz, 2 H, ArOCH_2), 1.78 (quintet, J = 7 Hz, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.20-1.50 (m, 14 H, 7 $\times$ CH_2), and 0.86 (t, J = 7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 192.23 (C=O), 159.71, 137.57, 129.97, 123.28, 121.97, 112.75, 68.31 (ArOCH_2), 31.89, 29.55, 29.35, 29.31, 29.12, 25.99, 22.67, and 14.11; IR (film) 2925, 2855, 2725, 1700 (C=O), 1600, 1585, 1485, 1450, 1385, 1285, and 1260 cm^{-1} ; MS (DCI) m/e 263 (MH^+).

For 2-decyloxybenzaldehyde (3f): from 2-hydroxybenzaldehyde (Aldrich Chemicals) via procedure B-1, scale = 7.50 mmol, yield = 60%; ^1H NMR (300 MHz, CDCl_3) δ 10.49 (s, 1 H, CHO), 7.80 (dd, J = 2, 8 Hz, 1 H, ArH), 7.50 (dt, J = 2, 8 Hz, 1 H, ArH), 6.94-7.01 (m, 2 H, ArH), 4.05 (t, J = 7 Hz, 2 H, ArOCH_2), 1.81 (quintet, J = 7 Hz, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.20-1.51 (m, 14 H, 7 $\times$ CH_2), and 0.85 (t, J = 7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 189.96 (C=O), 161.59, 135.90, 128.19, 124.89, 120.43, 112.47, 68.53 (ArOCH_2), 31.87, 29.54, 29.32, 29.30, 29.08, 26.05, 22.67, and 14.11;

IR (film) 2925, 2855, 1690 (C=O), 1600, 1585, 1485, 1460, 1390, 1300, 1285, 1240, 1190, 1160, and 755 cm^{-1} ; MS (DCI) m/e 263 (MH^+).

For 4-[(2E),(6E)-3,7-dimethyl-2,6-octadienoxy]benzaldehyde (3g):
5 from 4-hydroxybenzaldehyde (Aldrich Chemicals) via procedure B-1, scale = 11.3 mmol, yield = 84%; ^1H NMR (300 MHz, CDCl_3) δ 9.85 (s, 1 H, CHO), 7.80 (dt, J = 2, 8 Hz, 2 H, ArH), 6.98 (dt, J = 2, 8 Hz, 2 H, ArH), 5.43-5.48 (m, 1 H, C=CHCH₂O), 5.04-5.09 (m, 1 H, CH=C(CH₃)₂), 4.58 (d, J = 7 Hz, 2 H, ArOCH₂), 2.00-2.15 (m, 4 H, C=CHCH₂CH₂), 1.73 (s, 3 H, CH₃), 1.65 (s, 3 H, CH₃), and 1.58 (s, 3 H, CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 190.79 (C=O), 164.00, 142.13, 131.94, 129.80, 123.62, 118.59, 114.98, 65.24 (ArOCH₂), 39.50, 39.03, 37.26, 32.45, 26.52, 26.23, 25.67, 17.69, and 16.72; IR (film) 2970, 2925, 2855, 2735, 1695 (C=O), 1600, 1575, 1510, 1450, 1430, 1380, 1310, 1250, 1160, 1110, 990, and 830 cm^{-1} ; MS (DCI) m/e 259 (MH^+).
15

For 3,4-Bisdecyloxybenzaldehyde (3h): from 3,4-dihydroxybenzaldehyde (Aldrich Chemicals) via procedure B-2, scale = 72.4 mmol, yield = 53%; mp 59.5-60 $^{\circ}\text{C}$; UV_{max} (EtOH) 310 nm (ϵ = 9,200), 276 nm (ϵ = 11,000), 232 nm (ϵ = 15,400); ^1H NMR (300 MHz, CDCl_3) δ 9.81 (s, 1 H, CHO), 7.39 (d, J = 8 Hz, 1 H, ArH), 7.37 (s, 1 H, ArH), 6.93 (d, J = 8 Hz, 1 H, ArH), 4.05 (t, J = 7 Hz, 2 H, ArOCH₂), 4.03 (t, J = 7 Hz, 2 H, ArOCH₂), 1.77-1.88 (m, 4 H, 2 $\times$ ArOCH₂CH₂), 1.20-1.50 (m, 28 H, 14 $\times$ CH₂), and 0.86 (t, J = 7 Hz, 6 H, 2 $\times$ CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 190.98 (C=O), 154.68, 149.44, 129.87, 126.57, 111.76, 110.97, 69.13 (2 $\times$ ArOCH₂), 31.90, 29.57, 29.34, 29.07, 28.98, 25.97, 25.94, and 14.10; IR (film) 2955, 2920, 2850, 1690 (C=O), 1675, 1595, 1585, 1510, 1470, 1440, 1395, 1275, 1235, 1135, and 810 cm^{-1} ; MS (DCI) m/e 419 (MH^+). Anal. Calcd for $\text{C}_{27}\text{H}_{46}\text{O}_3$: C, 77.46; H, 11.07. Found: C, 77.19; H, 10.99.
25
30

For 3,4-Bispentyloxybenzaldehyde (3i): from 3,4-dihydroxybenzaldehyde (Aldrich Chemicals) via procedure B-2, scale = 109 mmol, yield = quantitative; mp 31-32.5 $^{\circ}\text{C}$; UV_{max} (EtOH) 310 nm (ϵ = 9,000), 276 nm (ϵ = 10,900), 232 nm (ϵ = 15,500); ^1H NMR (300 MHz, CDCl_3) δ 9.79 (s, 1 H, CHO), 7.38 (dd, J = 2, 8 Hz, 1 H, ArH), 7.36 (s, 1 H, ArH), 6.91 (d, J = 8 Hz, 1 H, ArH), 4.04 (t, J = 7 Hz, 2 H, ArOCH₂), 4.02 (t, J = 7 Hz, 2 H, ArOCH₂), 1.77-1.88 (m, 4 H, 2 $\times$ ArOCH₂CH₂), 1.20-1.50 (m,
35

8 H, 4 x CH₂), and 0.90 (t, *J* = 7 Hz, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 190.99 (C=O), 154.65, 149.40, 129.84, 126.61, 111.68, 110.84, 69.08 (2 x ArOCH₂), 28.74, 28.65, 28.16, 28.12, 22.42, and 14.02; IR (film) 2955, 2935, 2860, 1690 (C=O), 1675, 1595, 1585, 1510, 1465, 1440, 1395, 1275, 1240, 1165, 1135, 1050, 1025, 1000, 990, and 810 cm⁻¹; MS (DCI) *m/e* 279 (MH⁺). Anal. Calcd for C₁₇H₂₆O₃: C, 73.35; H, 9.41. Found: C, 73.61; H, 9.40.

Procedure C: 3-Arylpropionaldehydes via treatment of aryl iodides with allyl alcohol and palladium acetate

3-Arylpropionaldehydes were prepared according to the general procedure of T. Jeffery *J. Chem. Soc., Chem. Commun.* 1984, 1287. Upon consumption of all the aryl iodide as judged by ¹H NMR analysis of a small aliquot, the reaction mixture was partitioned between water and 2:1 hexane/ethyl acetate. The organic phase was washed with water (5x), dried with anhydrous sodium sulfate, decanted, and concentrated to give the crude product.

For 3-(5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-propionaldehyde (3j): scale = 27.6 mmol, purified by column chromatography (40:1 silica gel/crude product), yield = 82%. The precursor aryl iodide, 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-iodonaphthalene, was obtained from 5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalene (Maybridge Chemicals) via the method of W.W. Sy et al. *Synth. Commun.* 1990, 20, 877. ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, *J* = 2 Hz, 1 H, ArH), 7.42 (dd, *J* = 2, 8 Hz, 1 H, ArH), 7.03 (d, *J* = 8 Hz, 1 H, ArH), 1.65 (s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 x CH₃), 1.24 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 147.68, 144.59, 135.58, 134.57, 128.74, 91.18, 34.83, 34.78, 34.33, 34.13, 31.75, 31.71; IR (KBr) 2955, 2920, 2860, 1580, 1480, 1455, 1385, 1360, 1065, 815 cm⁻¹; MS (DCI) *m/e* 315(MH⁺), 314 (M⁺), 299 (M-CH₃)⁺. Anal. Calcd for C₁₄H₁₉I: C, 53.51; H, 6.09; I, 40.39. Found: C, 53.82; H, 6.08; I, 40.33. For 3j: ¹H NMR (300 MHz, CDCl₃) δ 9.84 (t, *J* = 1.5 Hz, 1 H, CHO), 7.25 (d, *J* = 8 Hz, 1 H, ArH), 7.13 (d, *J* = 2 Hz, 1 H, ArH), 6.97 (dd, *J* = 2, 8 Hz, 1 H, ArH), 2.89-2.95 (m, 2 H, CH₂), 2.75-2.81 (m, 2 H, CH₂), 1.69 (s, 4 H, CH₂CH₂), and 1.29 (s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 201.83 (C=O), 144.94,

142.73, 137.02, 126.63, 126.19, 125.40, 45.18, 35.02, 34.96, 34.10, 33.87, 31.77, and 27.77; IR (KBr) 2960, 2920, 2855, 1725 (C=O), 1455, 1385, 1360, and 820 cm^{-1} ; MS (DCI) m/e 245(MH^+), 227 (M-OH^+). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}$: C, 83.55; H, 9.90. Found: C, 83.85; H, 9.93.

5

For 3-(3-(1-Adamantyl)-4-hydroxyphenyl)propionaldehyde (**3k**): scale = 28.2 mmol, yield = 98%. The precursor aryl iodide, 2-adamantyl-4-iodophenol was prepared from 4-iodophenol and 1-adamantanol using the general procedure of Shreet et al. U.S. Patent 10 4,717,720, 1/1988. Scale = 80 mmol, yield = 58%; ^1H NMR (300 MHz, CDCl_3) δ 7.44 (d, $J = 2$ Hz, 1 H, ArH), 7.32 (dd, $J = 2, 8$ Hz, 1 H, ArH), 6.40 (d, $J = 8$ Hz, 1 H, ArH), 4.77 (s, 1 H, OH), 2.06 (s, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 154.18, 139.13, 136.05, 135.32, 118.87, 83.53, 40.16, 36.73, 36.80, and 28.80; IR (KBr) 3530 15 (OH), 2910, 2885, 2850, 1480, 1390, 1245, 1120, 820, and 805 cm^{-1} ; MS (DCI) m/e 355 (MH^+), 354 (M^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{OI}$: C, 54.25; H, 5.41. Found: C, 54.46; H, 5.44. Reaction of 2-adamantyl-4-iodophenol according to general procedure C gave **3k**: ^1H NMR (300 MHz, CDCl_3) δ 9.80 (t, $J = 1$ Hz, 1 H, CHO), 7.00 (d, $J = 2$ Hz, 1 20 H, ArH), 6.86 (dd, $J = 2, 8$ Hz, 1 H, ArH), 6.56 (d, $J = 8$ Hz, 1 H, ArH), 4.71 (s, 1 H, OH), 2.86 (t, $J = 7$ Hz, 2 H, CH_2), 2.73 (t, $J = 7$ Hz, 2 H, CH_2), 2.08 (br s, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 202.19 (C=O), 152.83, 136.51, 132.17, 127.04, 126.23, 116.82, 45.65, 40.50, 37.02, 36.64, 29.00, and 27.69; IR (KBr) 3340 (OH), 2910, 2890, 2850, 25 1710, 1510, 1425, 1370, and 1245 cm^{-1} ; MS (DCI) m/e 285 (MH^+), 284 (M^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2 \cdot 0.13 \text{H}_2\text{O}$: C, 79.59; H, 8.53. Found: C, 79.23; H, 8.40.

For 3-(4-(1-Adamantyl)-3-hydroxyphenyl)propionaldehyde (**3l**): 30 scale = 42.3 mmol, purified by column chromatography (40:1 silica gel/crude product; elution with methylene chloride followed by 5% methanol/methylene chloride), yield = 44%. The precursor aryl iodide, 2-adamantyl-5-iodophenol was prepared from 3-iodophenol as described in the experimental for **3c**. For **3l**: ^1H NMR (300 MHz, 35 $\text{DMSO}-d_6$) δ 9.67 (s, 1 H, CHO), 9.11 (s, 1 H, OH), 6.92 (d, $J = 8$ Hz, 1 H, ArH), 6.53-6.55 (m, 2 H, ArH), 2.68 (s, 4 H, $2 \times \text{CH}_2$), 2.01 (s, 9 H, adamantyl), and 1.68 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ

202.88 (C=O), 155.91, 138.85, 133.25, 126.05, 118.57, 116.18, 44.23, 39.96, 36.66, 35.84, 28.41, and 26.87; IR (KBr) 3445 (OH), 2910, 2890, 2845, 1720 (C=O), 1430, and 1225 cm^{-1} ; MS (DCI) m/e 285 (MH^+), 284 (M^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2 \cdot 0.15 \text{ H}_2\text{O}$: C, 79.49; H, 8.53.

5 Found: C, 79.62; H, 8.47.

For 3-[4-(1-Adamantyl)-3-*t*-

butyldimethylsilyloxyphenyl)propionaldehyde (**3m**): scale = 51.6 mmol, purified by column chromatography (40:1 silica gel/crude product; elution with 2:1 hexane/methylene chloride), yield = 70%.
10 The precursor aryl iodide, 2-adamantyl-5-iodo-1-(*t*-butyldimethylsiloxy)benzene, was prepared from 2-adamantyl-5-iodophenol (see **3c** for preparation) via treatment with *t*-butyldimethylsilyl chloride for 24 h at 60 °C. The procedure was taken
15 from a similar conversion described by Shreet et al. U.S. Patent 4,717,720, 1/1988. Purification by column chromatography (10:1 silica gel/crude product; elution with hexane) gave 2-adamantyl-5-iodo-1-(*t*-butyldimethylsiloxy)benzene: scale = 118 mmol, yield = 97%; ^1H NMR (300 MHz, CDCl_3) δ 7.19 (dd, $J = 2, 8$ Hz, 1 H, ArH), 7.09 (d, $J = 2$ Hz, 1 H, ArH), 6.90 (d, $J = 8$ Hz, 1 H, ArH), 2.04 (s, 9H, adamantyl), 1.74 (s, 6 H, adamantyl), 1.03 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$), and 0.34 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C
20 NMR (75 MHz, CDCl_3) δ 155.39, 139.48, 129.58, 128.80, 127.86, 90.43, 40.18, 36.97, 36.78, 28.92, 26.39 ($\text{SiC}(\text{CH}_3)_3$), 19.00 ($\text{SiC}(\text{CH}_3)_3$), and -3.51 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2930, 2910, 2875, 2855, 2845, 1575, 1480, 1390, 1265, 1250, 1240, 930, 850, 800, and 785 cm^{-1} ; MS (DCI) m/e 469 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{22}\text{H}_{33}\text{OISi}$: C, 56.40; H, 7.10. Found: C, 56.66; H, 7.25. Reaction of 2-adamantyl-5-iodo-1-(*t*-butyldimethylsiloxy)benzene according to general procedure C gave
30 **3m**: ^1H NMR (300 MHz, CDCl_3) δ 9.81 (s, 1 H, CHO), 7.11 (d, $J = 8$ Hz, 1 H, ArH), 6.70 (dd, $J = 2, 8$ Hz, 2 H, ArH), 6.61 (d, $J = 2$ Hz, 1 H, ArH), 2.83-2.89 (m, 2 H, CH_2), 2.71-2.76 (m, 2 H, CH_2), 2.06 (s, 9 H, adamantyl), 1.74 (s, 6 H, adamantyl), 1.03 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$), and 0.33 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 201.77 (C=O), 154.71, 138.46, 137.53, 127.18, 120.14, 119.05, 45.03, 40.43, 37.05, 36.56, 29.02, 27.42, 26.43 ($\text{SiC}(\text{CH}_3)_3$), 18.96 ($\text{SiC}(\text{CH}_3)_3$), and -3.34 ($\text{Si}(\text{CH}_3)_2$); IR (KBr) 2955, 2930, 2910, 2850,
35 1720 (C=O), 1415, 1250, 990, 855, and 780 cm^{-1} ; MS (DCI) m/e 399

(MH⁺), 398 (M⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₂₅H₃₈O₂Si: C, 75.32; H, 9.61. Found: C, 75.62; H, 9.66.

For 3-[2-(1-Adamantyl)-4-methoxyphenyl]propionaldehyde (3n):

- 5 Prepared by the following 5 step sequence. A solution of 2-(1-adamantyl)-1,4-hydroquinone (Miryan, N. I.; et al. *Ukr. Khim. Zh.* (Russ Ed.) 1990, 56, 183.) (1.88 g, 7.70 mmol) in acetone (100 mL) under a nitrogen atmosphere was treated with powdered potassium carbonate (1.06 g, 7.70 mmol) and dimethylsulfate (0.97 g, 7.70 mmol).
- 10 After stirring for 48 h at reflux, the reaction mixture was cooled and concentrated in vacuo. The residue was partitioned between ether and a saturated ammonium chloride solution. The organic phase was washed with water (5x) and brine, dried with magnesium sulfate, treated with activated charcoal, filtered through celite, concentrated in
- 15 vacuo to give an oil. Purification by column chromatography (20:1 silica gel/crude product; elution with methylene chloride) gave 1.0 g of an off-white solid. Trituration with ether gave 0.93 g (47%) of 2-(1-adamantyl)-4-methoxyphenol as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 8.75 (s, 1 H, OH), 6.64 (d, *J* = 8.5 Hz, 1 H, ArH), 6.59 (d, *J* = 3 Hz, 1 H, ArH), 6.55 (dd, *J* = 3, 8.5 Hz, 1 H, ArH), 3.62 (s, 3 H, OCH₃), 2.00-2.03
- 20 (m, 9 H, adamantyl), and 1.70 (s, 6 H, adamantyl); ¹³C NMR (300 MHz, CDCl₃) δ 151.98, 149.81, 136.51, 116.49, 112.75, 110.50, 55.14 (OCH₃), 39.72, 36.61, 36.17, and 28.39; IR (KBr) 3380, 2930, 2910, 2885, 2850, 1500, 1420, 1210, 1030, and 745 cm⁻¹; MS (DCI) *m/e* 259 (MH⁺), 258 (M⁺), 257 (M-H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₁₇H₂₂O₂: C, 79.03; H, 8.58. Found: C, 78.91; H, 8.51. A slurry of 2-(1-adamantyl)-4-methoxyphenol (0.93 g, 3.60 mmol) in methylene chloride (60 mL) cooled to -78 °C was treated with ethyldiisopropylamine (0.51 g, 3.96 mmol).
- 25 Trifluoromethanesulfonic anhydride (1.12 g, 3.96 mmol) was added dropwise to the stirred solution. After the addition was complete, the reaction mixture was stirred at 0 °C for 5 h and at room temperature for 18 h. The solvent was removed in vacuo and the residue was
- 30 partitioned between ethyl acetate and water. The organic phase was washed with water (5x), dried with anhydrous magnesium sulfate, filtered, and concentrated to give 1.36 g (96%) of 2-(1-adamantyl)-4-methoxyphenoxytrifluoromethanesulfonate. ¹H NMR (300 MHz, CDCl₃) δ 7.22 (d, *J* = 9 Hz, 1 H, ArH), 6.92 (d, *J* = 3 Hz, 1 H, ArH), 6.71 (dd,
- 35

$J = 3, 9$ Hz, 1 H, ArH), 3.79 (s, 3 H, OCH₃), 2.09 (s, 3 H, adamantyl), 2.02-2.03 (m, 6 H, adamantyl), and 1.74-1.76 (m, 6 H, adamantyl); ¹³C NMR (300 MHz, CDCl₃) δ 158.34, 143.10, 142.88, 122.11, 118.36 (q, $J_{\text{C,F}} = 318$ Hz, CF₃), 115.04, 110.84, 55.56 (OCH₃), 40.89, 37.13, 36.50, and 28.80; IR (KBr) 2910, 2855, 1580, 1480, 1415, 1270, 1245, 1220, 1210, 1195, 1140, 1035, 920, 890, 865, 800, and 580 cm⁻¹; MS (DCI) m/e 391 (MH⁺), 390 (M⁺), 389 (M-H)⁺, 255 (M-C₁₀H₁₅ + 2H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₁₈H₂₁O₄SF₃: C, 55.38; H, 5.42. Found: C, 55.48; H, 5.41. A solution of 2-(1-adamantyl)-4-methoxyphenoxytrifluoromethanesulfonate (1.51 g, 3.87 mmol), 3-tributylstannyl-(2E)-propenol (1.48 g, 4.25 mmol) (Jung, M. E.; Light, L.A. *Tetrahedron Lett.* 1982, 23, 3851), and bis-triphenylphosphinepalladium dichloride (0.05 g, 0.08 mmol) in dimethylformamide was heated at 90 °C for 16 h according to the general procedure of A. Echavarren and J. K. Stille *J. Am. Chem. Soc.* 1987, 109, 5478. Purification by column chromatography (25:1 silica gel/crude product; elution with 20% ethyl acetate/hexane) gave 0.99g (86%) of 3-[2-(1-adamantyl)-4-methoxyphenyl]-(2E)-propenol. ¹H NMR (300 MHz, CDCl₃) δ 7.35 (d, $J = 15$ Hz, 1 H, ArCH=CH), 7.30 (d, $J = 8.5$ Hz, 1 H, ArH), 6.89 (d, $J = 3$ Hz, 1 H, ArH), 6.68 (dd, $J = 3, 8.5$ Hz, 1 H, ArH), 5.93 (dt, $J = 15, 6$ Hz, 1 H, ArCH=CH), 3.79 (s, 3 H, OCH₃), 2.06-2.08 (m, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ¹³C NMR (300 MHz, CDCl₃) δ 159.19, 149.10, 132.98, 130.76, 129.28, 127.76, 112.94, 109.80, 64.19 (OCH₂), 55.15 (OCH₃), 41.89, 37.95, 36.84, and 29.09; IR (KBr) 3345 (OH), 2905, 2850, 1600, 1570, 1475, 1450, 1300, 1260, 1235, 1030, and 760 cm⁻¹; MS (DCI) m/e 299 (MH⁺), 298 (M⁺), 281 (M-OH)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₂₀H₂₆O₂: C, 80.50; H, 8.78. Found: C, 80.43; H, 8.87.

Hydrogenation of 3-[2-(1-adamantyl)-4-methoxyphenyl]-(2E)-propenol (0.99 g, 3.30 mmol) was conducted at 60 psi in ethanol using catalytic 10% palladium on charcoal. After 48 h, the solution was filtered through celite and concentrated in vacuo to give the crude product. Purification by column chromatography (20:1 silica gel/crude product; elution with methylene chloride) gave 3-[2-(1-adamantyl)-4-methoxyphenyl]-propanol (0.74 g, 75%). ¹H NMR (300 MHz, CDCl₃) δ 7.09 (d, $J = 8.5$ Hz, 1 H, ArH), 6.87 (d, $J = 3$ Hz, 1 H, ArH), 6.69 (dd, $J = 3, 8.5$ Hz, 1 H, ArH), 3.73-3.77 (m, 5 H, OCH₂ and OCH₃), 2.92-2.97 (m, 2 H, ArCH₂), 2.04-2.09 (m, 9 H, adamantyl), 1.81-1.91 (m, 2 H, ArCH₂CH₂), and 1.75-1.77 (s, 6 H, adamantyl); ¹³C NMR (300 MHz, CDCl₃) δ 157.43,

- 149.02, 132.74, 132.69, 113.02, 109.98, 63.04 (OCH₂), 55.11 (OCH₃), 42.10, 37.93, 36.85, 36.39, 29.91, and 29.19; IR (KBr) 3355 (OH), 2905, 2850, 1605, 1575, 1450, 1290, 1255, 1235, 1055, 1035, and 755 cm⁻¹; MS (DCI) *m/e* 301 (MH⁺), 300 (M⁺), 299 (M-H)⁺, 165 (M-C₁₀H₁₅)⁺, 135 (C₁₀H₁₅)⁺. Anal.
- 5 Calcd for C₂₀H₂₈O₂: C, 79.96; H, 9.39. Found: C, 79.63; H, 9.52.
- Oxidation of 3-[2-(1-Adamantyl)-4-methoxyphenyl]-propanol (0.62 g, 2.1 mmol) was carried out using catalytic tetrapropylammonium perruthenate using the general procedure of W. Griffith and S. Ley *Aldrichimica Acta* 1990, 23, 13. Purification by column
- 10 chromatography (40:1 silica gel/crude product; elution with ethyl acetate/hexane) gave 3-[2-(1-adamantyl)-4-methoxyphenyl]propanal (3n) (0.42 g, 68%). ¹H NMR (300 MHz, CDCl₃) δ 9.87 (s, 1 H, CHO), 7.04 (d, *J* = 8 Hz, 1 H, ArH), 6.90 (d, *J* = 3 Hz, 1 H, ArH), 6.71 (dd, *J* = 3, 8 Hz, 1 H, ArH), 3.79 (s, 3 H, OCH₃), 3.22 (m, 2 H, CH₂), 2.77 (m, 2 H, CH₂), 2.10
- 15 (s, 3 H, adamantyl), 2.03 (m, 6 H, adamantyl), and 1.77 (s, 6 H, adamantyl).

Example 3: General Procedure for Synthesis of 4

- 20 A solution of the phosphonate **2** (1.2 - 1.6 equivalents) and aldehyde **3** (1 equivalent) in anhydrous toluene (0.10-0.25 M) at room temperature under argon was treated dropwise with a solution of sodium ethoxide in ethanol (21 wt%, 1.1 - 1.5 equivalents). The reaction mixture was stirred at room temperature to 70 °C for 4-14 h.
- 25 The mixture was then partitioned between diethyl ether and saturated ammonium chloride solution, and the organic layer was washed further with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography (40:1 ratio of silica
- 30 gel/crude product; elution with 2-3% ethyl acetate in hexanes).

- For Ethyl (*E*)-2-(3-bromophenyl)-3-phenyl-propenoate (4a): scale = 2.46 mmol, yield = 87% [3.5:1 ratio of (*E*)/(*Z*) isomers]; ¹H NMR (300 MHz, CDCl₃) δ 7.83 (s, 1 H, C=CH from (*E*)-isomer), 7.62 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.13-7.48 (m, 9 H, ArH and C=CH from (*Z*)-isomer), 4.25 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.28 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃ from (*E*)-isomer), and 1.17 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃ from (*Z*)-isomer); ¹³C NMR (75

MHz, CDCl₃) δ 167.21 (C=O), 140.89, 138.01, 134.15, 132.70, 131.18, 130.85, 130.56, 130.07, 129.45, 129.30, 128.58, 128.46, 128.31, 125.12, 122.41, 61.50 (CO₂CH₂ from (Z)-isomer), 61.35 (CO₂CH₂ from (E)-isomer), 14.24 (CO₂CH₂CH₃ from (E)-isomer), and 13.81 (CO₂CH₂CH₃ from (Z)-isomer); IR (film) 2980, 1710 (C=O), 1560, 1475, 1450, 1370, 1245, 1210, 1180, 1075, 1040, and 690 cm⁻¹; MS (DCI) *m/e* 331/333 (MH⁺, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-propenoate (4b): scale = 8.63 mmol, yield = 63%; UV_{max} (CH₃OH) 300 nm (ϵ = 19,900); ¹H NMR (300 MHz, CDCl₃) δ 7.77 (s, 1 H, C=CH), 7.47 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.38 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.13-7.28 (m, 3 H, ArH), 6.92 (d, *J* = 2 Hz, 1 H, 3-ArH), 6.87 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 4.23 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.57 (br s, 4 H, CH₂CH₂), 1.27 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.20 (s, 6 H, 2 × CH₃) and 0.98 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.45 (C=O), 146.94, 144.85, 141.23, 138.82, 132.67, 131.12, 130.68, 130.25, 129.85, 129.11, 128.60, 128.41, 126.64, 122.61, 61.22 (CO₂CH₂), 34.79 (CH₂CH₂), 34.32, 33.96, 31.56 (CH₃), 31.42 (CH₃), and 14.29 (CO₂CH₂CH₃); IR (film) 2960, 2930, 2860, 1710 (C=O), 1620, 1605, 1560, 1490, 1470, 1460, 1365, 1280, 1245, 1215, 1175, 1070, 1040, and 830 cm⁻¹; MS (DCI) *m/e* 441/443 (MH⁺, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-propenoate (4c): scale = 5.0 mmol, yield = 64%; ¹H NMR (300 MHz, CDCl₃) δ 8.00 (s, 1 H, 3-ArH), 7.66 (s, 3 H, 3-ArH and C=CH), 7.41-7.51 (m, 3 H, ArH), 7.15-7.21 (m, 2 H, ArH), 6.81 (dd, *J* = 1, 9 Hz, 1 H, ArH), 4.29 (q, *J* = 6 Hz, 2 H, CO₂CH₂), 1.75 (s, 4 H, CH₂CH₂), and 1.27-1.41 (m, 15 H, 4 × CH₃ and CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.43 (C=O), 146.14, 145.06, 141.49, 138.27, 133.04, 131.81, 131.56, 131.39, 131.05, 130.85, 130.52, 130.00, 128.96, 126.94, 125.64, 125.60, 124.76, 122.40, 61.32 (CO₂CH₂), 34.97 (CH₂CH₂), 34.72, 34.58, 32.47 and 32.44 (4 × CH₃), and 14.32 (CO₂CH₂CH₃); IR (film) 2960, 2930, 1710 (C=O), 1615, 1470, 1365, 1240, 1185, 1165, and 1150 cm⁻¹; MS (DCI) *m/e* 493/491 (MH⁺, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-3-(4-decyloxyphenyl)propenoate (4d): scale = 9.60 mmol, yield = 79%; ¹H NMR (300 MHz, CDCl₃) δ 7.77 (s, 1 H, C=CH), 7.36-7.48 (m, 2 H, 2-ArH),

7.11-7.25 (m, 2 H, 2-ArH), 6.96 (d, $J = 8$ Hz, 2 H, 3-ArH), 6.67 (d, $J = 8$ Hz, 2 H, 3-ArH), 4.22 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 3.88 (t, $J = 7$ Hz, 2 H, ArOCH_2), 1.71 (quintet, $J = 7$ Hz, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.21-1.43 (m, 17 H, 7 $\times$ CH_2 and $\text{CO}_2\text{CH}_2\text{CH}_3$), and 0.85 (t, $J = 7$ Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.52 (C=O), 160.12, 140.72, 138.59, 132.79, 132.43, 130.70, 130.17, 128.67, 128.50, 126.46, 122.50, 114.32, 68.01 (ArOCH_2), 61.16 (CO_2CH_2), 31.88, 29.54, 29.34, 29.11, 25.96, 22.67, 14.29, and 14.12; IR (film) 2925, 2855, 1710 (C=O), 1600, 1570, 1560, 1510, 1470, 1365, 1300, 1250, 1210, 1170, 1070, 1040, 830, and 690 cm^{-1} ; MS (DCI) m/e 487/489 (MH $^+$, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-3-(3,4-bisdecyloxyphenyl)-propenoate (4e): scale = 3.2 mmol, yield = 46%; ^1H NMR (300 MHz, CDCl_3) δ 7.75 (s, 1 H, C=CH), 7.45 (dd, $J = 2, 6$ Hz, 1 H, 2-ArH), 7.41 (t, $J = 1$ Hz, 1 H, 2-ArH), 7.25 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.16 (dt, $J = 1, 8$ Hz, 1 H, 2-ArH), 6.77 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.70 (d, $J = 8, 1$ Hz, 3-ArH), 6.40 (d, $J = 2$ Hz, 1 H, 3-ArH), 4.23 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 3.94 (t, $J = 7$ Hz, 2 H, ArC^4OCH_2), 3.48 (t, $J = 7$ Hz, 2 H, ArC^3OCH_2), 1.71-1.78 (m, 2 H, $\text{ArC}^4\text{OCH}_2\text{CH}_2$), 1.60-1.65 (m, 2 H, $\text{ArC}^3\text{OCH}_2\text{CH}_2$), 1.17-1.29 (m, 31 H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and 14 $\times$ CH_2), and 0.83-0.87 (m, 6 H, 2 $\times$ CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.46 (C=O), 150.34 (3-ArC 4), 148.20 (3-ArC 3), 141.00, 138.90, 132.89, 130.59, 130.24, 128.76, 128.31, 126.65, 125.64, 114.15, 112.29, 68.87 (ArOCH_2), 68.46 (ArOCH_2), 61.14 (CO_2CH_2), 31.92, 31.89, 29.63, 29.57, 29.54, 29.37, 29.34, 29.03, 28.94, 25.93, 25.83, 22.69, 22.67, 14.29, and 14.13; IR (KBr) 2955, 2920, 2850, 1705 (C=O), 1515, 1465, 1275, 1250, 1225, 1190, and 1140 cm^{-1} ; MS (DCI) m/e 645/643 (MH $^+$, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-5-phenyl-2-pentenoate (4f): scale = 7.91 mmol, yield = 48%; ^1H NMR (300 MHz, CDCl_3) δ 7.42 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.06-7.28 (m, 8 H, 3 $\times$ 2-ArH, 4 $\times$ 5-ArH, and C=CH), 6.91 (dt, $J = 2, 8$ Hz, 1 H, 5-ArH), 4.18 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 2.72 (t, $J = 8$ Hz, 2 H, ArCH_2), 2.37 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), and 1.24 (t, $J = 7$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.44 (C=O), 144.41, 140.54, 137.21, 133.54, 130.43, 129.40, 128.34, 126.20, 121.80, 60.93 (CO_2CH_2), 34.81, 31.36, and 14.14 ($\text{CO}_2\text{CH}_2\text{CH}_3$); IR (film) 3060, 3025, 2980, 2935, 2860, 1710 (C=O), 1560, 1475, 1455, 1365, 1260, 1250, 1185, 1070, 1045, 790, 750, and 700 cm^{-1} ; MS (DCI) m/e 359/361 (MH $^+$, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenoate (4g): scale = 14.7 mmol, yield=64%; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.44 (m, 1 H, 2-ArH), 7.10-7.26 (m, 4 H, 3 × 2-ArH and C=CH), 7.04 (s, 1 H, 5-ArH), 6.82-6.89 (m, 2 H, 5-ArH), 4.21 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.71 (t, 2 H, *J* = 8 Hz, ArCH₂), 2.37 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.69 (m, 4 H, CH₂CH₂), and 1.23-1.33 (m, 15 H, 4 × CH₃ and CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.58 (C=O), 154.95, 144.90, 144.78, 142.73, 137.49, 137.37, 133.26, 132.55, 130.45, 60.99 (CO₂CH₂), 35.18, 35.14, 34.72, 34.20, 34.01, 31.96, 31.88, 31.62, and 14.29 (CO₂CH₂CH₃); IR (film) 2960, 2925, 2860, 1715 (C=O), and 1250 cm⁻¹; MS (DCI) *m/e* 469 (MH⁺); Exact mass spectrum (FAB) Calcd for C₂₇H₃₃BrO₂ (MH⁺): 469.1742. Found: 469.1745.

For Ethyl (2E),(4E)-2-(3-bromophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-hexadienoate (4h): scale = 8.19 mmol, yield = 45%; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, *J* = 12 Hz, 1 H, C=CH), 7.42-7.46 (m, 2 H, 2-ArH), 7.16-7.29 (m, 4 H, ArH), 7.10 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.43 (dd, *J* = 1.5, 12 Hz, 1 H, C=CH), 4.25 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.27 (d, *J* = 1.5 Hz, 3 H, C=CCH₃), 1.64 (br s, 4 H, CH₂CH₂), 1.27 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 1.23 (s, 12 H, 4 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.27 (C=O), 148.20, 146.20, 145.00, 139.00, 137.14, 133.32, 130.50, 129.36, 129.16, 126.64, 124.21, 123.32, 122.05, 61.01 (CO₂CH₂), 35.03, 34.88, 34.31, 34.20, 31.77, 31.69, 16.64 (C=CCH₃), and 14.33 (OCH₂CH₃); IR (film) 2960, 2930, 2860, 1705 (C=O), 1610, 1595, 1460, 1365, 1260, 1235, 1185, 1155, 1045, and 695 cm⁻¹; MS (DCI) *m/e* 481/483 (MH⁺, 1:1).

For Ethyl (E)-2-(3-bromophenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenoate (4i): scale = 9.79 mmol, yield = 55%; ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.41 (m, 1 H, 2-ArH), 7.07-7.17 (m, 4 H, 3 × 2-ArH and C=CH), 6.85 (dt, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.61 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.54 (d, *J* = 1 Hz, 1 H, 5-ArH), 4.18 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.75 (s, 3 H, OCH₃), 2.68 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.35 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.05 (br s, 9 H, adamantyl), 1.74 (br s, 6 H, adamantyl), and 1.22 (q, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.57 (C=O), 158.75, 144.70, 139.21, 137.29, 133.32, 132.48,

130.43, 129.41, 128.38, 126.49, 121.85, 120.25, 111.95, 60.99 (CO₂CH₂), 54.91 (OCH₃), 40.64, 37.13, 36.69, 34.60, 31.43, and 14.22 (CO₂CH₂CH₃); IR (film) 2905, 2850, 1715 (C=O), 1410, 1250, 1205, 1185, and 1040 cm⁻¹; MS (DCI) *m/e* 523/525 (MH⁺, 1:1).

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For Ethyl (E)-2-(3-bromophenyl)-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenoate (4j): scale = 10.1 mmol, yield = 76% (3:1 ratio of *E*:*Z* isomers); ¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) 7.43 (dd, *J* = 1, 8 Hz, 1 H, 2-ArH), 7.16-7.21 (m, 3 H, C=CH and 2 × 2-ArH), 6.93-6.96 (m, 2 H, 2-ArH and 5-ArH), 6.76 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.55 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.52 (br s, 1 H, OH), 4.25 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.68 (m, 2 H, ArCH₂), 2.36 (m, 2 H, ArCH₂CH₂), 2.13 (br s, 9 H, adamantyl), 1.81 (s, 6 H, adamantyl), and 1.30 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); (*Z*-isomer) 7.50 (m, 1 H, 2-ArH), 7.43 (m, 1 H, 2-ArH), 7.23 (m, 2 H, 2-ArH), 7.06 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.90 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.59 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.26 (m, 1 H, C=CH), 5.52 (br s, 1 H, OH), 4.32 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.78 (m, 4 H, ArCH₂CH₂), 2.13 (m, 9 H, adamantyl), 1.81 (s, 6 H, adamantyl), and 1.34 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ (*E* and *Z* isomers) 167.95 (C=O from *Z*-isomer), 167.13 (C=O from *E*-isomer), 153.21, 153.16, 145.55, 141.35, 140.11, 137.29, 136.29, 133.65, 133.15, 132.55, 132.14, 130.56, 130.51, 130.41, 129.76, 129.51, 128.43, 127.19, 126.38, 126.12, 122.37, 122.00, 116.83, 61.32 (CO₂CH₂ from *E*-isomer), 61.23 (CO₂CH₂ from *Z*-isomer), 40.54 (adamantyl CH₂), 37.17 (adamantyl CH₂), 36.67 (adamantyl quaternary), 34.93, 34.49 (CH₂), 32.20, 32.03 (CH₂), 29.13 (adamantyl CH), 15.23 (CO₂CH₂CH₃ from *Z*-isomer), and 14.29 (CO₂CH₂CH₃ from *E*-isomer); IR (film) 3440 (OH), 2905, 2850, 1700 (C=O), 1270, 1250, 1210, 1195, and 760 cm⁻¹; MS (DCI) *m/e* 509/511 (1:1, MH⁺); Exact mass spectrum (FAB) Calcd for C₂₉H₃₃BrO₃ (MH⁺): 531.1511. Found: 531.1492.

For Ethyl (E)-2-(3-bromophenyl)-3-(3,4-bis(pentyloxy)phenyl)-propenoate (4k): scale = 5.39 mmol, yield = 36%; ¹H NMR (300 MHz, CDCl₃) δ 7.75 (s, 1 H, C=CH), 7.40-7.47 (m, 2 H, 2-ArH), 7.25 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.16 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 6.77 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.70 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.40 (d, *J* = 2 Hz, 1 H, 3-ArH), 4.23 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.94 (t, *J* = 6.5 Hz, 2 H, ArOCH₂), 3.48 (t, *J* = 6.5

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Hz, 2 H, ArOCH₂), 1.72-1.82 (m, 2 H, ArOCH₂CH₂), 1.58-1.65 (m, 2 H, ArOCH₂CH₂), 1.20-1.44 (m, 8 H, 4 x CH₂), 1.25 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 0.86-0.94 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.46 (C=O), 150.37, 148.24, 140.99, 138.92, 132.92, 130.60, 130.24, 128.77, 128.35, 126.69, 125.65, 122.56, 114.21, 112.33, 68.88 (ArOCH₂), 68.46 (ArOCH₂), 61.22 (CO₂CH₂), 28.74, 28.64, 28.11, 28.01, 22.40, 14.30 (CO₂CH₂CH₃), 14.05, and 14.00; IR (film) 2955, 2935, 2870, 1710 (C=O), 1615, 1595, 1560, 1515, 1470, 1430, 1390, 1380, 1330, 1270, 1245, 1190, 1140, 1070, 1040, 1000, 805, and 690 cm⁻¹; MS (DCI) *m/e* 503/505 (MH⁺, 1:1).

For Ethyl (*E*)-2-(3-trifluoromethylphenyl)-3-(4-decyloxyphenyl)-propenoate (**4l**): scale = 11.9 mmol, yield = 63%, 12:1 mixture of *E*:*Z* isomers. ¹H NMR (300 MHz, CDCl₃) δ 7.83 (s, 1 H, C=CH), 7.58 (d, *J* = 9 Hz, 1 H, 2-ArH), 7.44-7.50 (m, 2 H, 2-ArH), 7.39 (d, *J* = 7 Hz, 1 H, 2-ArH), 6.92 (d, *J* = 9 Hz, 2 H, 3-ArH), 6.66 (d, *J* = 9 Hz, 2 H, 3-ArH), 4.23 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.95 (t, *J* = 6 Hz, 2 H, ArOCH₂ from minor isomer), 3.87 (t, *J* = 6 Hz, 2 H, ArOCH₂), 1.66-1.75 (m, 2 H, ArOCH₂CH₂), 1.20-1.38 (m, 17 H, 7 x CH₂ and CO₂CH₂CH₃), and 0.85 (t, *J* = 6 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.41 (C=O), 160.16 (3-ArC⁴), 141.04, 137.23, 133.52, 132.32 (3-ArC), 130.75, 129.02, 128.39, 127.02 (q, *J*_{C,f} = 4 Hz, 2-ArC), 126.33, 124.35 (q, *J*_{C,f} = 4 Hz, 2-ArC), 114.33 (3-ArC), 68.03 (CO₂CH₂), 61.20 (ArOCH₂), 31.87, 29.52, 29.32, 29.08, 25.94, 22.66, 14.23, and 14.10; IR (KBr) 2925, 2855, 1710 (C=O), 1600, 1510, 1325, 1310, 1250, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 477 (MH⁺).

For Ethyl (*E*)-2-(3-trifluoromethylphenyl)-3-(3-decyloxyphenyl)-propenoate (**4m**): scale = 5.4 mmol, yield = 50%; ¹H NMR (300 MHz, CDCl₃) δ 7.85 (s, 1 H, C=CH), 7.57 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.52 (s, 1 H, 2-ArH), 7.47 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.38 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.08 (t, *J* = 8 Hz, 1 H, 3-ArH), 6.75 (dt, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.65 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.42 (t, *J* = 2 Hz, 1 H, 3-ArH), 4.26 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.53 (t, *J* = 7 Hz, 2 H, ArOCH₂), 1.55-1.63 (m, 2 H, ArOCH₂CH₂), 1.22-1.30 (m, 17 H, 7 x CH₂ and CO₂CH₂CH₃), and 0.87 (t, *J* = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.07 (C=O), 158.76 (3-ArC³), 141.30, 136.99, 135.16, 133.47, 131.20, 129.32, 129.04, 126.99 (q, *J*_{C,f} = 4 Hz, 2-ArC), 124.44 (q, *J*_{C,f} = 4 Hz, 2-ArC), 123.43, 117.01, 114.84, 67.65 (CO₂CH₂), 61.41

(ArOCH₂), 31.89, 29.41, 29.31, 29.02, 25.84, 22.68, 14.21, and 14.11; IR (film) 3585, 2925, 2855, 1710 (C=O), 1325, 1230, and 1165 cm⁻¹; MS (DCI) *m/e* 477 (MH⁺).

5 For Ethyl (E)-2-(3-trifluoromethylphenyl)-3-(2-decyloxyphenyl)-propenoate (4n): scale = 8.0 mmol, yield = 72%, approx. 2:1 mixture of E:Z isomers. ¹H NMR (300 MHz, CDCl₃) δ 8.24 (s, 1 H, C=CH), 7.13-7.74 (m, 4 H, 2-ArH), 6.80-6.95 (m, 2 H, 3-ArH), 6.53-6.62 (m, 2 H, 3-ArH), 4.20-4.35 (m, 2 H, CO₂CH₂ for both isomers), 4.01 (t, *J* = 7 Hz, 2 H, CO₂CH₂ for both isomers), 1.75-1.88 (m, 2 H, OCH₂CH₂ for both isomers), 1.22-1.55 (m, 14 H, 7 × CH₂ for both isomers), 1.14 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃ for both isomers), and 0.84-0.91 (m, 3 H, CH₃ for both isomers).

15 For Ethyl (E)-2-(3-trifluoromethylphenyl)-3-[4-(2E),(6E)-3,7-dimethyl-octa-2,6-dienoxy]phenyl)-propenoate (4o): scale = 2.73 mmol, yield = 62%, 4:1 mixture of E:Z isomers. ¹H NMR (300 MHz, CDCl₃) δ 7.83 (s, 1 H, C=CH), 7.31-7.60 (m, 4 H, 2-ArH), 6.87-6.99 (m, 2 H, 3-ArH), 6.68 (dt, *J* = 2, 9 Hz, 2 H, 3-ArH), 5.40 (t, *J* = 6.5 Hz, 1 H, C=CHCH₂OAr), 5.02-5.08 (m, 1 H, CH=C(CH₃)₂), 4.55 (d, *J* = 6.5 Hz, 2 H, ArOCH₂ from minor isomer), 4.47 (d, *J* = 6.5 Hz, 2 H, ArOCH₂), 4.19-4.31 (m, 2 H, CO₂CH₂), 1.96-2.08 (m, 4 H, C=CHCH₂CH₂), 1.51-1.76 (m, 9 H, 3 × CH₃), 1.00-1.27 (m, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.41 (C=O), 159.91 (3-ArC⁴), 141.59, 141.01, 137.22, 133.53, 133.16, 132.30, 131.85, 130.76, 130.03, 129.68, 129.03, 128.57, 127.04 (q, *J*_{C,F} = 4 Hz, 2-ArC), 126.45, 124.40 (q, *J*_{C,F} = 4 Hz, 2-ArC), 123.70, 119.13, 118.96 (3-ArC), 114.68, 114.56 (3-ArC), 64.88 (ArOCH₂), 61.50, 61.21 (CO₂CH₂), 39.48, 29.71, 26.23, 25.67, 17.67, 16.64, 14.23 (CO₂CH₂CH₃), and 13.93; IR (film) 2980, 2930, 1710 (C=O), 1600, 1510, 1445, 1380, 1310, 1250, 1210, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 473 (MH⁺).

 For Ethyl (E)-2-(3-trifluoromethylphenyl)-3-(3,4-bisdecyloxyphenyl)-propenoate (4p): scale = 3.58 mmol, yield = 69%; ¹H NMR (300 MHz, CDCl₃) δ 7.80 (s, 1 H, C=CH), 7.40-7.59 (m, 4 H, 2-ArH), 6.75 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.69 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.31 (d, *J* = 2 Hz, 1 H, 3-ArH), 4.23 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.93 (t, *J* = 7 Hz, 2 H, ArOCH₂), 3.39 (t, *J* = 7 Hz, 2 H, ArOCH₂), 1.71-1.80 (m, 2 H, CH₂CH₂O),

1.53-1.61 (m, 2 H, CH₂CH₂O), 1.21-1.43 (m, 31 H, 14 x CH₂ and OCH₂CH₃), and 0.83-0.89 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.35, 150.43, 148.31, 141.33, 137.85, 133.66, 129.15, 128.33, 136.80 (q, *J*_{C,f} = 38 Hz, 2-ArC), 125.58, 124.25, 114.10, 112.40, 68.91 (CH₂O), 68.38 (CH₂O), 61.19 (CO₂CH₂), 31.91, 29.57, 29.35, 29.04, 28.93, 25.92, 25.76, 22.68, 14.25 (OCH₂CH₃), and 14.11; IR (film) 2925, 2855, 1710, 1595, 1515, 1470, 1430, 1390, 1325, 1310, 1270, 1250, 1165, 1130, 1095, 1075, 1045, and 700 cm⁻¹; MS (DCI) *m/e* 633 (MH⁺).

10 For Ethyl (E)-2-(3-trifluoromethylphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-propenoate (4q): scale = 4.1 mmol, yield = approx. 50%, 3:1 mixture of product (A) to starting material (B). ¹H NMR (300 MHz, CDCl₃) δ 10.09 (s, 1 H, CH=O, B), 8.24 (s, 1 H, ArH, B), 8.05 (s, 1 H, C=CH, A), 7.95 (s, 1 H, ArH, B), 7.83-7.84 (m, 1 H, ArH, A), 7.58-7.66 (m, 5 H, ArH), 7.40-7.49 (m, 3 H, ArH), 6.75 (dd, *J* = 2, 9 Hz, 1 H, ArH), 4.30 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.79 (s, 4 H, CH₂CH₂, B), 1.75 (s, 4 H, CH₂CH₂, A), 1.41 (s, 12 H, 4 x CH₃, B), 1.36 (br s, 12 H, 4 x CH₃, A), and 1.32 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 192.44 (C=O, B), 168.80 (C=O, A), 146.22, 145.12, 141.80, 136.90, 134.64, 133.74, 131.79, 131.54, 131.34, 130.82, 130.41, 128.92, 128.31, 127.24, 126.96, 126.84, 125.62, 125.43, 125.27, 124.74, 124.51, 121.65, 61.38 (CO₂CH₂), 34.91, 34.83, 34.70, 34.56, 32.41 (4 x CH₃), and 14.26 (CO₂CH₂CH₃); IR (KBr) 2960, 2930, 2860, 1710 (C=O, A), 1680 (C=O, B), 1470, 1320, 1310, 1240, and 1165 cm⁻¹; MS (DCI) *m/e* 481 (MH⁺, A) and 267 (MH⁺, B).

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For Ethyl (E)-2-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenoate (4r): scale = 4.09 mmol, yield = 56%; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (br d, *J* = 8 Hz, 1 H, 2-ArH), 7.37 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.30 (br s, 1 H, 2-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.16 (t, *J* = 8 Hz, 1 H, C=CH), 7.03 (d, *J* = 8 Hz, 5-ArH), 6.98 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.81 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 4.18 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.68 (t, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.32 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 x CH₃), 1.24 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 1.21 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.47 (C=O), 145.13, 144.80, 142.77, 137.37, 136.00, 133.22, 133.07, 130.26 (q, *J*_{C,f} = 32 Hz, 2-ArC), 128.32, 126.65, 126.50 (q, *J*_{C,f} = 4 Hz, 2-ArC), 125.65, 124.16 (q, *J*_{C,f} = 4 Hz, 2-ArC), 61.01 (CO₂CH₂), 35.10,

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34.64, 34.13, 33.95, 31.86, 31.77, 31.57, and 14.19 (CO₂CH₂CH₃); IR (film) 2960, 2930, 2860, 1715 (C=O), 1495, 1460, 1445, 1385, 1365, 1325, 1310, 1250, 1180, 1165, 1130, 1095, 1075, 1045, 810, and 700 cm⁻¹; MS (DCI) *m/e* 459 (MH⁺).

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For Ethyl (E)-2-(4-fluorophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenoate (4s): scale = 2.66 mmol, yield = 58%; ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, *J* = 8 Hz, 1 H, 5-ArH), 7.09 (t, *J* = 8 Hz, 1 H, C=CH), 6.80-6.98 (m, 6 H, 4 × 2-ArH and 2 × 5-ArH), 4.17 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.66 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.32 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 × CH₃), 1.24 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 1.21 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.97 (C=O), 162.02 (d, *J*_{C,F}¹ = 246 Hz, 2-ArC), 144.73, 144.31, 142.68, 137.58, 133.51, 131.26 (d, *J*_{C,F}³ = 8 Hz, 2-ArC), 125.58, 125.74, 114.72 (15 *J*_{C,F}² = 21 Hz, 2-ArC), 60.86 (CO₂CH₂), 35.11, 35.07, 34.67, 34.14, 33.95, 31.89, 31.80, 31.55, and 14.24 (CO₂CH₂CH₃); IR (film) 2960, 2925, 2860, 1715 (C=O), 1640, 1605, 1510, 1495, 1460, 1410, 1385, 1365, 1250, 1220, 1205, 1185, 1160, 1095, 1070, 1045, 840, 825, and 765 cm⁻¹; MS (DCI) *m/e* 409 (MH⁺).

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For Ethyl (E)-2-(3-fluorophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenoate (4t): scale = 2.29 mmol, yield = 57%; ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.24 (m, 2 H, 1 × 2-ArH and 1 × 5-ArH), 7.11 (t, *J* = 8 Hz, 1 H, C=CH), 6.98 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.94 (25 apparent tt, *J* = 2, 8 Hz, 1 H, 2-ArH), 6.82 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.67 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 6.58 (apparent dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 4.17 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.68 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.33 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 × CH₃), 1.24 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 1.21 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.65 (C=O), 162.30 (d, *J*_{C,F}¹ = 246 Hz, 2-ArC), 144.77, 144.63, 142.73, 137.49, 137.36 (d, *J*_{C,F}³ = 8 Hz, 2-ArC), 133.44, 129.25 (d, *J*_{C,F}³ = 9 Hz, 2-ArC), 126.56, 125.72, 125.35 (d, *J*_{C,F}⁴ = 3 Hz, 2-ArC), 116.64 (*J*_{C,F}² = 22 Hz, 2-ArC), 114.24 (*J*_{C,F}² = 22 Hz, 2-ArC), 60.92 (CO₂CH₂), 35.12, 35.08, 34.64, 34.14, 33.96, 31.87, 31.80, 31.55, and 14.23 (30 CO₂CH₂CH₃); IR (film) 2960, 2930, 2860, 1715 (C=O), 1640, 1610, 1585, 1490, 1460, 1440, 1410, 1385, 1365, 1260, 1230, 1190, 1175, 1135, 1070, 1045, 885, 825, and 790 cm⁻¹; MS (DCI) *m/e* 409 (MH⁺).

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For Ethyl (E)-2-phenyl-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenoate (4u): scale = 2.66 mmol, yield = 53%; ¹H NMR (300 MHz, CDCl₃) δ 7.23-7.30 (m, 3 H, 2-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 5-ArH), 7.08 (t, *J* = 8 Hz, 1 H, C=CH), 6.99 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.92-6.95 (m, 2 H, 2-ArH), 6.82 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 4.17 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.66 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.34 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 × CH₃), 1.24 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 1.21 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.18 (C=O), 144.59, 143.92, 142.58, 137.73, 135.25, 129.57, 127.82, 127.25, 126.53, 125.71, 60.76 (CO₂CH₂), 35.14, 35.09, 34.75, 34.15, 33.94, 31.88, 31.81, 31.47, and 14.25 (CO₂CH₂CH₃); IR (film) 2960, 2925, 2860, 1715 (C=O), 1495, 1460, 1445, 1385, 1365, 1250, 1205, 1185, 1070, 1045, 1030, 825, 775, and 700 cm⁻¹; MS (DCI) *m/e* 391 (MH⁺).

For Ethyl (E)-2-(3-trifluoromethylphenyl)-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenoate (4v): scale = 6.17 mmol, yield = 32% (3:1 *E*:*Z* isomers); ¹H NMR (300 MHz, CDCl₃) δ (*E*-isomer) 7.53 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.41 (m, 1 H, 2-ArH), 7.24 (s, 1 H, 2-ArH), 7.17 (m, 2 H, C=CH and 2-ArH), 6.89 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.72 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.51 (d, *J* = 8 Hz, 1 H, 5-ArH), 4.87 (s, 1 H, OH), 4.20 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.66 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.31 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.07 (m, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl); and 1.25 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); (*Z*)-isomer, partially obscured: 7.03 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.57 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.26 (m, 1 H, 5-ArH), 4.88 (s, 1 H, OH), 4.27 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.76 (m, 4 H, ArCH₂CH₂), and 1.29 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ (*E*- and *Z*-isomers) δ 166.64 (C=O), 152.88, 152.81, 145.32, 142.09, 138.93, 136.23, 135.99, 133.20, 133.12, 132.80, 132.34, 130.80, 130.26 (d, *J*_{C,f} = 32 Hz, 2-ArC), 128.63, 128.34, 127.24, 127.18, 126.49 (d, *J*_{C,f} = 4 Hz, 2-ArC), 126.31, 125.90, 124.19 (d, *J*_{C,f} = 4 Hz, 2-ArC), 116.74, 61.13 (CO₂CH₂ from *E*-isomer), 61.05 (CO₂CH₂ from *Z*-isomer), 40.54 (adamantyl CH₂ from *Z*-isomer), 40.49 (adamantyl CH₂ from *E*-isomer), 37.05 (adamantyl CH₂), 36.59 (adamantyl quaternary), 34.84 (CH₂ from *Z*-isomer), 34.42 (CH₂ from *E*-isomer), 32.13 (CH₂ from *Z*-isomer), 31.91 (CH₂ from *E*-isomer), 29.01 (adamantyl CH), and 14.19 (CO₂CH₂CH₃); IR (film) 3450 (OH), 2905, 2850, 1695 (C=O), 1325, 1255, 1210, 1180, and

760 cm^{-1} ; MS (DCI) m/e 499 (MH^+), 488 (M^+), 487 (M-H^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{30}\text{H}_{33}\text{O}_3\text{F}_3$: C, 72.27; H, 6.67. Found: C, 72.70; H, 7.01.

- 5 For Ethyl (*E*)-2-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-hydroxyphenyl]-2-pentenoate (4w): scale = 6.17 mmol, yield=32%; ^1H NMR (300 MHz, CDCl_3) δ 7.53-7.55 (d, J = 8 Hz, 1 H, 2-ArH), 7.41 (t, J = 8 Hz, 1 H, 2-ArH), 7.33 (s, 1 H, 2-ArH), 7.10-7.17 (m, 2 H, C=CH and 2-ArH), 7.07 (d, J = 8 Hz, 1 H, 5-ArH), 6.60 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.34 (d, J = 2 Hz, 1 H, 5-ArH), 4.83 (s, 1 H, OH), 4.19 (q, J = 7 Hz, 2 H, CO_2CH_2), 2.63 (t, J = 8 Hz, 2 H, ArCH_2), 2.32 (q, 2 H, ArCH_2CH_2), 2.08 (br s, 9 H, adamantyl), 1.75 (s, 6 H, adamantyl), and 1.24 (t, J = 7 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.60 (C=O), 154.40, 144.98, 139.21, 135.94, 134.40, 133.34, 133.13, 130.30 (d, $J^2_{\text{C,F}}$ = 32 Hz, 2-ArC), 128.40, 127.05, 126.47 (d, $J^3_{\text{C,F}}$ = 4 Hz, 2-ArC), 124.25 (d, $J^3_{\text{C,F}}$ = 4 Hz, 2-ArC), 124.08 (q, $J^1_{\text{C,F}}$ = 271 Hz, CF_3), 120.55, 116.73, 61.15 (CO_2CH_2), 40.59 (adamantyl CH_2), 37.04 (adamantyl CH_2), 36.40 (adamantyl quaternary), 34.00 (CH_2), 31.24 (CH_2), 29.01 (adamantyl CH), and 14.16 ($\text{CO}_2\text{CH}_2\text{CH}_3$); IR (KBr) 3460 (OH), 2905, 2850, 1695 (C=O), 1420, 1325, 1265, 1165, and 1125 cm^{-1} ; MS (DCI) m/e 499 (MH^+), 498 (M^+), 497 (M-H^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{30}\text{H}_{33}\text{O}_3\text{F}_3$: C, 72.27; H, 6.67. Found: C, 72.64; H, 6.60.

- 25 For Ethyl (*E*)-2-phenyl-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenoate (4x): scale = 7.00 mmol, yield = 59%; ^1H NMR (300 MHz, CDCl_3) δ 7.22-7.33 (m, 3 H, 2-ArH), 7.08 (t, J = 8 Hz, 1 H, C=CH), 7.06 (d, J = 8 Hz, 1 H, 5-ArH), 6.96-7.01 (m, 2 H, 2-ArH), 6.62 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.54 (d, J = 2 Hz, 1 H, 5-ArH), 4.16 (q, J = 7 Hz, 2 H, CO_2CH_2), 3.74 (s, 3 H, OCH_3), 2.67 (t, J = 8 Hz, 2 H, ArCH_2), 2.37 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 2.03-2.08 (m, 9 H, adamantyl), 1.74 (br s, 6 H, adamantyl), and 1.24 (t, J = 7 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 167.17 (C=O), 158.72, 143.76, 139.50, 136.36, 135.24, 134.57, 129.62, 127.84, 127.29, 126.36, 120.25, 111.97, 60.80 (CO_2CH_2), 54.89 (OCH_3), 40.66, 37.14, 36.68, 34.67, 31.32, 29.11, and 14.24 ($\text{CO}_2\text{CH}_2\text{CH}_3$); IR (film) 2905, 2850, 1710 (C=O), 1610, 1465, 1450, 1415, 1250, 1205, 1185, 1165, 1140, 1100, 1045, 1030, 760, and 700 cm^{-1} ; MS (DCI) m/e 445 (MH^+).

For Ethyl (*E*)-2-(3-trifluoromethylphenyl)-5-[2-(1-adamantyl)-4-methoxyphenyl]-2-pentenoate (4y): scale = 1.41 mmol, yield = 41%; ¹H NMR (300 MHz, CDCl₃) δ 7.54 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.43 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.35 (s, 1 H, 2-ArH), 7.18-7.28 (m, 2 H, C=CH and 2-ArH), 6.90 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.83 (d, *J* = 3 Hz, 1 H, 5-ArH), 6.63 (dd, *J* = 3, 8 Hz, 1 H, 5-ArH), 4.21 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.74 (s, 3 H, OCH₃), 2.97 (m, 2 H, ArCH₂), 2.35 (m, 2 H, ArCH₂CH₂), 2.03 (br s, 3 H, adamantyl), 1.91 (m, 6 H, adamantyl), 1.72 (m, 6 H, adamantyl), and 1.26 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.54 (C=O), 157.69, 149.05, 144.95, 136.04, 133.06, 132.66, 131.34, 130.40 (d, *J*_{cf}² = 32 Hz, 2-ArC), 128.41, 126.46 (d, *J*_{cf}³ = 4 Hz, 2-ArC), 124.30 (d, *J*_{cf}³ = 4 Hz, 2-ArC), 113.17, 110.00, 61.12 (CO₂CH₂), 55.09 (OCH₃), 42.10 (adamantyl CH₂), 37.85 (adamantyl quaternary), 36.74 (adamantyl CH₂), 33.31 (CH₂), 32.66 (CH₂), 29.07 (adamantyl CH), and 14.20 (CO₂CH₂CH₃); IR (film) 2910, 2850, 1715 (C=O), 1605, 1575, 1465, 1445, 1325, 1255, 1165, 1130, 1075, 760, 710, and 700 cm⁻¹; MS (DCI) *m/e* 513 (MH⁺), 135 (C₁₀H₁₅⁺). Exact mass spectrum (FAB) Calcd for C₃₁H₃₆O₃F₃ (MH⁺): 513.2617. Found: 513.2601.

For Ethyl (*E*)-2-(3-trifluorophenyl)-3-[4-(1-adamantyl)-3-methoxyphenyl]-propenoate (4z): scale = 4.26 mmol, yield = 65%; ¹H NMR (300 MHz, CDCl₃) δ 7.84 (s, 1 H, C=CH), 7.42-7.61 (m, 4 H, 2-ArH), 7.07 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.74 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.32 (d, *J* = 2 Hz, 1 H, 3-ArH), 4.25 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.31 (s, 3 H, OCH₃), 1.98 (br s, 9 H, adamantyl), 1.71 (s, 6 H, adamantyl), and 1.27 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.23 (C=O), 158.28, 141.14, 140.80, 137.50, 133.53, 132.40, 131.09 (d, *J*_{cf}² = 32 Hz, 2-ArC), 130.07, 129.17, 126.99 (d, *J*_{cf}³ = 4 Hz, 2-ArC), 126.56, 124.38 (d, *J*_{cf}³ = 4 Hz, 2-ArC), 124.01 (d, *J*_{cf}¹ = 271 Hz, CF₃), 112.59, 61.32 (CO₂CH₂), 54.17 (OCH₃), 40.26 (adamantyl CH₂), 37.14 (adamantyl quaternary), 36.99 (adamantyl CH₂), 28.92 (adamantyl CH), and 14.23 (CO₂CH₂CH₃); IR (film) 2905, 2850, 1710 (C=O), 1325, 1230, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 485 (MH⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₂₉H₃₁O₃F₃: C, 71.88; H, 6.45. Found: C, 70.46; H, 6.21.

For Ethyl (*E*)-2-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-*t*-butyldimethylsilyloxyphenyl]-2-pentenoate (4aa): scale = 4.94 mmol,

yield=59% ; ^1H NMR (300 MHz, CDCl_3) δ 7.53 (m, 1 H, ArH), 7.39 (m, 1 H, ArH), 7.33 (s, 1 H, ArH), 7.15 (m, 1 H, C=CH), 7.08 (m, 2 H, ArH), 6.60 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.47 (d, $J = 2$ Hz, 1 H, 5-ArH), 4.19 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 2.63 (m, 2 H, ArCH_2), 2.31 (m, 2 H, ArCH_2CH_2), 2.06 (m, 9 H, adamantyl), 1.74 (s, 6 H, adamantyl), 1.24 (t, $J = 7$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 0.99 (s, 9H, $\text{Si}(\text{CH}_3)_3$), and 0.25 (s, 6H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.41 (C=O), 154.58, 144.81, 138.73, 137.46, 135.97, 133.39, 133.05, 128.39, 127.09, 126.47 (d, $J_{\text{C},\text{H}} = 4$ Hz, 2-ArC), 124.23 (d, $J_{\text{C},\text{H}} = 4$ Hz, 2-ArC), 120.33, 119.06, 61.05 (CO_2CH_2), 40.43 (adamantyl CH_2), 37.05 (adamantyl CH_2), 36.55 (adamantyl quaternary), 34.25 (CH_2), 31.44 (CH_2), 29.03 (adamantyl CH), 26.38 ($\text{Si}(\text{CH}_3)_3$), 18.89 ($\text{Si}(\text{CH}_3)_3$), 14.19 ($\text{CO}_2\text{CH}_2\text{CH}_3$), and -3.43 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2955, 2930, 2905, 2855, 1715 (C=O), 1415, 1325, 1265, 860, 840, 780, and 760 cm^{-1} ; MS (DCI) m/e 613 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{36}\text{H}_{47}\text{O}_3\text{F}_3\text{Si}$: C, 70.56; H, 7.73. Found: C, 70.47; H, 7.66.

Example 4: General Procedure for Synthesis of 5

A solution of ester **4** (1 equivalent) in anhydrous THF (0.1-0.2 M) was cooled to -78°C under argon. A solution of diisobutylaluminum hydride (1M in hexanes, 2.5 equivalents) was added and the reaction mixture was allowed to warm to 0°C to room temperature. The reaction was quenched by slow addition of methanol followed by treatment with saturated ammonium chloride. The resulting mixture was stirred for 15 min and then partitioned between diethyl ether and 1 N HCl solution. The layers were agitated until all solid in the aqueous phase had dissolved. The organic layer was separated and washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification was achieved by column chromatography (30:1 - 40:1 ratio of silica gel/crude product; elution with 5% to 15% ethyl acetate in hexanes) to provide the target compound.

For (Z)-2-(3-Bromophenyl)-3-phenyl-2-propenol (**5a**): scale = 2.14 mmol, yield = 78%; ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.43 (m, 2 H, 2-ArH), 7.10-7.20 (m, 5 H, ArH), 6.96-7.00 (m, 2 H, ArH), 6.70 (br s, 1 H, C=CH), and 4.41 (d, $J = 1.5$ Hz, 2 H, CH_2OH); ^{13}C NMR (75 MHz, CDCl_3)

δ 140.81, 139.83, 135.86, 131.50, 130.63, 130.31, 129.22, 128.10, 127.70, 127.18, 122.76, and 68.35 (CH₂OH); IR (film) 3320 (OH), 3060, 3020, 1590, 1560, 1495, 1470, 1450, 1410, 1095, 1070, 1030, 1000, 920, 880, 790, 785, and 700 cm⁻¹; MS (DCI) *m/e* 288/290 (M⁺, 1:1), 271/273 (M⁺ - OH, 1:1).

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For (Z)-2-(3-Bromophenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-propenol (5b): scale = 5.44 mmol, yield = 99%; ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.47 (m, 2 H, 2-ArH), 7.18-7.28 (m, 2 H, 2-ArH), 7.13 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.88 (d, *J* = 2 Hz, 1 H, 3-ArH), 6.83 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.63 (br s, 1 H, C=CH), 4.42 (dd, *J* = 1.5, 7 Hz, 2 H, CH₂OH), 1.60 (br s, 4 H, CH₂CH₂), 1.20 (s, 6 H, 2 × CH₃) and 0.98 (s, 6 H, 2 × CH₃); IR (film) 3000-3300 (br, OH), 2950, 2920, 2860, 1555, 1500, 1470, 1460, 1415, 1360, 1350, 1035, 915, 820, and 700 cm⁻¹; MS (DCI) *m/e* 398/400 (M⁺, 1:1), 381/383 (M⁺ - OH, 1:1).

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For (Z)-2-(3-Bromophenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propenol (5c): scale = 2.66 mmol, yield = 87%; ¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 9 Hz, 2 H, ArH), 7.39-7.48 (m, 4 H, ArH), 7.13-7.15 (m, 2 H, ArH), 6.83-6.87 (m, 2 H, ArH and C=CH), 4.70 (dd, *J* = 1, 6 Hz, 2 H, CH₂OH), 1.73 (s, 4 H, CH₂CH₂), and 1.34-1.37 (m, 12 H, 4 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 144.72, 144.60, 140.93, 139.29, 132.65, 131.53, 130.87, 130.66, 130.56, 128.34, 128.02, 126.60, 125.89, 125.02, 124.64, 122.76, 68.55 (CH₂OH), 35.04 (CH₂CH₂), 34.58, 34.53, and 32.47 (4 × CH₃); IR (KBr) 3400 (br, OH), 2960, 2925, 2860, 1560, 1470, and 1360 cm⁻¹; MS (DCI) *m/e* 451/449 (MH⁺, 1:1), 433/431 (MH⁺ - H₂O, 1:1).

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For (Z)-2-(3-bromophenyl)-3-(4-decyloxyphenyl)-2-propenol (5d): scale = 7.40 mmol, yield = 78%; ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.42 (m, 2 H, 2-ArH), 7.12-7.24 (m, 2 H, 2-ArH), 6.89 (d, *J* = 8 Hz, 2 H, 3-ArH), 6.61-6.67 (m, 3 H, 2 × 3-ArH and C=CH), 4.39 (dd, *J* = 1, 6 Hz, 2 H, CH₂OH), 3.86 (t, *J* = 7 Hz, 2 H, ArOCH₂), 1.71 (quintet, *J* = 7 Hz, 2 H, ArOCH₂CH₂), 1.57 (t, *J* = 6 Hz, 1 H, OH), 1.18-1.43 (m, 14 H, 7 × CH₂), and 0.86 (t, *J* = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 158.33, 141.22, 137.61, 131.57, 130.48, 130.36, 128.11, 127.80, 127.62, 122.81, 114.09, 68.74 (CH₂OH), 67.91 (ArOCH₂), 31.89, 29.55, 29.37, 29.31, 29.21, 26.01, 22.68, and 14.12; IR (film) 3400 (br, OH), 2950, 2940, 2920, 2850, 1605,

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1590, 1555, 1510, 1475, 1400, 1395, 1375, 1300, 1250, 1175, 1090, 1060, 1050, 1030, 995, 975, 880, 830, 790, 775, and 720 cm^{-1} ; MS (DCI) m/e 444/446 (MH^+ , 1:1).

5 For (Z)-2-(3-Bromophenyl)-3-(3,4-bisdecyloxyphenyl)-2-propenol (5e): scale = 0.84 mmol, yield = 87%; ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.43 (m, 2 H, 2-ArH), 7.15-7.24 (m, 2 H, 2-ArH), 6.67 (d, J = 8 Hz, 1 H, 3-ArH), 6.59 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.58 (s, 1 H, C=CH), 6.42 (d, J = 2 Hz, 1 H, 3-ArH), 4.39 (br s, 2 H, CH_2OH), 3.91 (t, J = 7 Hz, 2 H, ArC^4OCH_2), 3.54 (t, J = 7 Hz, 2 H, ArC^3OCH_2), 1.75 (quint, J = 7 Hz, 2 H, $\text{ArC}^4\text{OCH}_2\text{CH}_2$), 1.59 (quint, J = 7 Hz, 2 H, $\text{ArC}^3\text{OCH}_2\text{CH}_2$), 1.24-1.40 (m, 28 H, 14 $\times$ CH_2), and 0.83-0.89 (m, 6 H, 2 $\times$ CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 148.44 (3-ArC⁴), 148.27 (3-ArC³), 141.50, 137.70, 131.80, 130.42, 128.52, 127.78, 122.83, 122.68, 113.90, 112.96, 69.05, 68.75, 68.65, 31.93, 29.65, 29.60, 29.57, 29.37, 29.20, 29.04, 25.98, 25.89, 22.70, and 14.12; IR (KBr) 3100-3400 (br, OH), 2955, 2920, 2850, 1515, 1470, 1425, 1270, 1235, and 1140 cm^{-1} ; MS (DCI) m/e 603/601 (MH^+ , 1:1), 585/583 ($\text{MH}^+ - \text{H}_2\text{O}$, 1:1).

20 For (Z)-2-(3-Bromophenyl)-5-phenyl-2-pentenol (5f): scale = 5.80 mmol, yield = 95%; ^1H NMR (300 MHz, CDCl_3) δ 7.39 (dt, J = 2, 8 Hz, 1 H, 2-ArH), 7.08-7.29 (m, 7 H, 3 $\times$ 2-ArH and 4 $\times$ 5-ArH), 6.98 (dt, J = 2, 8 Hz, 1 H, 5-ArH), 5.77 (t, J = 7.5 Hz, 1 H, C=CH), 4.25 (s, 2 H, CH_2OH), 2.67 (t, J = 7.5 Hz, 2 H, ArCH_2), and 2.30 (q, J = 7.5 Hz, 2 H, ArCH_2CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 141.17, 140.44, 139.72, 131.33, 130.10, 129.70, 128.78, 128.37, 128.22, 127.17, 125.85, 122.26, 67.70 (CH_2OH), 35.67, and 30.26; IR (film) 3350 (br, OH), 3085, 3060, 3025, 2920, 2860, 1590, 1560, 1495, 1475, 1455, 1410, 1365, 1100, 1080, 1070, 1030, 995, 790, 750, 700, and 670 cm^{-1} ; MS (DCI) m/e 299/301 ($\text{M}^+ - \text{OH}$, 1:1).

30 For (Z)-2-(3-Bromophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol (5g): scale = 3.2 mmol, yield = 87%; ^1H NMR (300 MHz, CDCl_3) δ 7.38 (ddd, J = 1, 2, 8 Hz, 1 H, 2-ArH), 7.27 (t, J = 2 Hz, 1 H, 2-ArH), 7.13-7.24 (m, 2 H, 2-ArH), 7.01 (d, J = 2 Hz, 1 H, 5-ArH), 6.95 (dt, J = 1, 8 Hz, 1 H, 5-ArH), 6.86 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 5.80 (m, 1 H, C=CH), 4.26 (m, 2 H, CH_2OH), 2.61 (t, J = 7 Hz, 2 H, ArCH_2), 2.28 (q, J = 7 Hz, 2 H, ArCH_2CH_2), 1.44 (m, 1 H, OH), 1.25 (s, 6 H,

2 x CH₃), and 1.24 (s, 6 H, 2 x CH₃); ¹³C NMR (CDCl₃) δ 144.66, 142.44, 140.63, 139.53, 138.19, 131.47, 130.18, 129.82, 129.42, 127.31, 126.47, 125.75, 122.34, 107.61, 67.88 (CH₂OH), 35.59, 35.18, 35.12, 34.16, 33.96, 31.93 (CH₃), 31.88, and 30.49; IR (film) 3335 (br, OH), 2960, 2925, 2860, 1470, 1460, 1360, 1070, 790, 760 cm⁻¹; MS (FAB) m/e 426/428 (MH⁺, 1:1). Anal. Calcd for C₂₅H₃₁BrO: C, 70.25; H, 7.31. Found: C, 70.15; H, 7.20.

For (2Z),(4E)-2-(3-Bromophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-hexadienol (5h): scale = 3.47 mmol, yield = 93%; ¹H NMR (300 MHz, CDCl₃) δ 7.49 (d, J = 2 Hz, 1 H, 2-ArH), 7.41 (dt, J = 2, 8 Hz, 1 H, 2-ArH), 7.19-7.27 (m, 4 H, 2 x 2-ArH and 2 x 5-ArH), 7.09 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.74 (dt, J = 1.5, 12 Hz, 1 H, C=CH), 6.45 (br d, J = 12 Hz, 1 H, C=CH), 4.46 (d, J = 1.5 Hz, 2 H, CH₂OH), 2.22 (d, J = 1.5 Hz, 3 H, C=CCH₃), 1.65 (br s, 4 H, CH₂CH₂), and 1.24 (s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 139.99, 139.07, 131.87, 130.46, 129.86, 127.82, 126.46, 125.19, 123.83, 123.08, 122.47, 122.15, 67.87 (CH₂OH), 35.12, 34.97, 34.30, 34.10, 31.81, 31.75, and 16.11 (C=CCH₃); IR (film) 3335 (br, OH), 2960, 2930, 2860, 1590, 1555, 1495, 1470, 1460, 1385, 1360, 1215, 1085, 1070, 885, 825, 785, 760, 700, and 680 cm⁻¹; MS (DCI) m/e 438/440 (M⁺, 1:1), 421/423 (M⁺ - OH).

For (Z)-2-(3-Bromophenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenol (5i): scale = 5.4 mmol, yield = 78%; ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.39 (m, 1 H, 2-ArH), 7.23 (t, J = 2 Hz, 1 H, 2-ArH), 7.16 (t, J = 8 Hz, 1 H, 2-ArH), 7.07 (d, J = 8 Hz, 1 H, 3-ArH), 6.94 (dt, J = 2, 8 Hz, 1 H, 2-ArH), 6.63 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.56 (d, J = 2 Hz, 1 H, 3-ArH), 5.77 (t, J = 8 Hz, 1 H, C=CH), 4.25 (d, J = 5 Hz, 2 H, CH₂OH), 3.75 (s, 3 H, OCH₃), 2.62 (t, J = 8 Hz, 2 H, ArCH₂), 2.28 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 2.05 (br s, 9 H, adamantyl), and 1.74 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 158.71, 140.60, 139.93, 139.67, 136.21, 131.49, 130.18, 129.81, 129.22, 127.30, 126.30, 122.32, 120.31, 112.00, 67.85 (CH₂OH), 54.92 (OCH₃), 40.64, 37.14, 36.66, 35.48, 30.33, and 29.10; IR (film) 3355 (br, OH), 2900, 2850, 1560, 1450, 1410, and 1245 cm⁻¹; MS (DCI) m/e 483/481 (MH⁺, 1:1), 465/463 (MH⁺ - H₂O, 1:1).

For (Z)-2-(3-Bromophenyl)-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenol (5j): scale = 2.6 mmol, yield = 95% (3:1, Z:E); ¹H NMR (300

MHz, CDCl₃) δ (Z-isomer) 7.37 (m, 1 H, 2-ArH), 7.17 (m, 2 H, 2-ArH), 6.99 (m, 1 H, 2-ArH), 5.77 (t, J = 7 Hz, 1 H, C=CH), 5.09 (br s, 1 H, ArOH), 4.26 (s, 2 H, CH₂OH), 2.57 (t, J = 7 Hz, 2 H, ArCH₂), 2.25 (q, J = 7 Hz, 2 H, ArCH₂CH₂), 2.06 (m, 9 H, adamantyl), and 1.76 (s, 6 H, adamantyl); (E-isomer, partially obscured) 7.55 (m, 1 H, 2-Ar), 5.91 (t, J = 8 Hz, 1 H, C=CH), 4.21 (s, 2 H, CH₂OH), 2.71 (t, J = 7 Hz, 2 H, ArCH₂), and 2.53 (q, J = 7 Hz, 2 H, ArCH₂CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 153.11, 152.77, 143.39, 140.62, 139.43, 138.33, 136.19, 133.05, 132.64, 131.45, 130.16, 129.99, 129.82, 129.60, 129.38, 127.59, 127.36, 127.15, 126.67, 126.36, 124.86, 122.60, 122.37, 116.83, 116.61, 67.91, 59.45, 40.55, 40.45, 37.08, 36.60, 35.31, 35.08, 31.04, 30.78, 29.05, and 25.61; IR (KBr) 3520 (OH), 3345 (br, OH), 2900, 2850, 1450, 1420, 1240, 1100, 995, and 785 cm⁻¹; MS (DCI) m/e 466/468 (M⁺, 1:1), 241, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₂₇H₃₁BrO₂: C, 69.38; H, 6.68. Found: C, 69.06; H, 6.91.

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For (Z)-2-(3-Bromophenyl)-3-(3,4-bis(pentyloxy)phenyl)-2-propenol (5k): scale = 1.67 mmol, yield = 94%; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.44 (m, 2 H, 2-ArH), 7.11-7.24 (m, 2 H, 2-ArH), 6.67 (d, J = 8 Hz, 1 H, 3-ArH), 6.60 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.58 (t, J = 1.5 Hz, 1 H, C=CH), 6.42 (d, J = 2 Hz, 1 H, 3-ArH), 4.39 (dd, J = 1.5, 6 Hz, 2 H, CH₂OH), 3.91 (t, J = 6.5 Hz, 2 H, 3-ArOCH₂), 3.54 (t, J = 6.5 Hz, 2 H, 3-ArOCH₂), 1.71-1.81 (m, 2 H, 3-ArOCH₂CH₂), 1.55-1.65 (m, 2 H, 3-ArOCH₂CH₂), 1.29-1.44 (m, 8 H, 4 $\times$ CH₂), and 0.86-0.92 (m, 6 H, 2 $\times$ CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 148.41, 148.23, 141.49, 137.69, 131.78, 130.43, 128.50, 127.79, 127.76, 122.83, 122.68, 113.81, 112.87, 69.00 (3-ArOCH₂), 68.75 (CH₂OH), 68.60 (3-ArOCH₂), 28.87, 28.70, 28.16, 28.05, 22.46, 22.40, 14.08 and 14.04; IR (film) 3355 (OH), 3265 (OH), 2955, 2930, 2870, 2855, 1515, 1465, 1430, 1270, 1235, 1170, 1140, 1085, 1070, 1035, 985, 800, and 785 cm⁻¹; MS (DCI) m/e 461/463 (MH⁺, 1:1), 443/445 (M⁺ - OH).

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For (Z)-2-(3-Trifluoromethylphenyl)-3-(4-decyloxyphenyl)-2-propenol (5l): scale = 7.4 mmol, yield = 80%; ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.54 (m, 2 H, 2-ArH), 7.39-7.42 (m, 2 H, 2-ArH), 6.85 (dt, J = 3, 8 Hz, 2 H, 3-ArH), 6.61-6.67 (m, 3 H, 2 $\times$ 3-ArH and C=CH), 4.44 (dd, J = 1, 6 Hz, 2 H, CH₂OH), 3.85 (t, J = 6 Hz, ArOCH₂), 1.71 (quint, J = 6 Hz, 2 H, ArOCH₂CH₂), 1.24-1.41 (m, 14 H, 7 $\times$ CH₂), 0.85 (t, J = 6 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 158.40 (3-ArC⁴), 139.86, 137.59, 132.57,

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130.42 (3-ArC), 129.20, 128.13, 127.99, 125.60 (q, $J_{\text{C},\text{F}} = 4$ Hz, 2-ArC), 124.16 (q, $J_{\text{C},\text{F}} = 4$ Hz, 2-ArC), 114.14 (3-ArC), 68.65, 67.93, 31.88, 29.54, 29.36, 29.30, 29.19, 25.99, 22.66, and 14.10; IR (KBr) 3550, 3400 (br, OH), 2960, 2940, 2920, 2850, 1605, 1510, 1475, 1420, 1390, 1325, 1310, 1255, 1180, and
5 1160 cm^{-1} ; MS (DCI) m/e 434 (M^+), 417 ($\text{MH}^+ - \text{H}_2\text{O}$).

For (Z)-2-(3-Trifluoromethylphenyl)-3-(3-decyloxyphenyl)-2-propenol (5m): scale = 2.7 mmol, yield = 68%; ^1H NMR (300 MHz, CDCl_3) δ 7.52-7.54 (m, 2 H, 2-ArH), 7.37-7.45 (m, 2 H, 2-ArH), 7.02 (t, $J = 8$
10 Hz, 1 H, 3-ArH), 6.72 (br s, 1 H, $\text{C}=\text{CH}$), 6.65 (dt, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.54 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.42 (t, $J = 2$ Hz, 1 H, 3-ArH), 4.46 (dd, $J = 1, 5$ Hz, 2 H, CH_2OH), 3.58 (t, $J = 7$ Hz, 2 H, ArOCH_2), 1.55-1.68 (m, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.21-1.37 (m, 14 H, $7 \times \text{CH}_2$), and 0.87 (t, $J = 7$ Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 158.74 (3-ArC), 139.90, 139.69, 136.94,
15 132.51, 129.24, 129.09, 128.17, 125.60 (q, $J_{\text{C},\text{F}} = 4$ Hz, 2-ArC), 124.24 (q, $J_{\text{C},\text{F}} = 4$ Hz, 2-ArC), 121.78, 114.48, 114.29, 68.31, 67.65, 31.89, 29.55, 29.31, 29.08, 25.88, 22.68, and 14.11; IR (film) 3330 (br, OH), 2925, 2855, 1600, 1570, 1470, 1435, 1325, 1265, 1165, and 1130 cm^{-1} ; MS (DCI) m/e 435 (MH^+), 417 ($\text{MH}^+ - \text{H}_2\text{O}$).

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For (Z)-2-(3-Trifluoromethylphenyl)-3-(2-decyloxyphenyl)-2-propenol (5n): scale = 5.7 mmol, yield = 99%, ca. 5:3 mixture of Z:E isomers. A solution of the crude mixture (2.46 g, 5.5 mmol) in pyridine (23 mL) at room temperature was treated with acetic
25 anhydride (0.73 g, 7.2 mmol) and 4,4-dimethylaminopyridine (10 mg). The solution was stirred for 1.5 h, and was then diluted with diethyl ether and poured into a separatory funnel containing 1 N HCl solution. The layers were agitated and separated, and the organic layer was washed with saturated sodium chloride solution, dried over
30 anhydrous magnesium sulfate, and concentrated in vacuo to yield 2.6 g of a yellow oil. The crude material was purified by column chromatography (40:1 ratio of silica gel/ crude product; elution with 5% to 10% ethyl acetate in hexanes) to afford 1.1 g (42%) of the acetate target compound as a single isomer: ^1H NMR (300 MHz, CDCl_3) δ 7.46-
35 7.48 (m, 2 H, 2-ArH), 7.31-7.39 (m, 2 H, 2-ArH), 7.09 (dt, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.98 (br s, 1 H, $\text{C}=\text{CH}$), 6.80 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.66 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.56 (t, $J = 8$ Hz, 1 H, 3-ArH), 4.94 (d, $J = 1$ Hz, 2 H,

CH₂OAc), 3.94 (t, $J = 7$ Hz, 2 H, ArOCH₂), 2.04 (s, 3 H, COCH₃), 1.78 (quint, $J = 7$ Hz, 2 H, OCH₂CH₂), 1.13-1.50 (m, 14 H, 7 × CH₂), and 0.86 (t, $J = 7$ Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.70 (C=O), 157.03 (3-ArC), 139.27, 134.33, 132.31, 130.09, 128.89, 128.80, 127.07, 125.64 (q, $J_{C,f}^3 = 4$ Hz, 2-ArC), 124.59, 124.06 (q, $J_{C,f}^3 = 4$ Hz, 2-ArC), 119.78, 111.62, 69.00, 68.30, 31.90, 29.62, 29.39, 29.33, 29.20, 26.09, 22.68, 20.92, 18.54, and 14.11; IR (film) 2925, 2855, 1740 (C=O), 1450, 1325, 1245, 1220, 1165, and 1125 cm⁻¹; MS (DCI) m/e 477 (MH⁺), 476 (M⁺). A solution of the acetate (1.04 g, 2.18 mmol) in methanol (10.9 mL) was treated with 2 N NaOH solution (4.4 mL, 8.7 mmol) and was stirred at reflux for 2 h. The solution was allowed to cool to room temperature and was poured into water and extracted with diethyl ether. Sodium chloride was added to the aqueous layer, which was extracted a second time with diethyl ether. The organic layers were combined, washed sequentially with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to afford 0.96 g of a colorless oil. Purification by column chromatography (20:1 silica gel/crude product; elution with 5% to 10% ethyl acetate in hexanes) afforded 0.87 g (92%) of the product (5n) as a clear, colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.51 (m, 2 H, 2-ArH), 7.31-7.40 (m, 2 H, 2-ArH), 7.09 (dt, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.95 (br s, 1 H, C=CH), 6.80 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.67 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.56 (t, $J = 8$ Hz, 1 H, 3-ArH), 4.52 (dd, $J = 1, 6$ Hz, 2 H, CH₂OH), 3.94 (t, $J = 7$ Hz, 2 H, OCH₂), 1.78 (quint, $J = 7$ Hz, 2 H, OCH₂CH₂), 1.21-1.48 (m, 14 H, 7 × CH₂), 0.87 (t, $J = 7$ Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 157.05 (3-ArC), 139.66, 132.42, 130.19, 128.83, 128.59, 125.52 (q, $J_{C,f}^3 = 4$ Hz, 2-ArC), 124.98, 124.49, 123.95 (q, $J_{C,f}^3 = 4$ Hz, 2-ArC), 119.80, 111.63, 68.41, 68.34, 31.90, 29.62, 29.58, 29.39, 29.34, 29.20, 26.10, 22.68, and 14.11; IR (film) 3380 (br, OH), 2925, 2855, 1580, 1325, 1245, and 1125 cm⁻¹; MS (DCI) m/e 435 (MH⁺), 434 (M⁺), 417 (MH⁺ - H₂O).

For (Z)-2-(3-Trifluoromethylphenyl)-3-[4-(2E),(6E)-3,7-dimethylocta-2,6-dienoxy]phenyl)-2-propenol (5o): scale = 2.0 mmol, yield = 67%; ¹H NMR (300 MHz, CDCl₃) δ 7.52-7.54 (m, 2 H, 2-ArH), 7.39-7.45 (m, 2 H, 2-ArH), 6.86 (d, $J = 8$ Hz, 2 H, 3-ArH), 6.63-6.68 (m, 3 H, 2 × 3-ArH and ArCH=C), 5.41 (dt, $J = 1, 6.5$ Hz, 1 H, C=CHCH₂O), 5.03-5.06 (m, 1 H, CH=C(CH₃)₂), 4.40-4.45 (m, 4 H, ArOCH₂ and CH₂OH), 2.02-2.10

(m, 4 H, C=CHCH₂CH₂), and 1.56-1.68 (m, 9 H, 3 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 158.14 (3-ArC), 141.22, 139.85, 137.67, 132.56, 131.81, 130.93, 130.41 (3-ArC), 129.20, 128.09, 125.61 (q, *J*_{C,f} = 4 Hz, 2-ArC), 124.15, 123.77, 119.31, 114.36 (3-ArC), 68.64 (CH₂OH), 64.81 (ArOCH₂),
5 39.50, 26.27, 25.66, 17.67, and 16.62; IR (film) 3360 (br, OH), 2970, 2920, 1605, 1510, 1325, 1305, 1245, 1175, and 1165 cm⁻¹; MS (DCI) *m/e* 431 (MH⁺), 413 (MH⁺ - H₂O).

For (Z)-2-(3-Trifluoromethylphenyl)-3-(3,4-bisdecyloxyphenyl)-2-propenol (5p): scale = 2.37 mmol, yield = 93%; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.55 (m, 4 H, 2-ArH), 6.66 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.65 (d, *J* = 2 Hz, 1 H, 3-ArH), 6.57 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.33 (t, *J* = 2 Hz, 1 H, C=CH), 4.43 (dt, *J* = 2, 8 Hz, CH₂OH), 3.90 (t, *J* = 7 Hz, 2 H, CH₂OAr), 3.46 (t, *J* = 7 Hz, 2 H, CH₂OAr), 1.69-1.79 (m, 2 H, CH₂CH₂O), 1.55-1.63
15 (m, 3 H, CH₂CH₂O and OH), 1.24-1.45 (m, 28 H, 14 × CH₂), 0.83-0.89 (m, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 148.47, 148.32, 140.22, 137.68, 132.69, 131.50 (q, *J*_{C,f} = 38 Hz, 2-ArC), 129.31, 128.40, 128.27, 125.73 (q, *J*_{C,f} = 4 Hz, 2-ArC), 124.07 (q, *J*_{C,f} = 4 Hz, 2-ArC), 122.65, 113.78, 113.00, 69.06 (CH₂O), 68.69 (CH₂O), 68.54 (CH₂O), 31.91, 29.59, 29.57, 29.33, 29.18, 29.01,
20 25.97, 25.82, 22.69, and 14.11; IR (KBr) 3400 (br, OH), 2960, 2920, 2850, 1515, 1475, 1430, 1330, 1270, 1235, 1170, 1140, 1125, 1100, 1070, and 1020 cm⁻¹; MS (DCI) *m/e* 590 (M⁺).

For (Z)-2-(3-trifluoromethylphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propenol (5q): scale = 3.0 mmol, obtained
25 1.14 g of a 2:1 mixture of target compound to impurity. Acetic anhydride (0.35 g, 3.5 mmol) and 4,4-dimethylaminopyridine (10 mg) were added to a stirred solution of the mixture (1.12 g) in pyridine (11.6 mL), and the solution was stirred at room temperature for 5 h. The
30 solution was diluted with diethyl ether and poured into 1 N HCl solution. The layers were agitated and separated, and the organic layer was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated to yield 1.14 g of a
pale yellow oil. Purification was accomplished by column
35 chromatography (40:1 silica gel/crude product; gradient elution with 3% to 15% ethyl acetate in hexanes) to afford 0.80 g (20:1 mixture of Z:E isomers) of the acetate. ¹H NMR (300 MHz, CDCl₃) δ 7.62 (s, 1 H, ArH),

7.54-7.58 (m, 3 H, ArH), 7.47 (s, 1 H, ArH), 7.37-7.40 (m, 3 H, ArH), 6.90 (br s, 1 H, C=CH), 6.77 (dd, $J = 2, 9$ Hz, 1 H, 3-ArH), 4.94 (d, $J = 1$ Hz, 2 H, CH₂OAc), 2.05 (s, 3 H, COCH₃), 1.72 (s, 4 H, CH₂CH₂), and 1.33 (br s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.72 (C=O), 145.04, 144.74, 139.17, 134.37, 132.70, 132.03, 131.81, 131.54, 131.01, 129.11, 128.70, 126.70, 125.56, 125.08, 124.64, 124.45, 69.28 (CH₂OAc), 34.99 (CH₂CH₂), 34.59, 34.52, 32.44 (4 x CH₃), and 20.95 (COCH₃); IR (KBr) 2960, 2950, 2925, 1735 (C=O), 1325, 1255, 1230, 1160, and 1125 cm⁻¹; MS (DCI) m/e 481 (MH⁺), 480 (M⁺), 421 (M⁺ - OAc). The acetate (0.77 g, 1.66 mmol) was dissolved in methanol (8.3 mL) and tetrahydrofuran (8.3 mL) and the stirred solution was treated with 2 N NaOH (3.33 mL, 6.66 mmol). The mixture was heated at reflux for 2.5 h. The solution was then allowed to cool to room temperature and was poured into saturated ammonium chloride solution and extracted twice with diethyl ether. The organic layers were combined, washed sequentially with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated to give 0.74 g of a clear colorless oil. Purification by column chromatography (20:1 silica gel/crude product; elution with 10% to 15% ethyl acetate in hexanes) gave 0.69 g (56% overall yield from ester) of the propenol **5q** as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.63 (s, 1 H, ArH), 7.54-7.59 (m, 3 H, ArH), 7.47 (s, 1 H, ArH), 7.35-7.42 (m, 3 H, ArH), 6.89 (s, 1 H, C=CH), 6.80 (dd, $J = 2, 9$ Hz, 1 H, 3-ArH), 4.52 (br s, 2 H, CH₂OH), 1.72 (s, 4 H, CH₂CH₂), and 1.34 (br s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 144.80, 144.67, 139.61, 139.21, 132.80, 132.46, 131.62, 131.30, 130.89, 129.16, 128.82, 128.36, 126.66, 125.75, 125.50 (q, $J_{C,F} = 4$ Hz, 2-ArC), 125.01, 124.64, 124.36 (q, $J_{C,F} = 4$ Hz, 2-ArC), 122.22, 68.52 (CH₂OH), 35.01 (CH₂CH₂), 34.58, 34.53, and 32.45 (4 x CH₃); IR (film) 3320 (br, OH), 2960, 2930, 1325, 1165, and 1130 cm⁻¹; MS (DCI) m/e 439 (MH⁺), 421 (MH⁺ - H₂O).

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For (Z)-2-(3-Trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol (**5r**): scale = 1.84 mmol, yield = 87%; ¹H NMR (300 MHz, CDCl₃) δ 7.50 (br d, $J = 8$ Hz, 1 H, 2-ArH), 7.37-7.42 (m, 3 H, 2-ArH), 7.17 (d, $J = 8$ Hz, 5-ArH), 6.99 (d, $J = 2$ Hz, 1 H, 5-ArH), 6.83 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 5.84 (t, $J = 8$ Hz, 1 H, C=CH), 4.29 (s, 2 H, CH₂OH), 2.61 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.25 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 x CH₃), and 1.22 (s, 6

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H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 144.68, 142.48, 139.56, 139.30, 138.08, 132.03, 130.50 (q, $J^2_{c,f}$ = 32 Hz, 2-ArC), 129.82, 128.71, 126.45, 125.69, 125.27 (q, $J^3_{c,f}$ = 4 Hz, 2-ArC), 123.91 (q, $J^3_{c,f}$ = 4 Hz, 2-ArC), 67.88 (OCH₂), 35.54, 35.14, 35.09, 34.13, 33.93, 31.87, 31.81, and 30.74; IR (film) 3320 (br, OH), 2960, 2925, 2860, 1460, 1365, 1325, 1310, 1165, 1130, 1110, 1070, 805, and 705 cm⁻¹; MS (DCI) *m/e* 399 (M⁺ - OH).

For (Z)-2-(4-Fluorophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol (5s): scale = 2.91 mmol, yield = 68%; ¹H NMR (300 MHz, CDCl₃) δ 7.17 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.92-6.99 (m, 5 H, 4 x 2-ArH and 1 x 5-ArH), 6.82 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 5.76 (t, *J* = 8 Hz, 1 H, C=CH), 4.25 (d, *J* = 5.5 Hz, 2 H, CH₂OH), 2.59 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.25 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.36 (t, *J* = 5.5 Hz, 1 H, OH), 1.24 (s, 6 H, 2 x CH₃), and 1.22 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 161.90 (d, $J^1_{c,f}$ = 246 Hz, 2-ArC), 144.62, 144.40, 139.82, 138.28, 134.16, 130.16 (d, $J^3_{c,f}$ = 8 Hz, 2-ArC), 128.70, 126.49, 126.30, 125.78, 115.12 ($J^2_{c,f}$ = 21 Hz, 2-ArC), 68.12 (CH₂OH), 35.58, 35.15, 35.10, 34.13, 33.94, 31.90, 31.85, and 30.45; IR (film) 3300 (br, OH), 2960, 2925, 2860, 1600, 1510, 1455, 1385, 1360, 1220, and 835 cm⁻¹; MS (DCI) *m/e* 349 (M⁺ - OH).

For (Z)-2-(3-Fluorophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol (5t): scale = 4.16 mmol, yield = 65%; ¹H NMR (300 MHz, CDCl₃) δ 7.16-7.28 (m, 2 H, 1 x 2-ArH and 1 x 5-ArH), 6.99 (d, *J* = 2 Hz, 5-ArH), 6.94 (apparent tt, *J* = 2, 8 Hz, 1 H, 2-ArH), 6.79-6.86 (m, 2 H, 1 x 5-ArH and 1 x 2-ArH), 6.71 (apparent dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 5.78 (t, *J* = 8 Hz, 1 H, C=CH), 4.26 (d, *J* = 5 Hz, 2 H, CH₂OH), 2.61 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.28 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.65 (br s, 4 H, CH₂CH₂), 1.40 (t, *J* = 5 Hz, 1 H, OH), 1.24 (s, 6 H, 2 x CH₃), and 1.23 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 162.64 (d, $J^1_{c,f}$ = 246 Hz, 2-ArC), 144.66, 142.45, 140.67 (d, $J^3_{c,f}$ = 8 Hz, 2-ArC), 139.73, 138.21, 129.69 (d, $J^3_{c,f}$ = 8 Hz, 2-ArC), 129.13, 126.48, 126.41, 125.76, 124.29 (d, $J^4_{c,f}$ = 5 Hz, 2-ArC), 115.52 ($J^2_{c,f}$ = 21 Hz, 2-ArC), 113.98 ($J^2_{c,f}$ = 21 Hz, 2-ArC), 67.92 (CH₂OH), 35.55, 35.15, 35.10, 34.15, 33.95, 31.89, 31.84, and 30.48; IR (film) 3300 (br, OH), 3020, 2960, 2925, 2860, 1610, 1580, 1490, 1460, 1435, 1410, 1385, 1360, 1260, 1235, 1220, 1190, 1090, 1070, 1005, 890, 825, 785, 760, 720, and 700 cm⁻¹; MS (DCI) *m/e* 349 (M⁺ - OH).

For (Z)-2-Phenyl-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol (5u): scale = 1.10 mmol, yield = 74%; ¹H NMR (300 MHz, CDCl₃) δ 7.23-7.32 (m, 3 H, 2-ArH), 7.16 (d, *J* = 8 Hz, 1 H, 5-ArH), 7.00-7.07 (m, 3 H, 1 × 5-ArH and 2 × 2-ArH), 6.84 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 5.76 (t, *J* = 8 Hz, 1 H, C=CH), 4.29 (s, 2 H, CH₂OH), 2.61 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.28 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.66 (br s, 4 H, CH₂CH₂), 1.44 (br s, 1 H, OH), 1.24 (s, 6 H, 2 × CH₃), and 1.22 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 144.57, 142.31, 140.77, 138.44, 138.33, 128.56, 128.26, 128.19, 127.10, 126.47, 126.36, 125.76, 68.10 (CH₂OH), 35.70, 35.18, 35.12, 34.15, 33.93, 31.91, 31.86, and 30.43; IR (film) 3340 (br, OH), 2960, 2925, 2860, 1495, 1455, 1440, 1385, 1360, 1090, 1070, 1025, 1000, 825, 760, and 700 cm⁻¹; MS (DCI) *m/e* 331 (MH⁺ - H₂O).

For (Z)-2-(3-Trifluoromethylphenyl)-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenol (5v): scale = 1.4 mmol, yield = 81%; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.42 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.34 (s, 1 H, 2-ArH), 7.23 (d, *J* = 7 Hz, 1 H, 2-ArH), 6.90 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.73 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.50 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.82 (m, 1 H, C=CH), 4.71 (s, 1 H, ArOH), 4.30 (d, *J* = 6 Hz, 2 H, CH₂OH), 2.58 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.23 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.07 (br s, 9 H, adamantyl), 1.75 (s, 6 H, adamantyl), and 1.44 (t, *J* = 6 Hz, 1 H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 152.63, 139.56, 139.30, 136.15, 133.13, 132.08, 130.63 (d, *J*_{C,F}² = 32 Hz, 2-ArC), 129.89, 128.72, 127.18, 126.32, 125.26 (d, *J*_{C,F}³ = 4 Hz, 2-ArC), 123.92 (d, *J*_{C,F}³ = 4 Hz, 2-ArC), 116.61, 67.92 (CH₂OH), 40.55 (adamantyl CH₂), 37.05 (adamantyl CH₂), 36.58 (adamantyl quaternary), 35.27, 30.76, and 29.02 (adamantyl CH); IR (KBr) 3430 (OH), 3250 (br, OH), 2900, 1325, 1170, 1160, 1125, 1075, and 990 cm⁻¹; MS (DCI) *m/e* 456 (M⁺), 455 (M-H)⁺, 241, 135 (C₁₀H₁₅⁺).
Anal. Calcd for C₂₈H₃₁F₃O₂: C, 73.66; H, 6.84. Found: C, 73.86; H, 6.87.

For (Z)-2-(3-Trifluoromethylphenyl)-5-[3-(1-adamantyl)-4-methoxyphenyl]-2-pentenol (5w): obtained from (Z)-2-(3-trifluoromethylphenyl)-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenol (5v) via treatment with dimethyl sulfate (0.25 g, 2.0 mmol) and potassium carbonate (0.19 g, 1.3 mmol) in refluxing acetone (10 mL) for 6 h. Scale = 0.87 mmol, yield = 78%; ¹H NMR (300 MHz,

CDCl₃) δ 7.51 (m, 1 H, 2-ArH), 7.42 (t, J = 8 Hz, 1 H, 2-ArH), 7.35 (s, 1 H, 2-ArH), 7.24 (m, 1 H, 2-ArH), 6.92 (m, 1 H, 5-ArH), 6.86 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.74 (d, J = 8 Hz, 1 H, 5-ArH), 5.84 (m, 1 H, C=CH), 4.30 (m, 2 H, CH₂OH), 3.78 (s, 3 H, OCH₃), 2.61 (t, J = 7 Hz, 2 H, ArCH₂), 2.25 (q, J = 7 Hz, 2 H, ArCH₂CH₂), 2.04 (br s, 9 H, adamantyl), 1.75 (s, 6 H, adamantyl), and 1.42 (t, J = 6 Hz, 1 H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 157.13, 139.57, 139.36, 138.28, 132.82, 132.08, 130.62 (d, $J^2_{C,f}$ = 32 Hz, 2-ArC), 129.91, 128.71, 126.82, 126.25, 125.91, 125.27 (d, $J^3_{C,f}$ = 4 Hz, 2-ArC), 123.90 (d, $J^3_{C,f}$ = 4 Hz, 2-ArC), 111.61, 67.92 (CH₂OH), 55.04 (OCH₃), 40.60 (adamantyl CH₂), 37.13 (adamantyl CH₂), 36.86 (adamantyl quaternary), 35.31, 30.77, and 29.10 (adamantyl CH); IR (film) 3345 (br, OH), 2905, 2850, 1325, 1235, 1165, and 1130 cm⁻¹; MS (DCI) m/e 470 (M⁺), 469 (M-H)⁺, 255, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₂₉H₃₃F₃O₂: C, 74.02; H, 7.07. Found: C, 73.96; H, 7.05.

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For (Z)-2-Phenyl-5-[3-(1-adamantyl)-4-methoxyphenyl]-2-pentenol (2.5:1, Z:E) (5x): obtained in three steps from (Z)-1-(*t*-butyldimethylsiloxy)-2-phenyl-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentene, a by-product in the synthesis of Zj. The bis-silyl ether (0.700 g, 1.14 mmol) was dissolved in 30 mL of 3:1:1 acetic acid/THF/H₂O, and stirred for 48 h. The solvent was removed in vacuo. A solution of the residue, 2-phenyl-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentenol (2.5:1, Z:E), in THF (10 mL) was treated with a 1.1 M solution of tetrabutylammonium fluoride in THF (1.44 mL, 1.59 mmol). This mixture was stirred for 30 min at rt and then quenched by the addition of saturated ammonium chloride solution (10 mL). This solution was partitioned between ether and water. The organic phase was separated, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 2-phenyl-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenol (2.5:1, Z:E): ¹H NMR (300 MHz, CDCl₃) δ (Z-isomer) 7.25-7.34 (m, 3 H, 2-ArH), 7.09-7.12 (m, 2 H, 2-ArH), 6.91 (d, J = 2 Hz, 1 H, 5-ArH), 6.75 (dd, J = 8, 2 Hz, 1 H, 5-ArH), 6.49 (d, J = 8 Hz, 1 H, 5-ArH), 5.75 (t, J = 7 Hz, 1 H, C=CH), 4.30 (m, 2 H, CH₂OH), 2.58 (t, J = 7 Hz, 2 H, ArCH₂), 2.28 (q, J = 7 Hz, 2 H, ArCH₂CH₂), 2.08 (s, 9 H, adamantyl), and 1.73 (s, 6 H, adamantyl); (E-isomer, partially obscured) 7.40 (m, 1 H, 2-ArH) 6.97 (d, J = 2 Hz, 1 H, 5-ArH), 6.86 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.51 (d, J = 8 Hz, 1

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H, 5-ArH), 5.91 (t, $J = 8$ Hz, 1 H, C=CH), and 2.71 (t, $J = 8$ Hz, 2 H, ArCH₂); IR (KBr) 3520 (OH), 3345 (OH), 2900, 2850, 1240, and 700 cm⁻¹; MS (DCI) m/e 389 (MH⁺), 388 (M⁺), 371, 241, 135 (C₁₀H₁₅⁺); Anal. Calcd for C₂₇H₃₂O₂ • 0.3 CH₃CO₂CH₂CH₃: C, 81.62; H, 8.36. Found: C, 81.62; H, 8.32. 2-Phenyl-5-[3-(1-adamantyl)-4-hydroxyphenyl]-2-pentenol (2.5:1, Z:E, 0.600 g, 1.55 mmol) was treated with dimethylsulfate (0.195 g, 1.55 mmol) and powdered potassium carbonate (0.214 g, 1.55 mmol) in refluxing acetone for 18 h. The cooled reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (elution with methylene chloride followed by 5% methanol/methylene chloride) to give 385 mg (84% overall yield) of **5x** as a 3:1 mixture of Z:E isomers. ¹H NMR (300 MHz, CDCl₃) δ (Z-isomer) 7.37-7.22 (m, 3 H, 2-ArH), 7.12 (m, 2 H, 2-ArH), 6.95 (d, $J = 2$ Hz, 1 H, 5-ArH), 6.88 (dd, $J = 8, 2$ Hz, 1 H, 5-ArH), 6.77 (d, $J = 8$ Hz, 1 H, 5-ArH), 5.78 (t, $J = 7$ Hz, 1 H, C=CH), 4.31 (m, 2 H, CH₂OH), 3.79 (s, 3 H, OCH₃), 2.58 (t, $J = 7$ Hz, 2 H, ArCH₂), 2.32 (q, $J = 7$ Hz, 2 H, ArCH₂CH₂), 2.02 (s, 9 H, adamantyl), and 1.76 (s, 6 H, adamantyl); (E-isomer, partially obscured) 7.41 (m, 1 H, 2-ArH), 5.92 (t, $J = 8$ Hz, 1 H, C=CH), and 2.73 (t, $J = 8$ Hz, 2 H, ArCH₂).

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For (Z)-2-(3-Trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-hydroxyphenyl]-2-pentenol (**5y**): scale = 1.8 mmol, yield = 83%; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (m, 1 H, 2-ArH), 7.40 (m, 1 H, 2-ArH), 7.35 (s, 1 H, 2-ArH), 7.15 (d, $J = 8$ Hz, 1 H, 2-ArH), 7.06 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.60 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.36 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.80 (m, 1 H, C=CH), 5.00 (s, 1 H, ArOH), 4.28 (m, 2 H, CH₂OH), 2.56 (t, $J = 7$ Hz, 2 H, ArCH₂), 2.23 (q, $J = 7$ Hz, 2 H, ArCH₂CH₂), 2.08 (br s, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 154.34, 139.88, 139.58, 139.23, 134.18, 132.09, 130.62 (d, $J^2_{C,F} = 32$ Hz, 2-ArC), 129.59, 128.76, 126.87, 125.26 (d, $J^3_{C,F} = 3$ Hz, 2-ArC), 124.09 (q, $J^1_{C,F} = 271$ Hz, CF₃), 123.97 (d, $J^3_{C,F} = 3$ Hz, 2-ArC), 120.63, 116.92, 67.79 (CH₂OH), 40.62 (adamantyl CH₂), 37.05 (adamantyl CH₂), 36.38 (adamantyl quaternary), 34.85, 30.11, and 29.03 (adamantyl CH); IR (film) 3500 (OH), 3280 (br, OH), 2910, 2870, 2850, 1420, 1320, 1310, 1165, 1125, 1085, and 1070 cm⁻¹; MS (DCI) m/e 455 (M-H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₂₈H₃₁F₃O₂: C, 73.66; H, 6.84. Found: C, 73.58; H, 6.84.

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For (Z)-2-(3-Trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenol (5z): obtained from (Z)-2-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-hydroxyphenyl]-2-pentenol (5y) via treatment with dimethyl sulfate (0.25 g, 2.0 mmol) and potassium carbonate (0.19 g, 1.3 mmol) in refluxing acetone (10 mL) for 56 h. Scale = 1.3 mmol, yield = 82%; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (m, 1 H, 2-ArH), 7.40 (m, 2 H, 2-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.07 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.63 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.55 (d, *J* = 2 Hz, 5-ArH), 5.84 (m, 1 H, C=CH), 4.29 (d, *J* = 1 Hz, 2 H, CH₂OH), 3.74 (s, 3 H, OCH₃), 2.63 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.27 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.05 (br s, 9 H, adamantyl), 1.74 (br s, 6 H, adamantyl), and 1.47 (br s, 1 H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 158.72, 139.85, 139.72, 139.30, 136.26, 132.08, 130.61 (d, *J*_{C,F}² = 32 Hz, 2-ArC), 129.62, 128.73, 126.31, 125.29 (d, *J*_{C,F}³ = 4 Hz, 2-ArC), 124.10 (q, *J*_{C,F}¹ = 271 Hz, CF₃), 123.93 (d, *J*_{C,F}³ = 4 Hz, 2-ArC), 120.29, 111.94, 67.83 (CH₂OH), 54.85 (OCH₃), 40.65 (adamantyl CH₂), 37.14 (adamantyl CH₂), 36.66 (adamantyl quaternary), 35.48, 33.31, and 29.10 (adamantyl CH); IR (film) 3355 (OH), 2905, 2850, 1325, 1250, 1165, 1130, 1100, and 1070 cm⁻¹; MS (DCI) *m/e* 470 (M⁺), 469 (M-H)⁺, 135 (C₁₀H₁₅)⁺. Exact mass spectrum (FAB) Calcd for C₂₉H₃₄F₃O₂ (MH⁺) 471.2511. Found: 471.2496. Anal. Calcd for C₂₉H₃₃F₃O₂ • 0.1 CH₂Cl₂: C, 72.96; H, 6.99. Found: C, 72.88; H, 7.10.

For (Z)-2-Phenyl-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenol (5aa): scale = 3.82 mmol, yield = 91%; ¹H NMR (300 MHz, CDCl₃) δ 7.20-7.33 (m, 3 H, 2-ArH), 7.03-7.07 (m, 3 H, 2 × 2-ArH and 1 × 5-ArH), 6.64 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.55 (d, *J* = 2 Hz, 1 H, 5-ArH), 5.75 (t, *J* = 8 Hz, 1 H, C=CH), 4.29 (s, 2 H, CH₂OH), 3.74 (s, 3 H, OCH₃), 2.62 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.30 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.03-2.08 (m, 9 H, adamantyl), and 1.74 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 158.68, 140.92, 140.22, 138.33, 136.10, 128.59, 128.26, 128.01, 127.11, 126.20, 120.32, 112.01, 68.06 (CH₂OH), 54.89 (OCH₃), 40.68, 37.14, 36.65, 35.62, 30.27, and 29.11; IR (film) 3350 (br, OH), 2904, 2848, 1610, 1494, 1452, 1412, 1246, 1162, 1138, 1102, 1090, 1042, 1026, 1002, 808, 760, and 702 cm⁻¹; MS (DCI) *m/e* 402 (M⁺), 385 (M⁺ - OH).

For (Z)-2-(3-Trifluoromethylphenyl)-5-[2-(1-adamantyl)-4-hydroxyphenyl]-2-pentenol (5bb): scale = 0.48 mmol, yield = 88%; ^1H NMR (300 MHz, CDCl_3) δ 7.52 (m, 1 H, 2-ArH), 7.43 (m, 2 H, 2-ArH), 7.33 (m, 1 H, 2-ArH), 6.93 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.82 (d, $J = 3$ Hz, 1 H, 5-ArH), 6.62 (dd, $J = 3, 8$ Hz, 1 H, 5-ArH), 5.90 (m, 1 H, C=CH), 4.34 (m, 2 H, CH_2OH), 3.74 (s, 3 H, OCH_3), 2.90 (m, 2 H, ArCH_2), 2.26 (m, 2 H, ArCH_2CH_2), 2.02 (br s, 3 H, adamantyl), 1.92 (m, 6 H, adamantyl), 1.73 (m, 6 H, adamantyl), and 1.51 (br s, 1 H, OH); ^{13}C NMR (75 MHz, CDCl_3) δ 157.52, 148.97, 139.52, 139.33, 132.67, 132.08, 130.75 (d, $J^2_{\text{C,F}} = 32$ Hz, 2-ArC), 129.59, 128.78, 125.17 (d, $J^3_{\text{C,F}} = 4$ Hz, 2-ArC), 124.03 (d, $J^3_{\text{C,F}} = 4$ Hz, 2-ArC), 113.02, 109.90, 67.83 (CH_2OH), 55.08 (OCH_3), 42.07 (adamantyl CH_2), 37.85 (adamantyl quaternary), 36.77 (adamantyl CH_2), 33.66, 32.35, and 29.10 (adamantyl CH); IR (film) 3390 (br, OH), 2910, 2850, 1325, 1165, 1125, and 1070 cm^{-1} ; MS (DCI) m/e 471 (MH^+), 470 (M^+), 469 (M-H^+), 255, 135 ($\text{C}_{10}\text{H}_{15}^+$).

For (Z)-2-(3-Trifluoromethylphenyl)-3-[4-(1-adamantyl)-3-methoxyphenyl]-2-propenol (5cc): scale = 2.48 mmol, yield = 90%; ^1H NMR (300 MHz, CDCl_3) δ 7.55 (m, 2 H, 2-ArH), 7.45 (m, 2 H, 2-ArH), 7.01 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.69 (s, 1 H, C=CH), 6.61 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.32 (d, $J = 2$ Hz, 1 H, 3-ArH), 4.44 (d, $J = 5$ Hz, 2 H, CH_2OH), 3.34 (s, 3 H, OCH_3), 1.98 (s, 9 H, adamantyl), and 1.69 (m, 7 H, 6 x adamantyl and OH); ^{13}C NMR (75 MHz, CDCl_3) δ 158.22, 140.17, 139.08, 138.14, 134.07, 132.56, 131.23 (d, $J^2_{\text{C,F}} = 32$ Hz, 2-ArC), 129.36, 127.99, 126.29, 125.75 (d, $J^3_{\text{C,F}} = 4$ Hz, 2-ArC), 124.16 (d, $J^3_{\text{C,F}} = 4$ Hz, 2-ArC), 122.11, 68.60 (CH_2OH), 54.25 (OCH_3), 40.42 (adamantyl CH_2), 37.06 (adamantyl CH_2), 36.83 (adamantyl quaternary), and 29.01 (adamantyl CH); IR (KBr) 3385 (br, OH), 2905, 2850, 1325, 1130, and 1070 cm^{-1} ; MS (DCI) m/e 443 (MH^+), 442 (M^+), 441 (M-H^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{27}\text{H}_{29}\text{F}_3\text{O}_2 \cdot 0.3 \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$: C, 72.23; H, 6.75. Found: C, 72.37; H, 6.59.

For (Z)-2-(3-Trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-*t*-butyldimethylsilyloxyphenyl]-2-pentenol (5dd): scale = 6.7 mmol, yield = 82%; ^1H NMR (300 MHz, CDCl_3) δ 7.51 (m, 1 H, 2-ArH), 7.40 (m, 2 H, 2-ArH), 7.19 (d, $J = 8$ Hz, 1 H, 2-ArH), 7.07 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.61 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.48 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.83 (m, 1 H,

C=CH), 4.29 (d, $J = 5$ Hz, 2 H, CH₂OH), 2.56 (t, $J = 7$ Hz, 2 H, ArCH₂), 2.23 (m, 2 H, ArCH₂CH₂), 2.06 (br s, 9 H, adamantyl), 1.74 (s, 6 H, adamantyl), 1.43 (m, 1 H, OH), 0.99 (s, 9 H, SiC(CH₃)₃), and 0.26 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 154.50, 139.76, 139.43, 139.28, 137.17, 132.07, 130.88, 129.50, 128.75, 126.88, 125.24 (d, $J_{\text{C,F}} = 4$ Hz, 2-ArC), 123.97 (d, $J_{\text{C,F}} = 4$ Hz, 2-ArC), 120.38, 119.15, 67.85 (CH₂OH), 40.46 (adamantyl CH₂), 37.07 (adamantyl CH₂), 36.52 (adamantyl quaternary), 35.16), 30.32, 29.04 (adamantyl CH), 26.39 (SiC(CH₃)₃), 18.90 (SiC(CH₃)₃), and -3.42 (Si(CH₃)₂); IR (film) 3320 (br, OH), 2930, 2905, 2850, 1325, 1265, 1255, 1165, 1130, 855, and 835 cm⁻¹; MS (DCI) m/e 571 (MH⁺), 570 (M⁺), 569 (M-H)⁺, 135 (C₁₀H₁₅⁺). Exact mass spectrum (FAB) Calcd for C₃₄H₄₅F₃O₂Si (M⁺): 570.3141. Found 570.3122.

Example 5: General Procedure for Synthesis of 6

A solution of alcohol **5** (1 equivalent) in anhydrous methylene chloride (0.1 - 0.2 M) was cooled to -10 to 0 °C under argon. The solution was treated with *t*-butyldimethylchlorosilane (1.3 equivalents) in one portion, followed by addition of 4-dimethylaminopyridine (0.05 equivalents). Triethylamine (1.4 equivalents) was added dropwise and the reaction mixture was stirred at 0 - 25 °C for 2-5 h. The mixture was then partitioned between diethyl ether and saturated ammonium chloride solution, and the organic layer was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification by column chromatography (20:1 ratio of silica gel/crude product; elution with hexanes to 2% to 4% ethyl acetate in hexanes) afforded the desired product.

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-3-phenyl-2-propene (**6a**): scale = 2.62 mmol, yield = 96%; ¹H NMR (300 MHz, CDCl₃) δ 7.39 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.35 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.06-7.24 (m, 5 H, ArH), 6.95-6.98 (m, 2 H, ArH), 6.70 (t, $J = 2$ Hz, 1 H, C=CH), 4.37 (d, $J = 2$ Hz, 2 H, CH₂OSi), 0.92 (s, 9 H, SiC(CH₃)₃), and 0.07 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 139.87, 136.30, 131.58, 130.35, 130.14, 129.17, 128.01, 127.72, 126.78, 125.87, 122.52, 67.80 (CH₂O), 29.71 (SiC(CH₃)₃), 25.91 (SiC(CH₃)₃), and -5.34 (Si(CH₃)₂); IR (film) 2955,

2930, 2885, 2855, 1560, 1472, 1250, 1125, 1075, 1005, 880, 840, 780, 750, and 695 cm^{-1} ; MS (DCI) m/e 401/403 (MH^+ , 1:1).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-propene (6b): scale = 5.41 mmol, yield = 98%; ^1H NMR (300 MHz, CDCl_3) δ 7.42 (dt, J = 2, 8 Hz, 1 H, 2-ArH), 7.38 (t, J = 2 Hz, 1 H, 2-ArH), 7.09-7.24 (m, 3 H, ArH), 6.85 (d, J = 2 Hz, 1 H, 3-ArH), 6.83 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.63 (s, 1 H, C=CH), 4.38 (s, 2 H, CH_2OSi), 1.60 (br s, 4 H, CH_2CH_2), 1.20 (s, 6 H, 2 $\times$ CH_3), 0.98 (s, 6 H, 2 $\times$ CH_3), 0.95 (s, 9 H, $\text{Si}(\text{C}(\text{CH}_3)_3)$), and 0.07 (s, 6 H, $\text{Si}(\text{CH}_3)_2$).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propene (6c): scale = 2.3 mmol, yield = 97%; ^1H NMR (300 MHz, CDCl_3) δ 7.61 (d, J = 6 Hz, 2 H, ArH), 7.37-7.60 (m, 4 H, ArH), 7.08-7.15 (m, 2 H, ArH), 6.83-6.87 (m, 2 H, ArH and C=CH), 4.22 (d, J = 1 Hz, 2 H, CH_2OSi), 1.73 (s, 4 H, CH_2CH_2), 1.27-1.30 (m, 12 H, 4 $\times$ CH_3), 0.95 (s, 9 H, $\text{Si}(\text{C}(\text{CH}_3)_3)$), and 0.10 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 153.16, 144.42, 141.47, 139.34, 133.13, 131.68, 131.62, 130.71, 131.36, 130.08, 128.02, 126.44, 126.38, 126.10, 124.95, 124.58, 122.51, 67.86 (CH_2OSi), 35.07 (CH_2CH_2), 34.55, 34.53, 32.48 (4 $\times$ CH_3), 29.72, 25.95 ($\text{Si}(\text{C}(\text{CH}_3)_3)$), 18.46 ($\text{Si}(\text{C}(\text{CH}_3)_3)$) and -5.29 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2955, 2930, 2860, 1470, 1360, 1255, 1125, and 1110 cm^{-1} ; MS (DCI) m/e 563/561 (MH^+ , 1:1), 433/431 (MH^+ - OTBDMS, 1:1).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-3-(4-decyloxyphenyl)-2-propene (6d): scale = 5.70 mmol, yield = 97%; ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.41 (m, 2 H, 2-ArH), 7.16 (t, J = 8 Hz, 1 H, 2-ArH), 7.09 (dt, J = 2, 8 Hz, 1 H, 2-ArH), 6.88 (d, J = 8 Hz, 2 H, 3-ArH), 6.61-6.66 (m, 3 H, 2 $\times$ 3-ArH and C=CH), 4.34 (d, J = 1 Hz, 2 H, CH_2OSi), 3.85 (t, J = 7 Hz, 2 H, ArOCH_2), 1.71 (quintet, J = 7 Hz, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.20-1.42 (m, 14 H, 7 $\times$ CH_2), 0.91 (s, 9 H, $\text{Si}(\text{C}(\text{CH}_3)_3)$), 0.85 (t, J = 7 Hz, 3 H, CH_3) and 0.06 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 158.02, 141.74, 137.65, 131.69, 130.35, 130.19, 130.17, 128.62, 127.83, 125.61, 122.54, 114.00, 68.08 (CH_2OSi), 67.88 (ArOCH_2), 31.89, 29.72, 29.56, 29.38, 29.32, 29.23, 26.02, 25.91 ($\text{Si}(\text{C}(\text{CH}_3)_3)$), 22.69, 18.43 ($\text{Si}(\text{C}(\text{CH}_3)_3)$), 14.13, and -5.40 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2955, 2930, 2855, 1605, 1560, 1510, 1470, 1300, 1250,

1180, 1130, 1110, 1070, 1025, 1005, 885, 840, 780, and 695 cm^{-1} ; MS (DCI) m/e 559/561 (MH^+ , 1:1).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-3-(3,4-bisdecyloxyphenyl)-2-propene (6e): scale = 1.6 mmol, yield = 100%; ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.40 (m, 2 H, 2-ArH), 7.21 (t, J = 9 Hz, 1 H, 2-ArH), 7.11 (dt, J = 1, 9 Hz, 1 H, 2-ArH), 6.66 (d, J = 8 Hz, 1 H, 3-ArH), 6.59 (dd, J = 2, 9 Hz, 1 H, 3-ArH⁶), 6.58 (br s, 1 H, C=CH), 6.40 (d, J = 2 Hz, 1 H, 3-ArH), 4.34 (d, J = 2 Hz, 2 H, CH_2OSi), 3.90 (t, J = 7 Hz, 2 H, ArC^4OCH_2), 3.53 (t, J = 7 Hz, 2 H, ArC^3OCH_2), 1.75 (quint, J = 7 Hz, 2 H, $\text{ArC}^4\text{OCH}_2\text{CH}_2$), 1.61 (quint, J = 7 Hz, 2 H, $\text{ArC}^3\text{OCH}_2\text{CH}_2$), 1.11-1.40 (m, 28 H, 14 $\times$ CH_2), 0.83-0.92 (m, 6 H, 2 $\times$ CH_3), 0.91 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$), and 0.05 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 148.24 (3-ArC), 148.11 (3-ArC), 142.01, 137.80, 131.92, 130.19, 130.12, 129.07, 127.85, 125.86, 122.51, 113.90, 113.04, 69.09, 68.61, 68.16, 31.93, 31.91, 29.65, 29.60, 29.57, 29.37, 29.22, 29.05, 25.98, 25.91 ($\text{SiC}(\text{CH}_3)_3$), 22.69, 18.43 ($\text{SiC}(\text{CH}_3)_3$), 14.12, and -5.35 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2955, 2925, 2855, 1515, 1470, 1270, 1260, 1240, 1140, 1085, and 1070 cm^{-1} ; MS (FAB) m/e 717/715 (MH^+ , 1:1).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-5-phenyl-2-pentene (6f): scale = 1.57 mmol, yield = 98%; ^1H NMR (300 MHz, CDCl_3) δ 7.39 (dt, J = 2, 8 Hz, 1 H, 2-ArH), 7.07-7.27 (m, 7 H, 3 $\times$ 2-ArH and 4 $\times$ 5-ArH), 6.98 (dt, J = 2, 8 Hz, 1 H, 5-ArH), 5.75 (tt, J = 1.5, 7.5 Hz, 1 H, C=CH), 4.25 (d, J = 1.5 Hz, 2 H, CH_2OSi), 2.65 (t, J = 7.5 Hz, 2 H, ArCH_2), 2.26 (q, J = 7.5 Hz, 2 H, ArCH_2CH_2), 0.87 (s, 9 H, $\text{Si}(\text{C}(\text{CH}_3)_3)$), and 0.00 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 141.43, 141.01, 139.35, 131.47, 129.77, 129.42, 128.15, 127.29, 126.51, 125.72, 121.94, 67.09 (CH_2OSi), 35.82, 30.16, 25.77 ($\text{SiC}(\text{CH}_3)_3$), 18.27 ($\text{SiC}(\text{CH}_3)_3$), and -5.52 ($\text{Si}(\text{CH}_3)_2$); IR (film) 3085, 3060, 3025, 3030, 2955, 2930, 2895, 2855, 1590, 1560, 1495, 1470, 1460, 1455, 1360, 1255, 1125, 1090, 1070, 1050, 1005, 840, 815, 775, 750, 700, and 675 cm^{-1} ; MS (FAB) m/e 429/431 (M^+ , 1:1), 373/375 ($\text{M}^+ - t\text{-Bu}$).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentene (6g): scale = 2.4 mmol, yield = 94%; ^1H NMR (300 MHz, CDCl_3) δ 7.35 (ddd, J = 1, 2, 8 Hz, 1 H, 2-ArH), 7.23 (t, J = 2 Hz, 1 H, 2-ArH), 7.18 (d, J = 8 Hz, 1 H, 2-

ArH), 7.13 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.01 (d, $J = 2$ Hz, 1 H, 5-ArH), 6.84-6.91 (m, 2 H, 5-ArH), 5.77 (t, $J = 7$ Hz, 1 H, C=CH), 4.22 (d, $J = 1$ H, 2 H, CH₂OSi), 2.60 (t, $J = 7$ Hz, 2 H, ArCH₂), 2.25 (q, $J = 7$ Hz, 2 H, ArCH₂CH₂), 1.65 (s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 × CH₃), 1.23 (s, 6 H, 2 × CH₃), 0.87 (s, 9 H, SiC(CH₃)₃), and 0.00 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 144.58, 142.27, 141.22, 139.19, 138.43, 131.63, 129.84, 129.55, 127.44, 127.13, 126.45, 126.37, 125.80, 122.03, 67.27 (CH₂OSi), 35.70, 35.21, 35.14, 34.15, 33.94, 31.93, 31.87, 30.32, 25.91 (SiC(CH₃)₃), and 18.39 (SiC(CH₃)₃); IR (film) 2955, 2930, 2855 1470, 1460, 1125, 840, and 775 cm⁻¹; MS (DCI) m/e 539/541 (M-H)⁺, 1:1). Anal. Calcd for C₃₁H₄₅OSiBr: C, 68.74; H, 8.37. Found: C, 69.02; H, 8.34.

For (2Z),(4E)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-hexadiene (6h): scale = 3.20 mmol, yield = 92%; ¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, $J = 2$ Hz, 1 H, 2-ArH), 7.39-7.43 (m, 1 H, 2-ArH), 7.19-7.28 (m, 4 H, 2 × 2-ArH and 2 × 5-ArH), 7.09 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.80 (dt, $J = 1.5, 12$ Hz, 1 H, C=CH), 6.45 (br d, $J = 12$ Hz, 1 H, C=CH), 4.46 (d, $J = 1.5$ Hz, 2 H, CH₂OSi), 2.20 (d, $J = 1.5$ Hz, 3 H, C=CCH₃), 1.67 (br s, 4 H, CH₂CH₂), 1.24 (s, 12 H, 4 × CH₃), 0.93 (s, 9 H, Si(C(CH₃)₃), and 0.09 (s, 6 H, Si(CH₃)₂); IR (film) 2955, 2930, 2860, 1555, 1495, 1470, 1460, 1405, 1390, 1360, 1255, 1215, 1190, 1125, 1070, 1050, 1030, 885, 840, 780, 700, and 680 cm⁻¹; MS (DCI) m/e 552/554 (M⁺, 1:1), 421/423 (M⁺ - OSi[C(CH₃)₃](CH₃)₂).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentene (6i): scale = 4.36 mmol, yield = 87%; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.36 (m, 1 H, 2-ArH), 7.18 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.12 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.07 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.88 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 6.63 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.56 (d, $J = 1$ Hz, 1 H, 3-ArH), 5.75 (t, $J = 8$ Hz, 1 H, C=CH), 4.20 (br s, 2 H, CH₂OSi), 3.76 (s, 3 H, OCH₃), 2.60 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.24 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.05 (br s, 9 H, adamantyl), 1.74 (br s, 6 H, adamantyl), 0.86 (s, 9 H, SiC(CH₃)₃), and -0.10 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 158.66, 141.72, 140.19, 139.33, 136.04, 131.63, 129.85, 129.54, 127.45, 126.88, 126.24, 122.00, 120.38, 112.03, 67.23 (CH₂OSi), 54.89 (OCH₃), 37.16, 36.64, 35.63, 30.22, 29.12, 25.89

(SiC(CH₃)₃), 18.38 (SiC(CH₃)₃), and -5.39 (Si(CH₃)₂); IR (film) 2950, 2930, 2905, 2850, 1470, 1460, 1455, 1410, 1250, and 1125 cm⁻¹; MS (DCI) *m/e* 595 (MH⁺), 465/463 (MH⁺ - OTBDMS, 1:1).

5 For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentene (6j): scale = 6.9 mmol, yield = 80%, ca. 3:1 mixture of *Z*:*E* isomers. This compound was prepared using a modified procedure of Shreet, B. et al, U.S. Patent 4,717,720, 1/1988. ¹H NMR (300 MHz, CDCl₃) δ (Z-isomer) 7.36 (dt, *J* =
10 8, 2 Hz, 1 H, 2-ArH), 7.24 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.15 (t, *J* = 8 Hz, 1 H, 2-ArH), 6.92-6.95 (m, 2 H, 2-ArH and 5-ArH), 6.77 (dd, *J* = 8, 2 Hz, 1 H, 5-ArH), 6.64 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.78 (t, *J* = 7 Hz, 1 H, C=CH), 4.22 (d, *J* = 1 H, 2 H, CH₂OSi), 2.58 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.22 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.05 (m, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl), 1.01 (s, 9
15 H, SiC(CH₃)₃), 0.88 (s, 9 H, SiC(CH₃)₃), 0.31 (s, 6 H, Si(CH₃)₂), and 0.00 (s, 6 H, Si(CH₃)₂); (E-isomer) 7.55 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.31 (m, 2 H, 2-ArH), 7.14 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.01 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.86 (dd, *J* = 8, 2 Hz, 1 H, 5-ArH), 6.72 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.82 (t, *J* = 7 Hz, 1 H, C=CH), 4.34 (s, 2 H, CH₂OSi), 2.68 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.52
20 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 1.12 (s, 9 H, SiC(CH₃)₃), 0.82 (s, 9 H, SiC(CH₃)₃), 0.32 (s, 6 H, Si(CH₃)₂), and 0.01 (s, 6 H, Si(CH₃)₂).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-bromophenyl)-3-(3,4-bis(pentyloxy)phenyl)-2-propene (6k): scale = 1.52 mmol, yield = 90%; ¹H
25 NMR (300 MHz, CDCl₃) δ 7.37-7.41 (m, 2 H, 2-ArH), 7.10-7.24 (m, 2 H, 2-ArH), 6.67 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.59 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.58 (t, *J* = 1.5 Hz, 1 H, C=CH), 6.41 (d, *J* = 2 Hz, 1 H, 3-ArH), 4.35 (d, *J* = 1.5 Hz, 2 H, CH₂OSi), 3.91 (t, *J* = 6.5 Hz, 2 H, 3-ArOCH₂), 3.53 (t, *J* = 6.5 Hz, 2 H, 3-ArOCH₂), 1.71-1.78 (m, 2 H, 3-ArOCH₂CH₂), 1.57-1.65 (m, 2 H, 3-ArOCH₂CH₂), 1.27-1.41 (m, 8 H), 0.86-0.93 (m, 15 H, 2 × CH₃ and
30 Si(C(CH₃)₃) and 0.06 (Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 148.22, 148.09, 142.00, 137.80, 131.91, 130.21, 130.12, 129.07, 127.86, 125.85, 122.51, 113.86, 113.00, 69.06 (3-ArOCH₂), 68.57 (3-ArOCH₂), 68.15 (CH₂OSi), 29.70, 28.90, 28.71, 28.05, 25.91 (SiC(CH₃)₃), 22.45, 22.40, 18.43 (SiC(CH₃)₃),
35 14.06, 14.03, and -5.35 (Si(CH₃)₂); IR (film) 2955, 2930, 2860, 1590, 1560, 1515, 1470, 1430, 1390, 1270, 1240, 1170, 1140, 1085, 1070, 1050, 1030, 1005,

890, 840, 810, 780, and 700 cm^{-1} ; MS (DCI) m/e 575/577 (MH^+ , 1:1), 443/445 (M^+ - $\text{OSi}[\text{C}(\text{CH}_3)_3](\text{CH}_3)_2$).

Example 6: General Procedure for Synthesis of 7

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Procedure A: A solution of aryl bromide **6** (1 equivalent) in anhydrous tetrahydrofuran (0.1 - 0.15 M) was cooled to -78°C under argon and treated with *t*-butyllithium solution (1.4-1.8 M in pentane, 2.1 equivalents). The pale yellow reaction mixture was stirred at -78°C for 30 min, and then added via cannula to a pre-cooled solution of ethyl chloroformate (1.5 - 3 equivalents) in anhydrous THF at -78°C . The resulting mixture was allowed to warm to room temperature, and then was poured into a separatory funnel containing diethyl ether and saturated ammonium chloride solution. The layers were agitated and separated, and the organic phase was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification by column chromatography (20:1 ratio of silica gel/crude product; elution with 1% to 2% ethyl acetate in hexanes) gave the desired product.

20 Procedure B: A solution of aryl bromide **6** (1 equivalent) in anhydrous tetrahydrofuran (0.1 M) was cooled to -78°C under argon and treated with *t*-butyllithium solution (1.4-1.8 M in pentane, 2 equivalents). The pale yellow reaction mixture was stirred at -78°C for 30 min, and then treated with anhydrous dimethylformamide (2 equivalents). The resulting mixture was allowed to warm to room temperature, and then was poured into a separatory funnel containing diethyl ether and saturated ammonium chloride solution. The layers were agitated and separated, and the organic phase was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude aldehyde (1 equivalent) was dissolved in methanol (0.1 M solution) and treated with sodium cyanide (5.4 equivalents), acetic acid (a few drops), and manganese dioxide (5:1 weight ratio of MnO_2 /crude aldehyde). The mixture was stirred at room temperature for 2-14 h and then diluted with methylene chloride and filtered through a one-inch pad of Celite. The filtrate was washed with water and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and

concentrated. Purification by column chromatography (20-40:1 ratio of silica gel/crude product; elution with 1% to 2% ethyl acetate in hexanes) gave the desired product.

5 For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-3-phenyl-2-propene (7a): via procedure A, scale = 2.48 mmol, yield = 46%; ¹H NMR (300 MHz, CDCl₃) δ 7.93-7.96 (m, 1 H, 2-ArH), 7.90 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.30-7.36 (m, 2 H, 2-ArH), 7.04-7.10 (m, 3 H, 3-ArH), 6.92-6.95 (m, 2 H, 3-ArH), 6.73 (t, *J* = 2 Hz, 1 H, C=CH), 4.41 (d, *J* = 2 Hz, 2 H, CH₂OSi), 4.34 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.35 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 0.91 (s, 9 H, Si(C(CH₃)₃), and 0.07 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 166.50 (C=O), 140.44, 139.41, 136.46, 133.73, 130.84, 129.70, 129.17, 128.62, 128.49, 127.97, 126.66, 125.81, 67.89 (CH₂OSi), 61.02 (CO₂CH₂), 25.91 (SiC(CH₃)₃), 18.42 (SiC(CH₃)₃), 14.30 (CO₂CH₂CH₃) and -5.34 (Si(CH₃)₂); IR (film) 2955, 2930, 2895, 2855, 1720 (C=O), 1470, 1465, 1370, 1265, 1195, 1125, 1110, 1080, 1020, 880, 840, 780, and 695 cm⁻¹; MS (FAB) *m/e* 395 (M-H⁺).

20 For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-propene (7b): via procedure A, scale = 4.77 mmol, yield = 73 %; ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.97 (m, 2 H, 2-ArH), 7.36-7.38 (m, 2 H, ArH), 7.05 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.75-6.83 (m, 2 H, 3-ArH), 6.64 (br s, 1 H, C=CH), 4.42 (d, *J* = 1.5 Hz, 2 H, CH₂OSi), 4.33 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.54 (br s, 4 H, CH₂CH₂), 1.34 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.19 (s, 3 H, CH₃), 1.18 (s, 3 H, CH₃), 0.98 (s, 6 H, 2 × CH₃), 0.95 (s, 9 H, Si(C(CH₃)₃), and 0.06 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 166.54 (C=O), 144.20, 143.57, 140.00, 139.30, 133.79, 133.26, 130.87, 129.94, 128.67, 128.34, 127.30, 126.67, 126.16, 126.10, 68.28 (CH₂OSi), 60.94 (CO₂CH₂), 34.96, 33.98, 33.86, 31.67, 31.42, 27.93, 25.91 (SiC(CH₃)₃), 18.42 (SiC(CH₃)₃), 14.31 (CO₂CH₂CH₃) and -5.33 (Si(CH₃)₂); IR (film) 2960, 2930, 2860, 1720 (C=O), 1470, 1460, 1280, 1260, 1195, 840, and 775 cm⁻¹; MS (DCI) *m/e* 506 (M⁺).

35 For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propene (7c): via procedure A, scale = 2.21 mmol, yield = 43%; ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.98 (m, 2 H, ArH), 7.58 (d, *J* = 9 Hz, 2 H, ArH), 7.45 (s, 1 H,

ArH), 7.27-7.36 (m, 3 H, ArH), 6.88 (s, 1 H, C=CH), 6.80 (dd, $J = 2, 9$ Hz, 1 H, ArH), 4.47 (d, $J = 1$ Hz, 2 H, CH₂OSi), 4.34 (q, $J = 7$ Hz, 2 H, CO₂CH₂), 1.72 (s, 4 H, CH₂CH₂), 1.29-1.38 (m, 15 H, 4 × CH₃ and CO₂CH₂CH₃), 0.94 (s, 9 H, SiC(CH₃)₃), and 0.10 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 166.58 (C=O), 144.38, 144.32, 139.95, 139.51, 134.07, 133.29, 131.66, 130.80, 130.64, 129.67, 128.56, 128.52, 127.93, 126.42, 126.31, 126.18, 124.92, 124.55, 67.95 (CH₂OSi), 61.02 (CO₂CH₂), 35.05, 34.51, 32.46, 25.95 (SiC(CH₃)₃), 18.45 (SiC(CH₃)₃), and 14.28; IR (film) 2960, 2930, 2860, 1720 (C=O), 1470, 1460, 1365, 1265, 1190, 1125, and 1110 cm⁻¹; MS (DCI) m/e 556 (MH⁺), 425 (MH⁺ - OTBDMS).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carbomethoxyphenyl)-3-(4-decyloxyphenyl)-2-propene (7d): scale = 2.11 mmol, yield = 89%; ¹H NMR (300 MHz, CDCl₃) δ 7.92-8.01 (m, 2 H, 2-ArH), 7.34-7.44 (m, 2 H, 2-ArH), 6.87 (d, $J = 8$ Hz, 2 H, 3-ArH), 6.60-6.67 (m, 3 H, 2 × 3-ArH and C=CH), 4.41 (d, $J = 1$ Hz, 2 H, CH₂OSi), 3.92 (s, 3 H, CO₂CH₃), 3.86 (t, $J = 7$ Hz, 2 H, ArOCH₂), 1.72 (quintet, $J = 7$ Hz, 2 H, ArOCH₂CH₂), 1.20-1.42 (m, 14 H, 7 × CH₂), 0.92 (s, 9 H, SiC(CH₃)₃), 0.85 (t, $J = 7$ Hz, 3 H, CH₃) and 0.08 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 166.92 (C=O), 157.78, 139.75, 138.05, 134.33, 133.89, 131.38, 130.84, 130.33, 130.20, 129.71, 128.56, 128.26, 125.40, 113.95, 68.01 (CH₂OSi), 67.72 (ArOCH₂), 52.00 (CO₂CH₃), 31.75, 29.42, 29.24, 29.18, 29.09, 25.88, 25.78 (SiC(CH₃)₃), 25.58, 22.55, 18.29 (SiC(CH₃)₃), 14.00, and -4.72 (Si(CH₃)₂); IR (film) 2950, 2930, 2855, 1730 (C=O), 1605, 1510, 1470, 1440, 1390, 1360, 1290, 1250, 1200, 1175, 1110, 1005, 985, 840, 780, 755, 730, and 695 cm⁻¹; MS (DCI) m/e 538 (M⁺).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-3-(3,4-bisdecyloxyphenyl)-2-propene (7e): via procedure A, scale = 1.29 mmol, yield = 44%; ¹H NMR (300 MHz, CDCl₃) δ 7.92-7.96 (m, 2 H, 2-ArH), 7.36-7.37 (m, 2 H, 2-ArH), 6.63 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.57 (br s, 1 H, C=CH), 6.55 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.38 (d, $J = 2$ Hz, 1 H, 3-ArH), 4.39 (d, $J = 2$ Hz, 2 H, CH₂OSi), 4.34 (q, $J = 6$ Hz, 2 H, CO₂CH₂), 3.89 (t, $J = 7$ Hz, 2 H, ArC⁴OCH₂), 3.48 (t, $J = 7$ Hz, 2 H, ArC³OCH₂), 1.73 (quint, $J = 7$ Hz, 2 H, ArC⁴OCH₂CH₂), 1.54-1.59 (m, 2 H, ArC³OCH₂CH₂), 1.36 (t, $J = 6$ Hz, 3 H, CO₂CH₂CH₃), 1.19-1.38 (m, 28 H, 14 × CH₂), 0.83-0.90 (m, 15 H, 2 × CH₃ and SiC(CH₃)₃) and 0.06 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 166.42 (C=O), 148.15 (3-ArC), 148.00 (3-ArC), 140.01, 138.39,

133.93, 130.90, 129.97, 129.22, 128.63, 128.30, 125.81, 122.40, 114.06, 112.99, 69.04, 68.57, 68.25, 61.00 (CH₂OSi), 31.90, 29.60, 29.40, 29.36, 29.22, 29.01, 25.98, 25.91 (SiC(CH₃)₃), 25.85, 24.14, 24.03, 22.68, 18.42 (SiC(CH₃)₃), 14.30, 14.12, and -5.34 (Si(CH₃)₂); IR (film) 2955, 2925, 2855, 1720 (C=O), 1515,
5 1470, 1265, 1240, 1140, 1085, and 1020 cm⁻¹; MS (FAB) *m/e* 709 (MH⁺).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-5-phenyl-2-pentene (7f): via procedure A, scale = 1.51 mmol, yield = 52%;
¹H NMR (300 MHz, CDCl₃) δ 7.94 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.82 (t, *J* =
10 2 Hz, 1 H, 2-ArH), 7.34 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.08-7.26 (m, 6 H, 1 × 2-ArH and 5 × 5-ArH), 5.80 (tt, *J* = 1.5, 7.5 Hz, 1 H, C=CH), 4.38 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 4.28 (d, *J* = 1.5 Hz, 2 H, CH₂OSi), 2.67 (t, *J* = 7.5 Hz, 2 H, ArCH₂), 2.26 (q, *J* = 7.5 Hz, 2 H, ArCH₂CH₂), 1.40 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 0.88 (s, 9 H, Si(C(CH₃)₃), and 0.02 (s, 6 H, Si(CH₃)₂); ¹³C
15 NMR (75 MHz, CDCl₃) δ 166.50 (C=O), 141.53, 139.75, 139.09, 133.17, 130.21, 129.60, 128.36, 128.10, 127.95, 126.51, 125.66, 67.21 (CH₂OSi), 60.83 (CO₂CH₂), 35.87, 30.17, 25.78 (SiC(CH₃)₃), 18.26 (SiC(CH₃)₃), 14.22 (CO₂CH₂CH₃), and -5.52 (Si(CH₃)₂); IR (film) 3085, 3065, 3030, 2955, 2930, 2895, 2855, 1720 (C=O), 1470, 1460, 1455, 1365, 1270, 1170, 1125, 1110, 1085,
20 1050, 1030, 840, 815, 775, 755, 700, and 675 cm⁻¹; MS (DCI) *m/e* 425 (MH⁺), 293 (M⁺ - OSi[(C(CH₃)₃)](CH₃)₂).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carbomethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentene (7g):
25 scale = 1.40 mmol, yield = 100%; ¹H NMR (300 MHz, CDCl₃) δ 7.92 (dt, *J* = 1, 8 Hz, 1 H, 2-ArH), 7.85 (t, *J* = 1 Hz, 1 H, 2-ArH), 7.33 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.12-7.17 (m, 2 H, 2-ArH and 5-ArH), 7.01 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.84 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 5.81 (br t, *J* = 7 Hz, 1 H, C=CH), 4.36 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 4.28 (d, *J* = 1 Hz, 2 H, CH₂OSi), 2.60 (t, *J* =
30 8 Hz, 2 H, ArCH₂), 2.24 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (s, 4 H, CH₂CH₂), 1.38 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.24 (s, 6 H, 2 × CH₃), 1.22 (s, 6 H, 2 × CH₃), 0.87 (s, 9 H, SiC(CH₃)₃), and 0.00 (s, 6 H, Si(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃) δ 166.64 (C=O), 144.56, 142.23, 139.63, 139.28, 138.54, 133.35, 130.28, 129.75, 128.04, 127.06, 126.40, 126.33, 125.76, 67.39
35 (CH₂OSi), 60.94 (CO₂CH₂), 35.74, 35.20, 35.13, 34.13, 33.92, 31.91, 31.85, 30.34, 25.91 (SiC(CH₃)₃), 18.39 (SiC(CH₃)₃), 14.35 (CO₂CH₂CH₃), and -5.36 (Si(CH₃)₂); IR (film) 2955, 2930, 2860, 1720 (C=O), 1270, 1120, 1110, and

840 cm^{-1} ; MS (FAB) m/e 534 (M^+), 533 (M-H^+). Anal. Calcd for $\text{C}_{34}\text{H}_{50}\text{O}_3\text{Si}$: C, 76.35; H, 9.42. Found: C, 76.78; H, 9.40.

For (2Z),(4E)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-hexadiene (7h): via procedure A, scale = 2.04 mmol, yield = 34%; ^1H NMR (300 MHz, CDCl_3) δ 7.95 (d, $J = 2$ Hz, 1 H, 2-ArH), 7.94 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.36-7.45 (m, 2 H, 2-ArH), 7.22 (d, $J = 2$ Hz, 1 H, 5-ArH), 7.15 (d, $J = 8$ Hz, 1 H, 5-ArH), 7.04 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.80 (br d, $J = 12$ Hz, 1 H, C=CH), 6.37 (br d, $J = 12$ Hz, 1 H, C=CH), 4.46 (s, 2 H, CH_2OSi), 4.35 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 2.20 (s, 3 H, C=CCH₃), 1.62 (br s, 4 H, CH_2CH_2), 1.36 (t, $J = 7$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.20 (s, 6 H, 2 $\times$ CH₃), 1.19 (s, 6 H, 2 $\times$ CH₃), 0.91 (s, 9 H, $\text{Si}(\text{C}(\text{CH}_3)_3)$), and 0.07 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.56 (C=O), 144.48, 143.88, 140.48, 140.42, 139.07, 137.49, 133.76, 130.42, 129.92, 128.35, 128.11, 126.31, 123.77, 123.06, 123.00, 122.60, 67.14 (CH_2OSi), 60.98 (CO_2CH_2), 35.12, 35.00, 34.24, 34.04, 31.74, 25.90 ($\text{SiC}(\text{CH}_3)_3$), 18.36 ($\text{SiC}(\text{CH}_3)_3$), 16.00 (C=CCH₃), 14.32 ($\text{CO}_2\text{CH}_2\text{CH}_3$), and -5.32 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2960, 2930, 2860, 1720 (C=O), 1470, 1460, 1390, 1365, 1260, 1215, 1110, 1085, 840, 780, and 755 cm^{-1} ; MS (DCI) m/e 546 (M^+), 415 ($\text{M}^+ - \text{OSi}[(\text{C}(\text{CH}_3)_3](\text{CH}_3)_2$).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carbomethoxyphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentene (7i): via procedure B, scale = 3.81 mmol, yield = 25%; ^1H NMR (300 MHz, CDCl_3) δ 7.91 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.83 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.31 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.14 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.04 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.63 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.55 (d, $J = 2$ Hz, 1 H, 3-ArH), 5.79 (br t, $J = 8$ Hz, 1 H, C=CH), 4.26 (d, $J = 2$ Hz, 2 H, CH_2OSi), 3.90 (s, 3 H, CO_2CH_3), 3.73 (s, 3 H, OCH_3), 2.60 (t, $J = 8$ Hz, 2 H, ArCH_2), 2.24 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), 2.04 (br s, 9 H, adamantyl), 1.74 (br s, 6 H, adamantyl), 0.86 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$), and -0.01 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 137.11 (C=O), 158.64, 140.29, 139.67, 139.30, 136.01, 133.50, 129.92, 129.78, 128.08, 126.87, 126.20, 120.34, 112.00, 67.32 (CH_2OSi), 54.86 (OCH_3), 52.09 (CO_2CH_3), 40.67, 37.15, 36.62, 35.65, 30.20, 29.11, 25.88 ($\text{SiC}(\text{CH}_3)_3$), and 18.38 ($\text{SiC}(\text{CH}_3)_3$); IR (film) 2950, 2930, 2905, 2850, 1725 (C=O), 1460, 1455, 1440, 1410, 1280, 1260, 1160, and 1120 cm^{-1} ; MS (DCI)

m/e 575 (MH^+), 574 (M^+), 573 ($M - H^+$), and 443 ($MH^+ - OSi[(C(CH_3)_3)(CH_3)_2]$).

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carboethoxyphenyl)-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentene (**7j**): via procedure A, scale = 3.6 mmol. Column chromatography on silica gel afforded 1.6 g of a ca. 1:1 mixture of **7j** (3:1, Z:E) and 1-(*t*-butyldimethylsiloxy)-2-phenyl-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentene (3:1, Z:E). Separate fractions were pooled and concentrated to give 0.800 g (36%) of the latter compound, 1-(*t*-butyldimethylsiloxy)-2-phenyl-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentene (3:1, Z:E): 1H NMR (300 MHz, $CDCl_3$) δ (Z-isomer) 7.20-7.32 (m, 3 H, 2-ArH), 7.04-7.07 (m, 2 H, 2-ArH), 6.94 (d, $J = 2$ Hz, 1 H, 5-ArH), 6.77 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.66 (d, $J = 8$ Hz, 1 H, 5-ArH), 5.77 (t, $J = 7$ Hz, 1 H, C=CH), 4.28 (d, $J = 1$ H, 2 H, CH_2OSi), 2.58 (t, $J = 7$ Hz, 2 H, $ArCH_2$), 2.26 (q, $J = 7$ Hz, 2 H, $ArCH_2CH_2$), 2.08 (m, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl), 1.03 (s, 9 H, $SiC(CH_3)_3$), 0.89 (s, 9 H, $SiC(CH_3)_3$), 0.32 (s, 6 H, $Si(CH_3)_2$), and 0.02 (s, 6 H, $Si(CH_3)_2$); (E-isomer, partially obscured) 7.40 (m, 1 H, 2-ArH), 6.90 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.72 (d, $J = 8$ Hz, 1 H, 5-ArH), 5.88 (t, $J = 7$ Hz, 1 H, C=CH), 4.41 (s, 2 H, CH_2OSi), 2.69 (t, $J = 7$ Hz, 2 H, $ArCH_2$), 1.04 (s, 9 H, $SiC(CH_3)_3$), 0.84 (s, 9 H, $SiC(CH_3)_3$), 0.34 (s, 6 H, $Si(CH_3)_2$), and 0.02 (s, 6 H, $Si(CH_3)_2$); IR (film) 2955, 2930, 2905, 2855, 1490, 1255, and 840 cm^{-1} ; MS (FAB) m/e 617 (MH^+), 616 (M^+). Anal. Calcd for $C_{39}H_{60}O_2Si_2$: C, 75.91; H, 9.80. Found: C, 75.62; H, 9.77.

For (Z)-1-(*t*-Butyldimethylsiloxy)-2-(3-carbomethoxyphenyl)-3-(3,4-bis(pentyloxy)phenyl)-2-propene (**7k**): via procedure B, scale = 1.33 mmol, yield = 84%; 1H NMR (300 MHz, $CDCl_3$) δ 7.91-7.95 (m, 2 H, 2-ArH), 7.36-7.38 (m, 2 H, 2-ArH), 6.63 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.62 (br s, $J = 1.5$ Hz, 1 H, C=CH), 6.56 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.37 (d, $J = 2$ Hz, 1 H, 3-ArH), 4.35 (d, $J = 1.5$ Hz, 2 H, CH_2OSi), 3.89 (t, $J = 6.5$ Hz, 2 H, $ArOCH_2$), 3.88 (s, 3 H, CO_2CH_3), 3.47 (t, $J = 6.5$ Hz, 2 H, $ArOCH_2$), 1.70-1.79 (m, 2 H, $ArOCH_2CH_2$), 1.55-1.60 (m, 2 H, $ArOCH_2CH_2$), 1.24-1.41 (m, 8 H, 2 $\times$ CH_2), 0.85-0.91 (m, 15 H, 2 $\times$ CH_3 and $Si(C(CH_3)_3)$), and 0.05 ($Si(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.89 (C=O), 148.15, 148.00, 140.09, 138.34, 134.08, 130.57, 130.01, 129.20, 128.69, 128.33, 125.81, 122.42,

114.03, 112.97, 69.01 (ArOCH₂), 68.53 (CH₂OSi), 68.19 (ArOCH₂), 52.11 (CO₂CH₃), 28.89, 28.66, 28.15, 28.01, 25.91 (SiC(CH₃)₃), 22.44, 22.36, 18.42 (SiC(CH₃)₃), 14.02 and -5.34 (Si(CH₃)₂); IR (film) 2955, 2930, 2860, 1725 (C=O), 1515, 1470, 1435, 1265, 1205, 1170, 1140, 1080, 1050, 1005, 840, and 780 cm⁻¹; MS (DCI) *m/e* 554 (MH⁺), 423 (M⁺ - OSi[C(CH₃)₃](CH₃)₂).

Example 7: General Procedure for Synthesis of 8

Ester Z was dissolved in a mixture of acetic acid/tetrahydrofuran/water (3:2:1, 0.03 M) and stirred at room temperature for 12-40 h. The mixture was then concentrated in vacuo and the residue was purified by column chromatography (20:1 to 30:1 ratio of silica gel/crude product; elution with 10% to 20% ethyl acetate in hexanes).

For (Z)-2-(3-Carboethoxyphenyl)-3-phenyl-2-propenol (8a): scale = 1.09 mmol, yield = 94%; ¹H NMR (300 MHz, CDCl₃) δ 7.93-7.98 (m, 2 H, 2-ArH), 7.34-7.38 (m, 2 H, 2-ArH), 7.07-7.10 (m, 3 H, 3-ArH), 6.93-6.98 (m, 2 H, 3-ArH), 6.73 (s, 1 H, C=CH), 4.47 (d, *J* = 5 Hz, 2 H, CH₂OH), 4.34 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.73 (t, *J* = 5 Hz, 1 H, OH, exch), and 1.35 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.42 (C=O), 140.45, 138.90, 136.03, 133.74, 131.06, 129.55, 129.22, 128.83, 128.73, 128.07, 127.42, 127.04, 68.37 (CH₂OH), 61.09 (CO₂CH₂), and 14.30 (CO₂CH₂CH₃); IR (film) 3400 (br, OH), 2980, 1720, 1370, 1265, 1195, 1110, 1090, 1022, 760, and 700 cm⁻¹; MS (DCI) *m/e* 282 (MH⁺).

For (Z)-2-(3-Carboethoxyphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-propenol (8b): scale = 3.35 mmol, yield = 91%; ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.99 (m, 2 H, 2-ArH), 7.37-7.44 (m, 2 H, ArH), 7.05 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.86 (d, *J* = 2 Hz, 1 H, 3-ArH), 6.76 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.65 (s, 1 H, C=CH), 4.45 (s, 2 H, CH₂OH), 4.33 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 1.51-1.59 (m, 5 H, CH₂CH₂ and OH, exch), 1.32 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.17 (s, 6 H, 2 x CH₃), and 0.93 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.42 (C=O), 144.35, 144.05, 139.47, 139.26, 133.71, 132.83, 131.13, 129.76, 128.92, 128.58, 127.76, 127.47, 126.63, 126.28, 68.78 (CH₂OH), 61.02 (CO₂CH₂), 34.92, 34.03, 33.88, 31.65, 31.44, 27.92, and 14.32 (CO₂CH₂CH₃); IR (film) 3100-3400 (br, OH),

2960, 2925, 2860, 1720 (C=O), 1460, 1365, 1285, 1265, 1200, 1110, 1085, 755, and 750 cm^{-1} ; MS (DCI) m/e 392 (M^+), 375 ($\text{M}^+ - \text{OH}$).

For (Z)-2-(3-Carboethoxyphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propenol (8c): scale = 0.95 mmol, yield = 97%; ^1H NMR (300 MHz, CDCl_3) δ 7.95-7.99 (m, 2 H, ArH), 7.59 (d, J = 12 Hz, 2 H, ArH), 7.47 (s, 1 H, ArH), 7.29-7.40 (m, 3 H, ArH), 6.88 (br s, 1 H, C=CH), 6.82 (dd, J = 1, 9 Hz, 1 H, ArH), 4.53 (dd, J = 1, 6 Hz, 2 H, CH_2OH), 4.34 (q, J = 7 Hz, 2 H, CO_2CH_2), 1.72 (s, 4 H, CH_2CH_2), and 1.31-1.36 (m, 15 H, 4 $\times$ CH_3 and $\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.47 (C=O), 144.62, 144.55, 139.96, 138.98, 134.08, 132.84, 131.64, 131.08, 130.81, 129.53, 128.76, 128.22, 128.08, 126.58, 125.98, 124.98, 124.56, 68.52 (CH_2OH), 61.07 (CO_2CH_2), 35.04 (CH_2CH_2), 34.56, 34.52, 32.46 (4 $\times$ CH_3), and 14.27 ($\text{CO}_2\text{CH}_2\text{CH}_3$); IR (KBr) 3400 (br, OH), 2960, 2930, 2860, 1720 (C=O), 1465, 1385, 1365, 1270, 1210, 1190, 1110, 1085, and 1020 cm^{-1} ; MS (DCI) m/e 443 (MH^+), 425 ($\text{MH}^+ - \text{OH}$).

For (Z)-2-(3-Carboethoxyphenyl)-3-(4-decyloxyphenyl)-2-propenol (8d): scale = 1.86 mmol, yield = 94%; ^1H NMR (300 MHz, CDCl_3) δ 7.96-8.00 (m, 2 H, 2-ArH), 7.34-7.43 (m, 2 H, 2-ArH), 6.88 (d, J = 8 Hz, 2 H, 3-ArH), 6.67 (s, 1 H, C=CH), 6.63 (d, J = 8 Hz, 2 H, 3-ArH), 4.46 (br s, 2 H, CH_2OH), 3.90 (s, 3 H, CO_2CH_3), 3.86 (t, J = 7 Hz, 2 H, ArOCH_2), 1.72 (quintet, J = 7 Hz, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.20-1.45 (m, 14 H, 7 $\times$ CH_2), and 0.87 (t, J = 7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 166.96 (C=O), 158.22, 139.39, 138.19, 133.98, 130.78, 130.45, 129.69, 128.92, 128.64, 128.25, 127.39, 114.05, 68.74 (CH_2OH), 67.88 (ArOCH_2), 52.19 (CO_2CH_3), 31.89, 29.56, 29.37, 29.31, 29.21, 26.01, 22.69, and 14.14; IR (film) 3400 (br, OH), 2925, 2855, 1725 (C=O), 1605, 1510, 1470, 1440, 1390, 1290, 1270, 1250, 1200, 1180, 1110, 1090, 1020, 980, 885, 825, 755, 710, and 700 cm^{-1} ; MS (DCI) m/e 424 (M^+), 407 ($\text{M}^+ - \text{OH}$).

For (Z)-2-(3-Carboethoxyphenyl)-3-(3,4-bisdecyloxyphenyl)-2-propenol (8e): scale = 0.53 mmol, yield = 96%; ^1H NMR (300 MHz, CDCl_3) δ 7.94-7.97 (m, 2 H, 2-ArH), 7.33-7.43 (m, 2 H, 2-ArH), 6.63 (d, J = 8 Hz, 1 H, 3-ArH), 6.62 (s, 1 H, C=CH), 6.56 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.40 (d, J = 2 Hz, 1 H, 3-ArH), 4.44 (d, J = 6 Hz, 2 H, CH_2OH), 4.34 (q, J = 7 Hz, 2 H, CO_2CH_2), 3.89 (t, J = 7 Hz, 2 H, ArC^4OCH_2), 3.49 (t, J = 7 Hz, 2 H,

ArC³OCH₂), 1.74 (quint, *J* = 7 Hz, 2 H, ArC⁴OCH₂CH₂), 1.55-1.61 (m, 2 H, ArC³OCH₂CH₂), 1.36 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.21-1.38 (m, 28 H, 14 × CH₂), and 0.83-0.89 (m, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.32 (C=O), 148.32 (3-ArC), 148.20 (3-ArC), 139.50, 138.32, 133.87, 131.17, 129.79, 128.87, 128.68, 128.54, 127.54, 122.53, 114.06, 112.93, 69.01, 68.76, 68.61, 61.07 (CO₂CH₂), 31.91, 29.60, 29.34, 29.19, 28.99, 25.97, 25.85, 22.68, 14.30, and 14.12; IR (KBr) 3500 (br, OH), 2960, 2920, 2850, 1720 (C=O), 1705 (C=O), 1515, 1295, 1265, 1235, and 1140 cm⁻¹; MS (FAB) *m/e* 595 (MH⁺).

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For (Z)-2-(3-Carboethoxyphenyl)-5-phenyl-2-pentenol (8f): scale = 0.78 mmol, yield = 99%; ¹H NMR (300 MHz, CDCl₃) δ 7.95 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.83 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.39 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.07-7.27 (m, 6 H, 1 × 2-ArH and 5 × 5-ArH), 5.81 (t, *J* = 7.5 Hz, 1 H, C=CH), 4.37 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 4.28 (s, 2 H, CH₂OH), 2.67 (t, *J* = 7.5 Hz, 2 H, ArCH₂), 2.31 (q, *J* = 7.5 Hz, 2 H, ArCH₂CH₂), and 1.39 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.40 (C=O), 141.27, 140.12, 138.53, 133.01, 130.48, 129.43, 128.57, 128.31, 128.24, 128.17, 125.78, 67.73 (CH₂OH), 60.93 (CO₂CH₂), 35.73, 30.26, and 14.22 (CO₂CH₂CH₃); IR (film) 3420 (br, OH), 3085, 3060, 3025, 2980, 2930, 2860, 1720 (C=O), 1495, 1455, 1390, 1370, 1280, 1225, 1170, 1110, 1085, 1020, 1000, 755, 700, and 675 cm⁻¹; MS (DCI) *m/e* 311 (MH⁺), 293 (M⁺ - OH).

For (Z)-2-(3-Carboethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol (8g): scale = 1.3 mmol, yield = 84%; ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.88 (s, 1 H, 2-ArH), 7.36 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.15-7.28 (m, 2 H, 2-ArH and 5-ArH), 7.00 (s, 1 H, 5-ArH), 6.84 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.83 (t, *J* = 7 Hz, 1 H, C=CH), 4.32-4.40 (m, 4 H, CO₂CH₂CH₃ and CH₂OH), 2.64 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.27 (q, *J* = 7 Hz, ArCH₂CH₂), 1.65 (s, 4 H, CH₂CH₂), 1.38 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.24 (s, 6 H, 2 × CH₃), and 1.22 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.54 (C=O), 144.63, 142.38, 139.99, 138.76, 138.31, 133.20, 130.55, 129.58, 129.35, 129.08, 128.33, 126.42, 125.72, 67.85 (CH₂OH), 61.03 (CO₂CH₂CH₃), 35.66, 35.18, 35.12, 34.14, 33.94, 31.91, 31.86, 30.51, and 14.36 (CO₂CH₂CH₃); IR (film) 3410 (OH), 2960, 2925, 2860, 1720 (C=O), 1270, 1025, and 755 cm⁻¹; MS (DCI) *m/e*

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421 (MH⁺), 403, 201; Exact mass spectrum (FAB) Calcd for C₂₈H₃₆O₃Na (MNa⁺): 443.2562. Found: 443.2544.

For (2Z),(4E)-2-(3-Carboethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-hexadienol (8h): scale = 0.64 mmol, yield = 93%; ¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, *J* = 2 Hz, 1 H, 2-ArH), 7.99 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.52 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.44 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.25 (d, *J* = 2 Hz, 1 H, 5-ArH), 7.20 (d, *J* = 8 Hz, 1 H, 5-ArH), 7.10 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.80 (br d, *J* = 12 Hz, 1 H, C=CH), 6.37 (br d, *J* = 12 Hz, 1 H, C=CH), 4.46 (br d, *J* = 6 Hz, 2 H, CH₂OH), 4.39 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.23 (s, 3 H, C=CCH₃), 1.65 (br s, 4 H, CH₂CH₂), 1.39 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.25 (t, *J* = 6 Hz, 1 H, OH), 1.23 (s, 6 H, 2 × CH₃), and 1.21 (s, 6 H, 2 × CH₃).

For (Z)-2-(3-Carbomethoxyphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenol (8i): scale = 0.96 mmol, yield = 98%; ¹H NMR (300 MHz, CDCl₃) δ 7.93 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.86 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.37 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.19 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.05 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.62 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.54 (d, *J* = 2 Hz, 1 H, 3-ArH), 5.81 (t, *J* = 8 Hz, 1 H, C=CH), 4.30 (br s, 2 H, CH₂OH), 3.90 (s, 3 H, CO₂CH₃), 3.73 (s, 3 H, OCH₃), 2.61 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.28 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.04 (br s, 9 H, adamantyl), and 1.73 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 166.00 (C=O), 158.66, 140.03, 138.74, 136.17, 133.31, 130.20, 129.64, 129.07, 128.40, 128.35, 126.25, 120.28, 111.95, 67.89 (CH₂OH), 54.89 (OCH₃), 52.17 (CO₂CH₃), 40.65, 37.13, 36.65, 35.52, 30.31, 29.70, and 29.08; IR (film) 3400 (br, OH), 2905, 2850, 1725 (C=O), 1450, 1440, 1410, 1285, 1270, 1245, and 1110 cm⁻¹; MS (DCI) *m/e* 461 (MH⁺), 460 (M⁺), 459 (M - H)⁺, and 443 (MH⁺ - H₂O).

For (Z)-2-(3-Carboethoxyphenyl)-5-[3-(1-adamantyl)-4-methoxyphenyl]-2-pentenol (8j). A ~1:1 mixture of Z:E (3:1, Z:E) and 1-(*t*-butyldimethylsiloxy)-2-phenyl-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentene (3:1, Z:E) (1.6 g) was dissolved in 30 mL of 3:1:1 acetic acid/THF/H₂O, and stirred for 48 h. The solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (elution with methylene chloride to 5%

- methanol/methylene chloride) to give 0.490 g of pure (Z)-2-(3-carboethoxyphenyl)-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentenol (74% based on ca. 800 mg of **7j** in the starting mixture): ¹H NMR (300 MHz, CDCl₃) δ 7.96 (dt, *J* = 8, 1 Hz, 1 H, 2-ArH), 7.89 (t, *J* = 1 Hz, 1 H, 2-ArH), 7.38 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.22 (m, 1 H, 2-ArH), 6.91 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.77 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.63 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.82 (t, *J* = 8 Hz, 1 H, C=CH), 4.23-4.40 (m, 4 H, CH₂OH and CO₂CH₂CH₃), 2.59 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.26 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.08 (s, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl), 1.39 (t, *J* = 8 Hz, 3 H, CO₂CH₂CH₃), 1.01 (s, 9 H, SiC(CH₃)₃), and 0.31 (s, 6 H, Si(CH₃)₂). (Z)-2-(3-Carboethoxyphenyl)-5-[3-(1-adamantyl)-4-*t*-butyldimethylsiloxyphenyl]-2-pentenol (490 mg) was converted in two steps to **8j** via treatment with tetrabutylammonium fluoride and then alkylation with dimethyl sulfate as described in the synthesis of **5x**.
- 15 Purification of **8j** by column chromatography on silica gel (elution with 30% ethyl acetate/hexane) gave 0.150 g of pure **8j** (37% for two steps): ¹H NMR (300 MHz, CDCl₃) δ 7.96 (dt, *J* = 1, 8 Hz, 1 H, 2-ArH), 7.89 (t, *J* = 1 Hz, 1 H, 2-ArH), 7.39 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.28 (m, 1 H, 2-ArH), 6.92 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.89 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.76 (d, *J* = 8 Hz, 1 H, 5-ArH), 5.83 (t, *J* = 8 Hz, 1 H, C=CH), 4.33-4.42 (m, 4 H, CH₂OH and CO₂CH₂CH₃), 3.80 (s, 3 H, OCH₃), 2.61 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.29 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.06 (s, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl), and 1.40 (t, *J* = 8 Hz, 3 H, CO₂CH₂CH₃).
- 25 For (Z)-2-(3-Carbomethoxyphenyl)-3-(3,4-bis(pentyloxy)phenyl)-2-propenol (**8k**): scale = 1.08 mmol, yield = 96%; ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.97 (m, 2 H, 2-ArH), 7.36-7.44 (m, 2 H, 2-ArH), 6.64 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.63 (br s, 1 H, C=CH), 6.57 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.39 (d, *J* = 2 Hz, 1 H, 3-ArH), 4.35 (dd, *J* = 1.5, 6 Hz, 2 H, CH₂OH), 3.90 (t, *J* = 6.5 Hz, 2 H, ArOCH₂), 3.87 (s, 3 H, CO₂CH₃), 3.48 (t, *J* = 6.5 Hz, 2 H, ArOCH₂), 1.70-1.79 (m, 2 H, ArOCH₂CH₂), 1.63 (t, *J* = 6 Hz, 1 H, OH), 1.55-1.65 (m, 2 H, ArOCH₂CH₂), 1.22-1.44 (m, 8 H, 4 × CH₂), and 0.88 (t, *J* = 7 Hz, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.80 (C=O), 148.33, 148.20, 139.61, 138.28, 134.00, 130.82, 129.85, 128.92, 128.67, 128.57, 127.59, 122.57, 114.04, 112.93, 68.99, 68.74, 68.58, 52.17 (CO₂CH₃), 28.88, 28.66, 28.15, 28.01, 22.44, 22.36, and 14.02; IR (film) 3430 (br, OH),
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2955, 2935, 2870, 1725 (C=O), 1510, 1470, 1440, 1265, 1235, 1205, 1170, 1140, 1110, 1090, 1020, and 760 cm^{-1} ; MS (DCI) m/e 441 (MH^+), 423 ($\text{M}^+ - \text{OH}$).

Example 8: General Procedure for Synthesis of 9

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Manganese dioxide (5:1 weight ratio MnO_2 /alcohol) was added in one portion to a solution of alcohol **8** in methylene chloride (0.1 M). The reaction mixture was stirred in a stoppered flask at room temperature for 4-18 h. Additional MnO_2 was added if necessary to
10 take the reaction to completion. The brown slurry was filtered through a one-inch pad of Celite and the collected solid was washed with methylene chloride. The filtrate was concentrated in vacuo, and the aldehyde product was used without purification.

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For (Z)-2-(3-Carboethoxyphenyl)-3-phenyl-2-propenal (**9a**): scale = 0.96 mmol, yield = 85%; ^1H NMR (300 MHz, CDCl_3) δ 9.80 (s, 1 H, CHO), 8.07-8.11 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.88 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.15-7.50 (m, 8 H, ArH), 4.35 (q, $J = 7$ Hz, 2 H, CO_2CH_2), and 1.35 (t, $J = 7$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$).

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For (Z)-2-(3-Carboethoxyphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-propenal (**9b**): scale = 2.13 mmol, yield = 90%; ^1H NMR (300 MHz, CDCl_3) δ 9.78 (s, 1 H, CHO), 8.09 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.92 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.55 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.38-7.43 (m, 2 H, ArH and C=CH), 7.20 (d, $J = 8$ Hz, 1 H, 3-ArH), 7.12 (d, $J = 2$ Hz, 1 H, 3-ArH), 6.97 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 4.36 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 1.60 (br s, 4 H, CH_2CH_2), 1.35 (t, $J = 7$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.22 (s, 6 H, 2 $\times$ CH_3), and 0.98 (s, 6 H, 2 $\times$ CH_3).

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For (Z)-2-(3-Carboethoxyphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propenal (**9c**): scale = 0.89 mmol, yield = 88%; ^1H NMR (300 MHz, CDCl_3) δ 9.80 (s, 1 H, CHO), 8.08 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.93 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.74 (s, 1 H, ArH or C=CH), 7.66 (s, 2 H, ArH), 7.57 (s, 1 H, ArH or C=CH), 7.36-7.49 (m, 3 H, ArH), 6.92 (dd, $J = 2, 9$ Hz, 1 H, ArH), 4.33 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 1.73 (s, 4 H, CH_2CH_2), and 1.31-1.41 (m, 15 H, 4 $\times$ CH_3 and OCH_2CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 193.57 (CH=O), 166.32 (C=O), 151.49, 146.93,
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145.45, 140.18, 134.18, 133.89, 132.32, 132.11, 131.33, 131.15, 130.79, 130.55, 129.51, 128.86, 127.35, 125.90, 125.33, 124.88, 61.09 (CO₂CH₂), 34.88 (CH₂CH₂), 34.78, 34.60, 32.43 and 32.39 (4 x CH₃), and 14.28 (CO₂CH₂CH₃); IR (KBr) 2960, 2930, 1720 (ester C=O), 1685 (CH=O), 1470, 1365, 1270, 1210, 1190, 1110, and 1090 cm⁻¹; MS (DCI) *m/e* 441 (MH⁺).

For (Z)-2-(3-Carboethoxyphenyl)-3-(4-decyloxyphenyl)-2-propenal (9d): scale = 1.70 mmol, yield = 80%; ¹H NMR (300 MHz, CDCl₃) δ 9.72 (s, 1 H, CHO), 8.08 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.91 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.51 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.39 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.37 (s, 1 H, C=CH), 7.12 (d, *J* = 8 Hz, 2 H, 3-ArH), 6.72 (d, *J* = 8 Hz, 2 H, 3-ArH), 3.92 (t, *J* = 7 Hz, 2 H, ArOCH₂), 3.90 (s, 3 H, CO₂CH₃), 1.75 (quintet, *J* = 7 Hz, 2 H, ArOCH₂CH₂), 1.20-1.46 (m, 14 H, 7 x CH₂), and 0.87 (t, *J* = 7 Hz, 3 H, CH₃).

For (Z)-2-(3-Carboethoxyphenyl)-3-(3,4-bisdecyloxyphenyl)-2-propenal (9e): scale = 0.46 mmol, yield = 93%; ¹H NMR (300 MHz, CDCl₃) δ 9.70 (s, 1 H, CHO), 8.05 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 8.03 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.50 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.39 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.33 (s, 1 H, C=CH), 6.87 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.73 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.55 (d, *J* = 2 Hz, 1 H, 3-ArH), 4.33 (q, *J* = 6 Hz, 2 H, CO₂CH₂), 3.95 (t, *J* = 7 Hz, 2 H, ArC⁴OCH₂), 3.45 (t, *J* = 7 Hz, 2 H, ArC³OCH₂), 1.77 (quint, *J* = 7 Hz, 2 H, ArC⁴OCH₂CH₂), 1.55-1.60 (m, 2 H, ArC³OCH₂CH₂), 1.35 (t, *J* = 6 Hz, 3 H, CO₂CH₂CH₃), 1.19-1.40 (m, 28 H, 14 x CH₂), and 0.83-0.88 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 193.45 (CH=O), 166.14 (C=O), 151.46, 151.17, 148.36, 139.63, 134.55, 134.15, 131.28, 130.79, 129.24, 129.00, 126.27, 126.01, 114.42, 112.32, 68.91, 68.57, 61.09 (CO₂CH₂), 31.91, 29.57, 29.33, 28.98, 28.85, 25.91, 25.78, 22.68, 14.30, and 14.12; IR (KBr) 2960, 2920, 2875, 2850, 1715 (ester C=O), 1675 (CH=O), 1665, 1615, 1595, 1570, 1515, 1475, 1430, 1285, 1270, 1245, 1210, 1145, and 1120 cm⁻¹; MS (FAB) *m/e* 593 (MH⁺).

For (Z)-2-(3-Carboethoxyphenyl)-5-phenyl-2-pentenal (9f): scale = 0.76 mmol, yield = 88%; ¹H NMR (300 MHz, CDCl₃) δ 9.62 (s, 1 H, CHO), 8.04 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.80 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.45 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.11-7.31 (m, 6 H, 1 x 2-ArH and 5 x 5-ArH), 6.79 (t, *J* = 7.5 Hz, 1 H, C=CH), 4.40 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.85 (t, *J* = 7.5

Hz, 2 H, ArCH₂), 2.68 (q, *J* = 7.5 Hz, 2 H, ArCH₂CH₂), and 1.40 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); MS (DCI) *m/e* 309 (MH⁺).

For (Z)-2-(3-Carbomethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenal (9g): scale = 0.62 mmol, yield = 100%; ¹H NMR (300 MHz, CDCl₃) δ 9.62 (s, 1 H, CHO), 8.01 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.82 (s, 1 H, 2-ArH), 7.41 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.21 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.09 (d, *J* = 7 Hz, 1 H, 5-ArH), 7.03 (s, 1 H, 5-ArH), 6.88 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.82 (t, *J* = 7 Hz, 1 H, C=CH), 4.38 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.78 (m, 2 H, ArCH₂), 2.64 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 1.66 (s, 4 H, CH₂CH₂), 1.39 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.26 (s, 6 H, 2 × CH₃), and 1.23 (s, 6 H, 2 × CH₃).

For (2Z),(4E)-2-(3-Carboethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-hexadienal (9h): scale = 0.54 mmol, yield = 89%; ¹H NMR (300 MHz, CDCl₃) δ 9.72 (s, 1 H, CHO), 8.02 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.94 (d, *J* = 2 Hz, 1 H, 2-ArH), 7.79 (br d, *J* = 12 Hz, 1 H, C=CH), 7.48-7.59 (m, 2 H, 2-ArH), 7.35 (d, *J* = 2 Hz, 1 H, 5-ArH), 7.27 (d, *J* = 8 Hz, 1 H, 5-ArH), 7.17 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.74 (br d, *J* = 12 Hz, 1 H, C=CH), 4.36 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 2.43 (d, *J* = 1.5 Hz, 3 H, C=CCH₃), 1.66 (br s, 4 H, CH₂CH₂), 1.36 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.23 (s, 6 H, 2 × CH₃), and 1.21 (s, 6 H, 2 × CH₃).

For (Z)-2-(3-Carbomethoxyphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenal (9i): scale = 0.93 mmol, yield = 88%; ¹H NMR (300 MHz, CDCl₃) δ 9.59 (s, 1 H, CHO), 7.99 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.79 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.41 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.10 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.08 (d, *J* = 8 Hz, 1 H, 3-ArH), 6.79 (t, *J* = 7 Hz, 1 H, C=CH), 6.65 (dd, *J* = 2, 8 Hz, 1 H, 3-ArH), 6.56 (d, *J* = 2 Hz, 1 H, 3-ArH), 3.89 (s, 3 H, CO₂CH₃), 3.74 (s, 3 H, OCH₃), 2.78 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.64 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.08 (br s, 9 H, adamantyl), and 1.74 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 193.08 (CH=O), 166.76 (ester C=O), 158.88, 155.58, 143.64, 138.64, 136.75, 133.98, 132.77, 130.49, 130.22, 129.16, 128.34, 126.55, 120.23, 111.82, 54.91 (OCH₃), 52.16 (CO₂CH₃), 40.64, 37.50, 37.11, 36.72, 34.40, 31.38, and 29.09.

For (Z)-2-(3-Carboethoxyphenyl)-5-[3-(1-adamantyl)-4-methoxyphenyl]-2-pentenal (9j): scale = 0.32 mmol, yield = 93%; ^1H NMR (300 MHz, CDCl_3) δ 9.61 (s, 1 H, CHO), 8.02 (dt, $J = 8, 1$ Hz, 1 H, 2-ArH), 7.81 (t, $J = 1$ Hz, 1 H, 2-ArH), 7.44 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.19 (dt, $J = 8, 1$ Hz, 1 H, 2-ArH), 6.89-6.95 (m, 2 H, 5-ArH and C=CH), 6.75-6.83 (m, 2 H, 5-ArH), 4.37 (q, $J = 7$ Hz, 2 H, CO_2CH_2), 3.80 (s, 3 H, OCH_3), 2.76 (t, $J = 7$ Hz, 2 H, ArCH_2), 2.64 (q, $J = 7$ Hz, 2 H, ArCH_2CH_2), 2.04 (s, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl), and 1.39 (t, $J = 7$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$).

For (Z)-2-(3-Carbomethoxyphenyl)-3-(3,4-bis(pentyloxy)phenyl)-2-propenal (9k): scale = 0.99 mmol, yield = 96%; ^1H NMR (300 MHz, CDCl_3) δ 9.72 (s, 1 H, CHO), 8.07 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.93 (t, $J = 2$ Hz, 1 H, 2-ArH), 7.53 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.42 (dt, $J = 2, 8$ Hz, 1 H, 2-ArH), 7.35 (s, 1 H, C=CH), 6.90 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.75 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.39 (d, $J = 2$ Hz, 1 H, 3-ArH), 3.98 (t, $J = 6.5$ Hz, 2 H, 3-ArOCH₂), 3.89 (s, 3 H, CO_2CH_3), 3.47 (t, $J = 6.5$ Hz, 2 H, 3-ArOCH₂), 1.75-1.86 (m, 2 H, 3-ArOCH₂CH₂), 1.56-1.66 (m, 2 H, 3-ArOCH₂CH₂), 1.25-1.49 (m, 8 H), and 1.86-1.96 (m, 6 H, 2 x CH₃).

Example 9: General Procedure for Synthesis of 10

A solution of 18-crown-6 (5 equivalents) and bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate (1.1 equivalents) in anhydrous tetrahydrofuran was cooled to -78°C under argon. A solution of potassium bistrimethylsilylamide (0.5 M in toluene, 1.1 equivalents) was added, followed by addition of a solution of the aldehyde **2** (1 equivalent) in tetrahydrofuran (0.05 M final concentration). The reaction mixture was allowed to warm to room temperature and then was poured into a separatory funnel containing diethyl ether and saturated ammonium chloride solution. The layers were agitated and separated. The ether layer was washed further with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification was accomplished by column chromatography (30:1 to 40:1 ratio of silica gel/crude product; elution with 5% ethyl acetate/hexanes) to provide the target compound.

For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-5-phenyl-2,4-pentadienoate (10a): scale = 0.82 mmol, yield = 93%; ^1H NMR (300 MHz, CDCl_3) δ 7.94 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.86 (t, J = 2 Hz, 1 H, 4-ArH), 7.30-7.37 (m, 2 H, 4-ArH), 7.08-7.11 (m, 3 H, 5-ArH), 6.91-6.94 (m, 2 H, 5-ArH), 6.86 (s, 1 H, C=CH), 6.67 (d, J = 12 Hz, 1 H, CH=CHCO₂), 5.87 (d, J = 12 Hz, 1 H, CH=CHCO₂), 4.32 (q, J = 7 Hz, 2 H, CO₂CH₂), 3.31 (s, 3 H, CO₂CH₃), and 1.34 (t, J = 7 Hz, 3 H, CO₂CH₂CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 166.72 (C=O), 166.35 (C=O), 142.77, 138.38, 136.95, 135.77, 135.09, 134.24, 130.82, 130.47, 129.58, 128.72, 128.52, 128.10, 127.70, 120.58, 61.01 (CO₂CH₂), 51.27 (CO₂CH₃) and 14.28 (CO₂CH₂CH₃); IR (film) 2980, 2950, 1720 (C=O), 1435, 1265, 1195, 1175, 1110, 1085, 1020, 760, and 700 cm^{-1} ; MS (DCI) m/e 336 (M^+).

For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-pentadienoate (10b): scale = 1.05 mmol, yield = 83%; UV_{max} (CH_3OH) 308 nm (ϵ = 20,100), 228 nm (ϵ = 22,700); ^1H NMR (300 MHz, CDCl_3) δ 7.94-7.98 (m, 1 H, 4-ArH), 7.90 (t, J = 2 Hz, 1 H, 4-ArH), 7.37-7.43 (m, 2 H, 4-ArH), 7.06 (d, J = 8 Hz, 1 H, 5-ArH), 6.80 (s, 2 H, 5-ArH and C=CH), 6.73 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.64 (d, J = 12 Hz, 1 H, CH=CHCO₂), 5.80 (d, J = 12 Hz, 1 H, CH=CHCO₂), 4.32 (q, J = 7 Hz, 2 H, CO₂CH₂), 3.25 (s, 3 H, CO₂CH₃), 1.50-1.58 (m, 4 H, CH₂CH₂), 1.33 (t, J = 7 Hz, 3 H, CO₂CH₂CH₃), 1.17 (s, 6 H, 2 $\times$ CH₃), and 0.92 (s, 6 H, 2 $\times$ CH₃); ^{13}C NMR (75 MHz, CDCl_3) δ 166.90 (C=O), 166.38 (C=O), 145.04, 144.45, 142.72, 138.85, 136.23, 136.03, 134.26, 132.64, 130.88, 130.70, 128.67, 128.60, 127.81, 127.30, 126.39, 119.65, 60.95 (CO₂CH₂), 51.24 (OCH₃), 34.88, 34.13, 33.89, 31.61, 31.38, and 14.31 (CO₂CH₂CH₃); IR (film) 2960, 2930, 2860, 1720 (C=O), 1460, 1440, 1280, 1265, 1195, 1170, 1110, 1085, and 755 cm^{-1} ; MS (DCI) m/e 447 (MH^+), 415 ($\text{M}^+ - \text{OCH}_3$).

For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoate (10c): scale = 0.76 mmol, yield = 94%; ^1H NMR (300 MHz, CDCl_3) δ 7.96 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.91 (t, J = 2 Hz, 1 H, 4-ArH), 7.58 (d, J = 12 Hz, 2 H, ArH), 7.47 (s, 1 H, ArH), 7.29-7.40 (m, 3 H, ArH), 7.01 (br s, 1 H, C=CH), 6.75 (dd, J = 2, 9 Hz, 1 H, ArH), 6.72 (dd, J = 1, 12 Hz, 1 H,

CH=CHCO₂), 5.88 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 4.32 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.30 (s, 3 H, CO₂CH₃), 1.72 (s, 4 H, CH₂CH₂), and 1.29-1.36 (m, 15 H, 4 × CH₃ and CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.89 (C=O), 166.41 (C=O), 145.12, 144.69, 142.97, 138.61, 136.51, 135.74, 134.51, 132.58, 131.54, 131.10, 130.82, 130.50, 129.22, 128.76, 128.49, 126.62, 125.82, 125.21, 124.62, 120.37, 61.01 (CO₂CH₃), 51.28 (CO₂CH₂), 35.00, 34.60, 34.52, 32.44, and 14.24 (CO₂CH₂CH₃); IR (film) 2960, 2860, 1720 (C=O), 1365, 1270, 1195, 1175, and 1110 cm⁻¹; MS (DCI) *m/e* 497 (MH⁺), 465 (MH⁺ - CH₃OH).

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For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-5-(4-decyloxyphenyl)-2,4-pentadienoate (10d): scale = 1.37 mmol, yield = 98%; ¹H NMR (300 MHz, CDCl₃) δ 7.95 (dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 7.88 (t, *J* = 2 Hz, 1 H, 4-ArH), 7.34-7.41 (m, 2 H, 4-ArH), 6.82 (d, *J* = 8 Hz, 2 H, 5-ArH), 6.81 (s, 1 H, C=CH), 6.63 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.61 (d, *J* = 8 Hz, 2 H, 5-ArH), 5.79 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.88 (s, 3 H, CO₂CH₃), 3.85 (t, *J* = 7 Hz, 2 H, ArOCH₂), 3.26 (s, 3 H, CO₂CH₃), 1.70 (quintet, *J* = 7 Hz, 2 H, ArOCH₂CH₂), 1.17-1.42 (m, 14 H, 7 × CH₂), and 0.85 (t, *J* = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.90 (C=O), 158.86, 142.94, 138.88, 135.64, 134.91, 134.48, 131.09, 130.58, 128.66, 128.00, 119.42, 114.11, 67.91 (ArOCH₂), 52.17 (CO₂CH₃), 51.24 (CO₂CH₃), 31.88, 29.54, 29.36, 29.31, 29.16, 25.98, 22.68, and 14.12; IR (film) 2925, 2855, 1725 (C=O), 1600, 1510, 1470, 1435, 1280, 1270, 1250, 1195, 1175, 1110, 1085, 1070, 1000, 825, 755, and 710 cm⁻¹; MS (DCI) *m/e* 479 (MH⁺), 447 (M⁺ - OCH₃).

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For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoate (10e): scale = 0.41 mmol, yield = 86%; ¹H NMR (300 MHz, CDCl₃) δ 7.90-7.96 (m, 2 H, 4-ArH), 7.38-7.48 (m, 2 H, 4-ArH), 6.79 (s, 1 H, C=CH), 6.56-6.65 (m, 3 H, 2 × 5-ArH and CH=CHCO₂), 6.32 (d, *J* = 2 Hz, 1 H, 5-ArH), 4.78 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 4.33 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.90 (t, *J* = 7 Hz, 2 H, ArC⁴OCH₂), 3.45 (t, *J* = 7 Hz, 2 H, ArC³OCH₂), 3.25 (s, 3 H, CO₂CH₃), 1.74 (quint, *J* = 7 Hz, 2 H, ArC⁴OCH₂CH₂), 1.54-1.60 (m, 2 H, ArC³OCH₂CH₂), 1.35 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.19-1.40 (m, 28 H, 14 × CH₂), and 0.83-0.88 (m, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.93 (C=O), 166.27 (C=O), 149.06, 148.17, 142.78, 135.03, 134.97, 134.45,

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130.93, 130.75, 128.62, 128.54, 128.37, 123.68, 119.28, 114.05, 112.67, 68.93, 68.57, 61.03 (CO₂CH₂), 51.22 (CO₂CH₃), 31.91, 29.58, 29.37, 29.34, 29.13, 28.98, 25.95, 25.83, 22.68, 14.30, and 14.12; IR (film) 2925, 2855, 1720 (C=O), 1510, 1470, 1265, 1200, 1170, and 1140 cm⁻¹; MS (DCI) *m/e* 649 (MH⁺).

For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-7-phenyl-2,4-heptadienoate (10f): scale = 0.65 mmol, yield = 77%; UV_{max} (CH₃OH) 262 nm (ϵ = 10,600); ¹H NMR (300 MHz, CD₃OD) δ 7.89 (dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 7.70 (t, *J* = 2 Hz, 1 H, 4-ArH), 7.39 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.04-7.22 (m, 6 H, 1 $\times$ 4-ArH and 5 $\times$ 7-ArH), 6.60 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.06 (t, *J* = 7.5 Hz, 1 H, C=CH), 5.74 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 4.35 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.14 (s, 3 H, CO₂CH₃), 2.68 (t, *J* = 7.5 Hz, 2 H, ArCH₂), 2.32 (q, *J* = 7.5 Hz, 2 H, ArCH₂CH₂), and 1.38 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 168.68 (C=O), 167.89 (C=O), 142.98, 142.46, 139.60, 139.43, 139.33, 135.01, 131.44, 131.26, 129.47, 129.35, 129.30, 129.10, 127.02, 120.01, 62.21 (CO₂CH₂), 51.61 (CO₂CH₃), 36.37, 32.30, and 14.63 (CO₂CH₂CH₃); IR (film) 3060, 3025, 2980, 2950, 2855, 1720 (C=O), 1455, 1435, 1370, 1270, 1195, 1170, 1110, 1085, 1020, 760, and 700 cm⁻¹; MS (DCI) *m/e* 365 (MH⁺), 333 (M⁺ - OCH₃).

For Methyl (2Z),(4Z)-4-(3-carbomethoxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (10g): scale = 0.62 mmol, yield = 85%; ¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.85 (s, 1 H, 4-ArH), 7.36 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.15-7.24 (m, 2 H, 4-ArH and 7-ArH), 7.00 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.84 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.57 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.07 (t, *J* = 7 Hz, 1 H, C=CH), 5.73 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 4.36 (q, *J* = 7 Hz, 2 H, CO₂CH₂), 3.21 (s, 3 H, OCH₃), 2.63 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.35 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (s, 4 H, CH₂CH₂), 1.38 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), 1.24 (s, 6 H, 2 $\times$ CH₃), and 1.22 (s, 6 H, 2 $\times$ CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.80 (C=O), 166.47 (C=O), 144.71, 142.48, 142.26, 138.53, 138.20, 137.98, 137.28, 133.51, 130.29, 130.12, 128.21, 128.06, 126.46, 126.39, 125.64, 119.07, 61.01 (CO₂CH₂), 51.09 (OCH₃), 35.22, 35.15, 35.09, 34.15, 33.94, 31.89, 31.84, 31.13, and 14.35 (CO₂CH₂CH₃); IR (film) 2960, 2925, 1720 (C=O), 1270, and 1170 cm⁻¹; MS (DCI) *m/e* 475 (MH⁺), 474

(M⁺); Exact mass spectrum (FAB) Calcd for C₃₁H₃₈O₄Na: 497.2668 (MNa⁺). Found: 497.2652.

For Methyl (2Z),(4Z),(6E)-4-(3-carboethoxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4,6-octatrienoate (10h): scale = 0.47 mmol, yield = 74%; UV_{max} (CH₃OH) 348 nm (ϵ = 14,300); ¹H NMR (300 MHz, CD₃OD) δ 7.95 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.91 (d, J = 2 Hz, 1 H, 4-ArH), 7.41-7.51 (m, 2 H, 4-ArH), 7.04-7.22 (m, 4 H, 3 x 7-ArH and C=CH), 6.81 (d, J = 12 Hz, 1 H, CH=CHCO₂), 6.41 (br d, J = 12 Hz, 1 H, C=CH), 5.82 (d, J = 12 Hz, 1 H, CH=CHCO₂), 4.35 (q, J = 7 Hz, 2 H, CO₂CH₂), 3.15 (s, 3 H, CO₂CH₃), 2.25 (d, J = 1.5 Hz, 3 H, C=CCH₃), 1.63 (s, 4 H, CH₂CH₂), 1.35 (t, J = 7 Hz, 3 H, CO₂CH₂CH₃), 1.21 (s, 6 H, 2 x CH₃), and 1.16 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 168.50 (C=O), 167.90 (C=O), 145.89, 145.69, 143.19, 140.96, 140.17, 138.62, 135.27, 134.69, 132.02, 131.50, 129.44, 129.26, 127.62, 124.73, 124.09, 123.55, 120.03, 62.29 (CO₂CH₂), 51.64 (OCH₃), 36.18, 36.09, 35.18, 35.04, 32.21, 32.08, 16.20 (C=CCH₃), and 14.62 (CO₂CH₂CH₃); IR (film) 2960, 2930, 2860, 1720 (C=O), 1460, 1440, 1365, 1265, 1205, 1170, 1110, 1085, and 760 cm⁻¹; MS (DCI) m/e 487 (MH⁺), 455 (M⁺ - OCH₃).

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For Methyl (2Z),(4Z)-4-(3-carbomethoxyphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoate (10i): scale = 0.81 mmol, yield = 69%; ¹H NMR (300 MHz, CDCl₃) δ 7.91 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.84 (t, J = 2 Hz, 1 H, 4-ArH), 7.36 (t, J = 8 Hz, 1 H, 4-ArH), 7.21 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.05 (d, J = 8 Hz, 1 H, 7-ArH), 6.62 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 6.54-6.58 (m, 2 H, 7-ArH and CH=CHCO₂), 6.05 (t, J = 8 Hz, 1 H, C=CH), 5.72 (d, J = 12 Hz, 1 H, CH=CHCO₂), 3.89 (s, 3 H, ArCO₂CH₃), 3.73 (s, 3 H, OCH₃), 3.21 (s, 3 H, CO₂CH₃), 2.63 (t, J = 8 Hz, 2 H, ArCH₂), 2.36 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 2.04 (br s, 9 H, adamantyl), and 1.73 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 166.40 (C=O), 166.30 (C=O), 142.20, 139.71, 138.19, 137.30, 136.27, 133.62, 130.16, 129.96, 128.23, 128.10, 126.31, 120.22, 119.17, 111.94, 54.89 (OCH₃), 52.12 (ArCO₂CH₃), 51.06 (CO₂CH₃), 40.66, 37.13, 36.66, 35.12, 30.94, and 29.10.

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For Methyl (2Z),(4Z)-4-(3-carboethoxyphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoate (10j): scale = 0.29 mmol, yield = 76%; ¹H NMR (300 MHz, CDCl₃) δ 7.92 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.83

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(t, $J = 2$ Hz, 1 H, 4-ArH), 7.37 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.25 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 6.91 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.87 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.73 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.57 (d, $J = 13$ Hz, 1 H, CH=CHCO₂), 6.06 (t, $J = 8$ Hz, 1 H, C=CH), 5.73 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 4.36 (q, $J = 7$ Hz, 2 H, CO₂CH₂), 3.77 (s, 3 H, OCH₃), 3.20 (s, 3 H, CO₂CH₃), 2.62 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.34 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.03 (s, 9 H, adamantyl), 1.74 (s, 6 H, adamantyl), and 1.38 (t, $J = 7$ Hz, 3 H, CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.83 (C=O), 166.50 (C=O), 157.13, 142.28, 138.67, 138.33, 138.22, 137.28, 133.55, 132.72, 130.28, 130.12, 128.18, 128.07, 126.72, 126.23, 119.01, 111.59, 61.02 (CO₂CH₂), 55.06, 51.09, 40.56, 37.13, 36.86, 35.01, 31.44, 29.10, and 14.34 (CO₂CH₂CH₃); IR (film) 2905, 2850, 1720 (C=O), 1495, 1270, and 1235 cm⁻¹; MS (DCI) m/e 529 (MH⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₄H₄₀O₅: C, 77.24; H, 7.63. Found: C, 77.55; H, 7.56.

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For Methyl (2Z),(4Z)-4-(3-carbomethoxyphenyl)-5-(3,4-bis(pentyloxy)phenyl)-2,4-pentadienoate (10k): scale = 0.63 mmol, yield = 85%; ¹H NMR (300 MHz, CDCl₃) δ 7.91-7.96 (m, 2 H, 4-ArH), 7.36-7.45 (m, 2 H, 4-ArH), 6.79 (s, 1 H, C=CH), 6.56-6.66 (m, 3 H, 2 x 5-ArH and CH=CHCO₂), 6.31 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.78 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 3.89 (t, $J = 6.5$ Hz, 2 H, ArOCH₂), 3.87 (s, 3 H, CO₂CH₃), 3.44 (t, $J = 6.5$ Hz, 2 H, ArOCH₂), 3.25 (s, 3 H, CO₂CH₃), 1.70-1.80 (m, 2 H, ArOCH₂CH₂), 1.54-1.60 (m, 2 H, ArOCH₂CH₂), 1.25-1.43 (m, 8 H, 4 x CH₂), and 0.86-0.94 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.92 (C=O), 166.75 (C=O), 149.06, 148.16, 142.76, 139.05, 136.06, 134.93, 134.58, 130.81, 130.59, 128.67, 128.59, 128.34, 123.71, 119.30, 114.00, 112.65, 68.91 (ArOCH₂), 68.52 (ArOCH₂), 52.16 (CO₂CH₃), 51.22 (CO₂CH₃), 28.81, 28.64, 28.13, 27.99, 22.43, 22.35, and 14.02; IR (film) 2955, 2870, 1725 (C=O), 1595, 1510, 1470, 1435, 1265, 1200, 1170, 1140, 1110, and 1000 cm⁻¹; MS (DCI) m/e 495 (MH⁺), 463 (M⁺ - OCH₃).

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Example 10a: General Procedure for Synthesis of 11a-j

A mixture of ester 10 in methanol/tetrahydrofuran/2N sodium hydroxide solution (1:1:1, 0.1 M) was heated at reflux for 1-4 h. The reaction mixture was then allowed to cool to room temperature and 10% hydrochloric acid solution was added until the solution reached

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pH 1. The resulting cloudy mixture was extracted with methylene chloride (2 to 4 portions), and the organic phase was washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was evaporated from pentane (3 portions) and then dried in vacuo.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-5-phenyl-2,4-pentadienoic acid (11a): scale = 2.05 mmol, yield = 99%; UV_{max} (CH₃OH) 269 nm (ϵ = 14,700), 222 nm (ϵ = 23,500); ¹H NMR (300 MHz, CD₃OD) δ 7.90-7.95 (m, 1 H, 4-ArH), 7.86 (t, J = 2 Hz, 1 H, 4-ArH), 7.37-7.41 (m, 2 H, 4-ArH), 7.06-7.13 (m, 3 H, 5-ArH), 6.95-6.98 (m, 2 H, 5-ArH), 6.90 (s, 1 H, C=CH), 6.71 (d, J = 12 Hz, 1 H, CH=CHCO₂), and 5.92 (d, J = 12 Hz, 1 H, CH=CHCO₂); ¹³C NMR (75 MHz, CD₃OD) δ 170.12 (C=O), 169.54 (C=O), 143.47, 140.11, 138.83, 137.47, 135.51, 135.15, 132.14, 130.66, 129.91, 129.63, 129.09, 128.67, and 122.57; IR (film) 2200-3400 (br, CO₂H), 1695 (C=O), 1625, 1600, 1580, 1435, 1305, 1275, 1250, 1230, 950, 910, 750, and 690 cm⁻¹; MS (DCI) m/e 295 (MH⁺). Anal. Calcd for C₁₈H₁₄O₄: C, 73.46; H, 4.79. Found: C, 73.40; H, 4.78.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-pentadienoic acid (11b): scale = 1.35 mmol, yield = 98%; UV_{max} (CH₃OH) 308 nm (ϵ = 15,200), 228 nm (ϵ = 21,100); ¹H NMR (300 MHz, CD₃OD) δ 7.91-7.96 (m, 1 H, 4-ArH), 7.89 (t, J = 2 Hz, 1 H, 4-ArH), 7.42-7.46 (m, 2 H, 4-ArH), 7.13 (d, J = 8 Hz, 1 H, 5-ArH), 6.82 and 6.85 (2 s, 3 H, 2 x 5-ArH and C=CH), 6.68 (d, J = 12 Hz, 1 H, CH=CHCO₂), 5.86 (d, J = 12 Hz, 1 H, CH=CHCO₂), 1.52-1.65 (m, 4 H, CH₂CH₂), 1.19 (s, 6 H, 2 x CH₃), and 0.89 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.29 (C=O), 169.63 (C=O), 145.89, 145.32, 143.52, 140.66, 137.87, 136.09, 135.52, 134.32, 132.35, 129.81, 128.71, 127.46, 121.76, 36.04, 35.05, 34.82, 32.03, and 31.87; IR (film) 2500-3400 (br, CO₂H), 1695 (C=O), 1615, 1585, 1440, 1415, 1365, 1285, 1225, and 910 cm⁻¹; MS (DCI) m/e 405 (MH⁺), 387 (M⁺ - OH). Anal. Calcd for C₂₆H₂₈O₄ · 0.4 H₂O: C, 75.85; H, 7.05. Found: C, 75.89; H, 6.96.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid (11c): scale = 0.69 mmol, yield = 100%; mp 211-213 °C; UV_{max} (CH₃OH) 332 nm (ϵ =

21,100), 284 nm ($\epsilon = 21,700$); ^1H NMR (300 MHz, DMSO- d_6) δ 7.86 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 7.74 (s, 1 H, 4-ArH), 7.69 (d, $J = 12$ Hz, 2 H, 5-ArH), 7.56 (s, 1 H, ArH), 7.34-7.44 (m, 3 H, ArH), 7.00 (s, 1 H, C=CH), 6.67-6.74 (m, 2 H, ArH and CH=CHCO₂), 5.94 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 1.67 (s, 4 H, CH₂CH₂), and 1.29 (br s, 12 H, 4 $\times$ CH₃); ^{13}C NMR (75 MHz, DMSO- d_6) δ 167.13 (C=O), 167.02 (C=O), 144.56, 144.29, 141.53, 138.47, 136.94, 133.90, 133.36, 132.54, 131.27, 130.80, 130.61, 130.24, 128.72, 128.52, 126.38, 125.29, 124.84, 124.47, 122.48, 34.48, 34.28, 34.21, and 32.18; IR (KBr) 3430 (br, CO₂H), 3010, 2960, 2925, 2865, 1690 (C=O), 1615, 1435, 1290, 1260, and 1225 cm⁻¹; MS (DCI) m/e 455 (MH⁺) and 411 (MH⁺ - CO₂H). Anal. Calcd for C₃₀H₃₀O₄ $\cdot$ 0.67 H₂O: C, 77.20; H, 6.77. Found: C, 77.21; H, 6.58.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-5-(4-decyloxyphenyl)-2,4-pentadienoic acid (11d): scale = 1.27 mmol, yield = 94%; UV_{max} (CH₃OH) 314 nm ($\epsilon = 19,700$), 228 nm ($\epsilon = 23,000$); ^1H NMR (300 MHz, CD₃OD) δ 7.93-7.96 (m, 1 H, 4-ArH), 7.88 (t, $J = 2$ Hz, 1 H, 4-ArH), 7.38-7.41 (m, 2 H, 4-ArH), 6.87 (d, $J = 8$ Hz, 2 H, 5-ArH), 6.86 (s, 1 H, C=CH), 6.63-6.69 (m, 3 H, CH=CHCO₂ and 2 $\times$ 5-ArH), 5.85 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 3.87 (t, $J = 7$ Hz, 2 H, ArOCH₂), 1.70 (quintet, $J = 7$ Hz, 2 H, ArOCH₂CH₂), 1.21-1.42 (m, 14 H, 7 $\times$ CH₂), and 0.88 (t, $J = 7$ Hz, 3 H, CH₃); ^{13}C NMR (75 MHz, CD₃OD) δ 169.25 (C=O), 160.30, 143.78, 140.51, 136.75, 135.62, 132.16, 129.82, 129.71, 121.47, 115.08, 68.92 (ArOCH₂), 33.07, 30.69, 30.50, 30.46, 30.34, 27.12, 23.74, and 14.45; IR (KBr) 2400-3500 (br, CO₂H), 2950, 2920, 2850, 1695 (C=O), 1605, 1510, 1465, 1440, 1420, 1300, 1255, 1175, 1025, 935, 915, 890, 830, and 750 cm⁻¹; MS (DCI) m/e 451 (MH⁺). Anal. Calcd for C₂₈H₃₄O₅: C, 74.64; H, 7.61. Found: C, 74.50; H, 7.56.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid (11e): scale = 0.32 mmol, yield = 100%; UV_{max} (CH₂Cl₂) 342 nm ($\epsilon = 20,200$); ^1H NMR (300 MHz, CDCl₃) δ 8.01 (s, 1 H, 4-ArH), 7.92-7.96 (m, 1 H, 4-ArH), 7.40-7.45 (m, 2 H, 4-ArH), 6.91 (s, 1 H, C=CH), 6.75 (d, $J = 13$ Hz, 1 H, CH=CHCO₂), 6.64 (d, $J = 8.5$ Hz, 1 H, 5-ArH), 6.58 (dd, $J = 2, 8.5$ Hz, 1 H, 5-ArH), 6.31 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.79 (d, $J = 13$ Hz, 1 H, CH=CHCO₂), 3.89 (t, $J = 7$ Hz, 2 H, ArC⁴OCH₂), 3.42 (t, $J = 7$ Hz, 2 H, ArC³OCH₂), 1.73 (quint, $J = 7$ Hz, 2 H,

ArC⁴OCH₂CH₂), 1.50-1.60 (m, 2 H, ArC³OCH₂CH₂), 1.21-1.38 (m, 28 H, 14 × CH₂), and 0.82-0.87 (m, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 173.39 (C=O), 171.72 (C=O), 149.30, 149.14, 141.84, 138.74, 138.66, 136.11, 135.36, 130.94, 129.64, 129.39, 129.14, 128.07, 123.97, 117.78, 114.15, 112.58, 68.91, 68.50, 31.90, 29.58, 29.36, 29.33, 29.09, 28.94, 25.94, 24.78, 22.68, and 14.12; IR (KBr) 2955, 2925, 2850, 2665, 1700 (C=O), 1585, 1515, 1435, 1310, 1270, 1240, and 1140 cm⁻¹; MS (DCI) *m/e* 607 (MH⁺), 563 (M - 2 × CO₂H + 2H)⁺. Anal. Calcd for C₃₈H₅₄O₆: C, 75.21; H, 8.97. Found: C, 75.22; H, 8.97.

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For (2Z),(4Z)-4-(3-Carboxyphenyl)-7-phenyl-2,4-heptadienoic acid (11f): scale = 0.40 mmol, yield = 85%; UV_{max} (CH₃OH) 262 nm (ε = 8,800); ¹H NMR (300 MHz, CD₃OD) δ 7.90 (dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 7.80 (t, *J* = 2 Hz, 1 H, 2-ArH), 7.38 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.06-7.27 (m, 6 H, 1 × 2-ArH and 5 × 5-ArH), 6.58 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.04 (t, *J* = 7.5 Hz, 1 H, C=CH), 5.76 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 2.68 (t, *J* = 7.5 Hz, 2 H, ArCH₂), and 2.33 (q, *J* = 7.5 Hz, 2 H, ArCH₂CH₂); ¹³C NMR (75 MHz, CD₃OD) δ 170.10 (C=O), 143.14, 142.60, 139.70, 139.13, 137.78, 134.94, 131.66, 129.49, 129.43, 129.34, 129.14, 126.96, 121.16, 36.41, and 32.43; IR (film) 2400-3500 (br, CO₂H), 1695 (C=O), 1620, 1605, 1585, 1440, 1290, 1245, 1170, 915, 885, 755, 725, and 700 cm⁻¹; MS (DCI) *m/e* 323 (MH⁺), 305 (M⁺ - OH). Anal. Calcd for C₂₀H₁₈O₄ · 0.1 H₂O: C, 74.11; H, 5.66. Found: C, 74.08; H, 5.61.

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For (2Z),(4Z)-4-(3-Carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (11g): scale = 2.21 mmol, yield = 75%; ¹H NMR (300 MHz, CD₃OD) δ 7.89 (dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 7.82 (t, *J* = 2 Hz, 1 H, 4-ArH), 7.34 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.15 (m, 2 H, 4-ArH and 7-ArH), 6.99 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.80 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.58 (dd, *J* = 1, 12 Hz, 1 H, CH=CHCO₂), 6.06 (t, *J* = 8 Hz, 1 H, C=CH), 5.75 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 2.61 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.29 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.65 (s, 4 H, CH₂CH₂), 1.23 (s, 6 H, 2 × CH₃), and 1.20 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.10 (C=O), 169.78 (C=O), 145.62, 143.35, 143.25, 139.75, 139.46, 139.04, 138.28, 134.96, 131.69, 129.37, 129.08, 127.72, 127.52, 127.48, 126.85, 120.99, 36.37, 36.32, 36.19, 35.06, 34.85, 32.67, 32.34, and 31.43; IR (film) 2400-3500 (br, CO₂H), 2960, 2925, 2860, 1695 (C=O), and 755 cm⁻¹; MS (DCI)

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m/e 434 ($M + 2H$)⁺. Anal. Calcd for $C_{28}H_{32}O_4 \cdot 0.1 H_2O$: C, 77.43; H, 7.47. Found: C, 77.22; H, 7.47.

For (2Z),(4Z),(6E)-4-(3-Carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4,6-octatrienoic acid (11h): scale = 0.30 mmol, yield = 67%; UV_{max} (CH₃OH) 348 nm (ϵ = 33,200); ¹H NMR (300 MHz, CD₃OD) ¹H NMR (300 MHz, CD₃OD) δ 7.94-7.98 (m, 2 H, 4-ArH), 7.43-7.47 (m, 2 H, 4-ArH), 7.05-7.25 (m, 4 H, 3 x 7-ArH and C=CH), 6.73 (d, J = 12 Hz, 1 H, CH=CHCO₂), 6.48 (br d, J = 12 Hz, 1 H, C=CH), 5.84 (d, J = 12 Hz, 1 H, CH=CHCO₂), 2.25 (d, J = 1.5 Hz, 3 H, C=CCH₃), 1.65 (s, 4 H, CH₂CH₂), 1.22 (s, 6 H, 2 x CH₃), and 1.18 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.56 (C=O), 169.89 (C=O), 145.71, 142.66, 142.46, 141.08, 140.26, 138.66, 135.20, 133.36, 132.39, 131.89, 129.58, 129.21, 127.59, 124.76, 124.07, 123.78, 121.58, 36.24, 36.13, 35.19, 35.03, 32.21, 32.10, and 16.19 (C=CCH₃); IR (film) 2400-3600 (br, CO₂H), 2960, 2925, 2860, 1690 (C=O), 1585, 1445, 1295, 1255, and 1225 cm⁻¹; MS (DCI) m/e 445 (MH⁺), 399 (M⁺ - CO₂H). Anal. Calcd for $C_{29}H_{32}O_4 \cdot 0.33 H_2O$: C, 77.30; H, 7.31. Found: C, 77.36; H, 7.20.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid (11i): scale = 0.54 mmol, yield = 100%; UV_{max} (CH₃OH) 280 nm (ϵ = 8,600), 270 nm (ϵ = 10,500); ¹H NMR (300 MHz, CD₃OD) δ 7.90 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.84 (t, J = 2 Hz, 1 H, 4-ArH), 7.35 (t, J = 8 Hz, 1 H, 4-ArH), 7.17 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.01 (d, J = 8 Hz, 1 H, 7-ArH), 6.56-6.61 (m, 3 H, 2 x 7-ArH and CH=CHCO₂), 6.05 (t, J = 8 Hz, 1 H, C=CH), 5.76 (d, J = 12 Hz, 1 H, CHCO₂), 3.72 (s, 3 H, OCH₃), 2.64 (t, J = 8 Hz, 2 H, ArCH₂), 2.33 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 2.06 (br s, 6 H, adamantyl), 2.01 (br s, 3 H, adamantyl), and 1.73 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CD₃OD) δ 170.10 (C=O), 169.78 (C=O), 160.11, 143.20, 141.32, 139.76, 139.06, 138.07, 137.13, 134.96, 131.72, 131.59, 129.38, 129.12, 127.15, 121.49, 121.07, 113.16, 55.34 (OCH₃), 41.94, 38.28, 37.74, 36.08, 32.42, and 30.63; IR (KBr) 3420 (br, CO₂H), 2905, 2850, 1695 (C=O), 1450, 1415, 1290, and 1245 cm⁻¹; MS (DCI) m/e 487 (MH⁺) and 443 (MH⁺ - CO₂H). Anal. Calcd for $C_{31}H_{34}O_5 \cdot 0.33 H_2O$: C, 75.58; H, 7.09. Found: C, 75.59; H, 7.02.

For (2Z),(4Z)-4-(3-Carboxyphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid (**11j**): scale = 0.21 mmol, yield = 87%; ^1H NMR (300 MHz, CD_3OD) δ 7.81 (d, J = 8 Hz, 1 H, 4-ArH), 7.68 (s, 1 H, 4-ArH), 7.39 (t, J = 8 Hz, 1 H, 4-ArH), 7.24 (d, J = 8 Hz, 1 H, 4-ArH), 6.77-6.88 (m, 3 H, 7-ArH), 6.55 (d, J = 13 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 6.00 (t, J = 7 Hz, $\text{C}=\text{CH}$), 5.76 (d, J = 12 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.71 (s, 3 H, OCH_3), 2.55 (t, J = 8 Hz, 2 H, ArCH_2), 2.22 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 1.95 (m, 9 H, adamantyl), and 1.68 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 167.29 ($\text{C}=\text{O}$), 167.01 ($\text{C}=\text{O}$), 156.67, 141.05, 138.05, 137.26, 137.13, 136.19, 133.14, 132.58, 130.54, 129.67, 128.05, 127.83, 126.30, 126.12, 121.06, 111.92, 55.13 (OCH_3), 40.12, 36.57, 36.24, 34.34, 31.23, and 28.38; IR (KBr) 2400-3500 (br, CO_2H), 2905, 2850, 1695 ($\text{C}=\text{O}$), 1495, 1445, 1285, 1260, and 1235 cm^{-1} ; MS (DCI) m/e 487 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{O}_5$: C, 76.52; H, 7.04. Found: C, 76.19; H, 7.14.

Example 10b: Synthesis of **11k**

For (2Z),(4Z)-3-Methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid (**11k**). A suspension of potassium *t*-butylate (1.40 g, 12.5 mmol) in THF (40 mL) was cooled under a nitrogen atmosphere to -5°C . A solution of 4-(3-carbomethoxyphenyl)-3-methyl-2-butenolate (Tramposch, K. M. et al. *Biochemical and Biophysical Research Communications* 1992, 189, 272) (1.66 g, 6.00 mmol) in THF (5 mL) was added to the slurry. The mixture was stirred at 0°C for 30 min. A solution of 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenaldehyde (**3b**) (1.33 g, 5.00 mmol) in THF (5 mL) was added slowly to the reaction mixture. After stirring for 30 min at 0°C , 4 mL of water was added. After 3 h of additional stirring, the solution was acidified with 1 N HCl to pH 2. This acidic solution was poured into a separatory funnel and shaken with ether. The organic phase was washed with water and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by passage through a silica gel pad using gradient elution (methylene chloride to 5% methanol/methylene chloride). Removal of the solvents gave an oil which was dissolved in acetonitrile to precipitate **11k** as a white solid (1.34 g, 55%): mp $186-7^\circ\text{C}$; UV_{max} ($\text{CH}_3\text{CH}_2\text{OH}$) 318 nm (ϵ = 16,000), 222 nm (ϵ = 45,000); ^1H

NMR (300 MHz, one drop of DMSO- d_6 in $CDCl_3$) δ 7.95 (s, 1 H, ArH), 7.88 (d, J = 8 Hz, 1 H, ArH), 7.54 (d, J = 13 Hz, 2 H, ArH), 7.39-7.42 (m, 2 H, ArH), 7.31 (d, J = 8.5 Hz, 1 H, ArH), 7.20 (t, J = 8 Hz, 1 H, ArH), 6.85 (dd, J = 8.5, 1 Hz, 1 H, ArH), 6.64 (s, 1 H, ArCH=C), 5.82 (d, J = 1 Hz, 1 H, C=CHCO₂), 1.84 (s, 3 H, C=CCH₃), 1.68 (s, 4 H, CH₂CH₂), and 1.29 (s, 12 H, 4 $\times$ CH₃); ¹³C NMR (75 MHz, $CDCl_3$) δ 168.96 (C=O), 168.80 (C=O), 156.12, 144.38, 144.25, 140.50, 138.24, 134.70, 133.18, 131.52, 130.85, 130.78, 130.71, 128.86, 128.42, 128.30, 128.15, 126.28, 124.88, 124.41, 119.55, 34.91, 34.40, 34.36, 32.33, and 24.19; IR (KBr) 2965, 2925, 2860, 1690 (C=O), 1650, 1465, 1360, 1300, 1250, 960 cm^{-1} ; MS (DCI) m/e 469 (MH⁺), 425. Anal. Calcd for C₃₁H₃₂O₄: C, 79.48; H, 6.84. Found: C, 79.30; H, 7.08.

Example 11: General Procedure for Synthesis of 12

Manganese dioxide (5:1 weight ratio MnO₂/alcohol) was added in one portion to a solution of alcohol 5 in methylene chloride (0.1 M). The reaction mixture was stirred in a stoppered flask at room temperature for 4-40 h. Additional MnO₂ was added if necessary to take the reaction to completion. The brown slurry was filtered through a one-inch pad of Celite and the collected solid was washed with methylene chloride. The filtrate was concentrated in vacuo, and the aldehyde product was used without purification.

For (Z)-2-(3-trifluoromethylphenyl)-3-(4-decyloxyphenyl)-2-propenal (12a): scale = 5.9 mmol, yield = 90%; ¹H NMR (300 MHz, $CDCl_3$) δ 9.69 (s, 1 H, CHO), 7.63 (d, J = 8 Hz, 1 H, 2-ArH), 7.53 (t, J = 8 Hz, 1 H, 2-ArH), 7.47 (s, 1 H, C=CH), 7.38 (d, J = 8 Hz, 1 H, 2-ArH), 7.36 (s, 1 H, 2-ArH), 7.09 (dt, J = 3, 9 Hz, 2 H, 3-ArH), 6.73 (dt, J = 3, 9 Hz, 2 H, 3-ArH), 3.91 (t, J = 7 Hz, 2 H, ArOCH₂), 1.73 (quint, J = 7 Hz, 2 H, ArOCH₂CH₂), 1.16-1.40 (m, 14 H, 7 $\times$ CH₂), 0.85 (t, J = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, $CDCl_3$) δ 193.14 (C=O), 161.31 (3-ArC), 151.30, 138.01, 134.67, 133.10, 132.74 (3-ArC), 129.34, 126.49 (q, $\beta_{C,f}$ = 4 Hz, 2-ArC), 125.79, 124.98 (q, $\beta_{C,f}$ = 4 Hz, 2-ArC), 114.69 (3-ArC), 68.19 (ArOCH₂), 40.60, 31.87, 29.52, 29.30, 29.04, 25.92, and 14.10; IR (KBr) 2960, 2920, 2870, 2850, 1675 (C=O), 1600, 1570, 1510, 1475, 1425, 1325, 1310, 1260, 1180, and 1165 cm^{-1} ; MS (DCI) m/e 433 (MH⁺).

For (Z)-2-(3-trifluoromethylphenyl)-3-(3-decyloxyphenyl)-2-propenal (12b): scale = 1.8 mmol, yield = 95%; ^1H NMR (300 MHz, CDCl_3) δ 9.75 (s, 1 H, CHO), 7.62 (d, J = 8 Hz, 1 H, 2-ArH), 7.56 (t, J = 8 Hz, 1 H, 2-ArH), 7.48 (s, 1 H, 2-ArH), 7.41 (s, 1 H, C=CH), 7.38 (d, J = 8 Hz, 1 H, 2-ArH), 7.15 (t, J = 8 Hz, 1 H, 3-ArH), 6.85 (dt, J = 2, 8 Hz, 1 H, 3-ArH), 6.78 (d, J = 8 Hz, 1 H, 3-ArH), 6.58 (t, J = 2 Hz, 1 H, 3-ArH), 3.57 (t, J = 7 Hz, 2 H, ArOCH_2), 1.57-1.65 (m, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.21-1.37 (m, 14 H, 7 $\times$ CH_2), and 0.87 (t, J = 7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 193.16 (C=O), 158.98 (3-ArC), 151.28, 140.32, 134.50, 134.37, 134.00, 129.68, 129.34, 126.50 (q, $J_{\text{C,F}}$ = 4 Hz, 2-ArC), 125.04 (q, $J_{\text{C,F}}$ = 4 Hz, 2-ArC), 123.60, 118.21, 115.02, 67.78 (ArOCH_2), 31.89, 29.53, 29.31, 29.27, 28.98, 25.83, 22.68, and 14.11; IR (film) 2925, 2855, 1690 (C=O), 1580, 1325, 1270, and 1165 cm^{-1} ; MS (DCI) m/e 433 (MH^+).

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For (Z)-2-(3-trifluoromethylphenyl)-3-(2-decyloxyphenyl)-2-propenal (12c): scale = 2.0 mmol, yield = 93%; ^1H NMR (300 MHz, CDCl_3) δ 9.77 (s, 1 H, CHO), 7.87 (s, 1 H, C=CH), 7.58 (d, J = 8 Hz, 1 H, 2-ArH), 7.39-7.47 (m, 2 H, 2-ArH), 7.38 (d, J = 8 Hz, 1 H, 2-ArH), 7.25 (dt, J = 2, 8 Hz, 1 H, 3-ArH), 6.92 (d, J = 8 Hz, 1 H, 3-ArH), 6.77 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.61 (t, J = 8 Hz, 1 H, 3-ArH), 4.03 (t, J = 7 Hz, 2 H, ArOCH_2), 1.85 (quint, J = 7 Hz, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.22-1.54 (m, 14 H, 7 $\times$ CH_2), and 0.87 (t, J = 7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 193.46 (C=O), 157.90 (3-ArC), 146.68, 139.54, 134.30, 133.16, 132.11, 130.30, 129.04, 126.58 (q, $J_{\text{C,F}}$ = 4 Hz, 2-ArC), 124.82 (q, $J_{\text{C,F}}$ = 4 Hz, 2-ArC), 122.47, 119.97, 111.95, 68.62 (OCH_2), 31.89, 29.59, 29.57, 29.37, 29.32, 29.13, 26.12, 22.68, and 14.11; IR (film) 2925, 2855, 1690 (C=O), 1600, 1455, 1325, 1250, and 1165 cm^{-1} ; MS (DCI) m/e 433 (MH^+).

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For (Z)-2-(3-trifluoromethylphenyl)-3-[4-(2E),(6E)-3,7-dimethylocta-2,6-dienoxy]phenyl)-2-propenal (12d): scale = 1.35 mmol, yield = 92%; ^1H NMR (300 MHz, CDCl_3) δ 9.70 (s, 1 H, CHO), 7.63 (d, J = 8 Hz, 1 H, 2-ArH), 7.53 (t, J = 8 Hz, 1 H, 2-ArH), 7.47 (s, 1 H, $\text{ArCH}=\text{C}$), 7.39 (d, J = 8 Hz, 1 H, 2-ArH), 7.36 (s, 1 H, 2-ArH), 7.10 (dt, J = 3, 9 Hz, 2 H, 3-ArH), 6.75 (dt, J = 3, 9 Hz, 2 H, 3-ArH), 5.41 (dt, J = 1, 7 Hz, 1 H, C=CHCH₂O), 5.03-5.06 (m, 1 H, CH=C(CH₃)₂), 4.51 (d, J = 7 Hz, 2 H, ArOCH_2), 2.03-2.12 (m, 4 H, C=CHCH₂CH₂), and 1.55-1.69 (m, 9 H, 3 $\times$ CH_3); ^{13}C NMR (75

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MHz, CDCl₃) δ 193.11 (C=O), 161.06 (3-ArC), 151.22, 141.89, 138.07, 134.66, 133.10, 132.71 (3-ArC), 131.89, 131.48, 129.34, 126.52 (q, $J^3_{C,f}$ = 4 Hz, 2-ArC), 125.90, 124.99 (q, $J^3_{C,f}$ = 4 Hz, 2-ArC), 123.65, 118.74, 114.92 (3-ArC), 65.03 (ArOCH₂), 39.48, 26.22, 25.66, 17.67, and 16.67; IR (KBr) 2970, 2915, 2890, 1675, 1600, 1570, 1510, 1425, 1325, 1310, 1255, 1180, 1160, and 1115 cm⁻¹; MS (DCI) m/e 429 (MH⁺).

For (Z)-2-(3-trifluoromethylphenyl)-3-(3,4-bisdecyloxyphenyl)-2-propenal (12e): scale = 2.11 mmol, yield = 94%; ¹H NMR (300 MHz, CDCl₃) δ 9.72 (s, 1 H, CHO), 7.40-7.68 (m, 4 H, 2-ArH), 7.37 (s, 1 H, C=CH), 6.91 (dd, J = 2, 8 Hz, 1 H, 3-ArH), 6.79 (d, J = 8 Hz, 1 H, 3-ArH), 6.50 (d, J = 2 Hz, 1 H, 3-ArH), 4.00 (t, J = 7 Hz, 2 H, CH₂OAr), 3.45 (t, J = 7 Hz, 2 H, CH₂OAr), 1.75-1.88 (m, 2 H, CH₂CH₂OAr), 1.55-1.67 (m, 2 H, CH₂CH₂OAr), 1.20-1.48 (m, 28 H, 14 $\times$ CH₂), and 0.83-0.95 (m, 6 H, 2 $\times$ CH₃).

For (Z)-2-(3-trifluoromethylphenyl)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2-propenal (12f): scale = 1.6 mmol, yield = 78%; ¹H NMR (300 MHz, CDCl₃) δ 9.80 (s, 1 H, CHO), 7.75 (s, 1 H, ArH), 7.64-7.68 (m, 3 H, ArH), 7.58 (s, 1 H, ArH), 7.45-7.55 (m, 3 H, 2 $\times$ ArH and C=CH), 4.42 (d, J = 8 Hz, 1 H, ArH), 6.90 (dd, J = 2, 9 Hz, 1 H, ArH), 1.74 (s, 4 H, CH₂CH₂), and 1.35 (br s, 12 H, 4 $\times$ CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 193.26 (C=O), 151.94, 147.10, 145.58, 139.48, 133.30, 132.41, 132.20, 131.33, 130.22, 129.22, 127.41, 126.73, 125.95, 125.15, 124.91, 34.86 (CH₂CH₂), 34.81, 34.61, and 32.43 and 32.38 (4 $\times$ CH₃); IR (KBr) 2960, 2930, 1685 (C=O), 1605, 1325, 1165, and 1125 cm⁻¹.

For (Z)-2-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenal (12g): scale = 1.39 mmol, yield = 89%; ¹H NMR (300 MHz, CDCl₃) δ 9.80 (s, 1 H, CHO), 7.50 (br d, J = 8 Hz, 1 H, 2-ArH), 7.39 (t, J = 8 Hz, 1 H, 2-ArH), 7.31 (s, 1 H, 2-ArH), 7.21 (d, J = 8 Hz, 1 H, 2-ArH), 7.10 (d, J = 8 Hz, 1 H, 5-ArH), 7.04 (d, J = 2 Hz, 1 H, 5-ArH), 6.88 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 6.82 (t, J = 8 Hz, 1 H, C=CH), 2.79 (t, J = 8 Hz, 2 H, ArCH₂), 2.65 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 1.65 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 $\times$ CH₃), and 1.22 (s, 6 H, 2 $\times$ CH₃).

For (Z)-2-(4-fluorophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenal (12h): scale = 1.94 mmol, yield = 95%; ¹H NMR (300 MHz, CDCl₃) δ 9.61 (s, 1 H, CHO), 7.24 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.98-7.08 (m, 3 H, ArH), 6.85-6.93 (m, 3 H, ArH), 6.76 (t, *J* = 8 Hz, 1 H, C=CH), 2.79 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.65 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 × CH₃), and 1.23 (s, 6 H, 2 × CH₃).

For (Z)-2-(3-fluorophenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenal (12i): scale = 2.73 mmol, yield = 94%; ¹H NMR (300 MHz, CDCl₃) δ 9.59 (s, 1 H, CHO), 7.22-7.31 (m, 2 H, 1 × 2-ArH and 1 × 5-ArH), 7.03 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.98 (apparent tt, *J* = 2, 8 Hz, 1 H, 2-ArH), 6.88 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.79 (t, *J* = 8 Hz, 1 H, C=CH), 6.72 (dd, *J* = 2, 8 Hz, 1 H, 2-ArH), 6.63 (apparent dt, *J* = 2, 8 Hz, 1 H, 2-ArH), 2.79 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.64 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.27 (s, 6 H, 2 × CH₃), and 1.24 (s, 6 H, 2 × CH₃).

For (Z)-2-phenyl-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenal (12j): scale = 0.78 mmol, yield = 95%; ¹H NMR (300 MHz, CDCl₃) δ 9.61 (s, 1 H, CHO), 7.28-7.38 (m, 3 H, 2-ArH), 7.22 (d, *J* = 8 Hz, 1 H, 5-ArH), 7.05 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.92-7.00 (m, 2 H, 2-ArH), 6.88 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.75 (t, *J* = 8 Hz, 1 H, C=CH), 2.78 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.66 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.66 (br s, 4 H, CH₂CH₂), 1.26 (s, 6 H, 2 × CH₃), and 1.24 (s, 6 H, 2 × CH₃).

For (Z)-2-(3-trifluoromethylphenyl)-5-[3-(1-adamantyl)-4-methoxyphenyl]-2-pentenal (12k): scale = 0.60 mmol, yield = 100%; ¹H NMR (300 MHz, CDCl₃) δ 9.63 (s, 1 H, CHO), 7.61 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.50 (t, *J* = 8 Hz, 1 H, 2-ArH), 7.30 (s, 1 H, 2-ArH), 7.19 (d, *J* = 8 Hz, 1 H, 2-ArH), 6.96 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.92 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.85 (t, *J* = 8 Hz, 1 H, C=CH), 6.80 (d, *J* = 8 Hz, 1 H, 5-ArH), 3.83 (s, 3 H, OCH₃), 2.80 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.65 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.07 (s, 9 H, adamantyl), and 1.78 (s, 6 H, adamantyl).

For (Z)-2-(3-Phenyl)-5-[3-(1-adamantyl)-4-methoxyphenyl]-2-pentenal (12l): scale = 0.96 mmol, yield = 89%, ca. 6:1 mixture of Z:E

isomers. ^1H NMR (300 MHz, CDCl_3) δ (Z-isomer) 9.60 (s, 1 H, CHO), 7.33-7.39 (m, 3 H, 2-ArH), 7.03-7.07 (m, 2 H, 2-ArH), 6.98 (d, $J = 2$ Hz, 1 H, 5-ArH), 6.93 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.78 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.75 (t, $J = 8$ Hz, 1 H, C=CH), 3.80 (s, 3 H, OCH_3), 2.79 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.64 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.02 (s, 9 H, adamantyl), and 1.76 (s, 6 H, adamantyl).

For (Z)-2-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenal (12m): scale = 1.06 mmol, yield = 87%; ^1H NMR (300 MHz, CDCl_3) δ 9.58 (s, 1 H, CHO), 7.57 (d, $J = 8$ Hz, 1 H, 2-ArH), 7.45 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.30 (s, 1 H, 2-ArH), 7.09 (m, 2 H, 2-ArH and 5-ArH), 6.82 (t, $J = 7$ Hz, 1 H, C=CH), 6.65 (dd, $J = 1, 8$ Hz, 1 H, 5-ArH), 6.57 (d, $J = 2$ Hz, 1 H, 5-ArH), 3.76 (s, 3 H, OCH_3), 2.79 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.63 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.04 (s, 9 H, adamantyl), and 1.76 (s, 6 H, adamantyl).

For (Z)-2-phenyl-5-[4-(1-adamantyl)-3-methoxyphenyl]-2-pentenal (12n): scale = 3.48 mmol, yield = 86%; ^1H NMR (300 MHz, CDCl_3) δ 9.62 (s, 1 H, CHO), 7.30-7.40 (m, 3 H, 2-ArH), 7.11 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.96-7.03 (m, 2 H, 2-ArH), 6.75 (t, $J = 8$ Hz, 1 H, C=CH), 6.68 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.58 (d, $J = 2$ Hz, 1 H, 5-ArH), 3.77 (s, 3 H, OCH_3), 2.79 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.68 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.07 (br s, 9 H, adamantyl), and 1.76 (br s, 6 H, adamantyl).

For (Z)-2-(3-trifluoromethylphenyl)-5-[2-(1-adamantyl)-4-methoxyphenyl]-2-pentenal (12o): scale = 0.30 mmol, yield = 100%; ^1H NMR (300 MHz, CDCl_3) δ 9.65 (s, 1 H, CHO), 7.60 (d, $J = 8$ Hz, 1 H, 2-ArH), 7.49 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.33 (s, 1 H, 2-ArH), 7.26 (m, 1 H, 2-ArH), 6.97 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.89 (m, 2 H, 5-ArH and C=CH), 6.67 (dd, $J = 3, 8$ Hz, 1 H, 5-ArH), 3.77 (s, 3 H, OCH_3), 3.08 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.65 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.04 (s, 3 H, adamantyl), 1.94 (s, 6 H, adamantyl), and 1.74 (m, 6 H, adamantyl).

For (Z)-2-(3-trifluoromethylphenyl)-3-[4-(1-adamantyl)-3-methoxyphenyl]-2-propenal (12p): scale = 2.13 mmol, yield = 94%; ^1H NMR (300 MHz, CDCl_3) δ 9.74 (s, 1 H, CHO), 7.65 (d, $J = 8$ Hz, 1 H, 2-ArH), 7.57 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.51 (s, 1 H, 2-ArH), 7.41 (m, 2 H, 2-

ArH and C=CH), 7.15 (d, $J = 8$ Hz, 1 H, 3-ArH), 6.88 (dd, $J = 2, 8$ Hz, 1 H, 3-ArH), 6.49 (d, $J = 2$ Hz, 1 H, 3-ArH), 3.34 (s, 3 H, OCH₃), 2.00 (s, 9 H, adamantyl), and 1.72 (s, 6 H, adamantyl).

5 For (Z)-2-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-*t*-butyldimethylsilyloxyphenyl]-2-pentenal (12q): scale = 1.43 mmol, yield = 90%; ¹H NMR (300 MHz, CDCl₃) δ 9.60 (s, 1 H, CHO), 7.59 (d, $J = 8$ Hz, 1 H, 2-ArH), 7.46 (t, $J = 8$ Hz, 1 H, 2-ArH), 7.31 (s, 1 H, 2-ArH), 7.11 (m, 2 H, 2-ArH and 5-ArH), 6.82 (t, $J = 7$ Hz, 1 H, HC=CCHO), 6.65 (dd, $J = 1, 8$ Hz, 1 H, 5-ArH), 6.52 (d, $J = 2$ Hz, 1 H, 5-ArH), 2.73 (t, $J = 7$ Hz, 2 H, CH₂Ar), 2.61 (q, $J = 7$ Hz, 2 H, ArCH₂CH₂), 2.07 (s, 9 H, adamantyl), 1.76 (s, 6 H, adamantyl), 1.01 (s, 9 H, *t*-butyl), and 0.28 (s, 6 H, Si(CH₃)₂).

Example 12: General Procedure for Synthesis of 13

15 A solution of 18-crown-6 (5 equivalents) and bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate (1.1 equivalents) in anhydrous tetrahydrofuran was cooled to -78 °C under argon. A solution of potassium bistrimethylsilylamide (0.5 M in toluene, 1.1 equivalents) was added, followed by addition of a solution of the aldehyde 12 (1 equivalent) in tetrahydrofuran (0.05 M final concentration). The reaction mixture was allowed to warm to room temperature and then was poured into a separatory funnel containing diethyl ether and saturated ammonium chloride solution. The layers were agitated and separated. The ether layer was washed further with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification was accomplished by column chromatography (40:1 ratio of silica gel/crude product; elution with 3 to 5% ethyl acetate/hexanes) to provide the target compound.

30 For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-5-(4-decyloxyphenyl)-2,4-pentadienoate (13a): scale = 2.8 mmol, yield = 75%; ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.53 (m, 4 H, 4-ArH), 6.78-6.86 (m, 3 H, 2 x 5-ArH and C=CH), 6.60-6.66 (m, 3 H, 2 x 5-ArH and CH=CHCO₂), 5.81 (d, $J = 16$ Hz, 1 H, CH=CHCO₂), 3.86 (t, $J = 6$ Hz, 2 H, ArOCH₂), 3.25 (s, 3 H, CO₂CH₃), 1.71 (quintet, $J = 6$ Hz, 2 H, ArOCH₂CH₂), 1.24-1.50 (m, 14 H, 7 x CH₂), and 0.85 (t, $J = 6$ Hz, 3 H, CH₃); ¹³C NMR (75 MHz,

CDCl₃) δ 166.82 (C=O), 159.02 (5-Ar), 142.64, 139.32, 136.11, 134.47, 133.26, 131.54, 131.03 (5-ArC), 129.01, 127.73, 126.42 (q, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 124.13 (q, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 119.68, 114.18 (5-ArC), 67.96 (ArOCH₂), 51.22 (CO₂CH₃), 31.87, 29.53, 29.35, 29.30, 29.14, 25.97, 22.66, and 14.10; IR (film) 2925, 2855, 1730 (C=O), 1600, 1510, 1325, 1310, 1255, 1175, and 1165 cm⁻¹; MS (DCI) *m/e* 489 (MH⁺).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-5-(3-decyloxyphenyl)-2,4-pentadienoate (13b): scale = 0.90 mmol, yield = 95%; ¹H NMR (300 MHz, CDCl₃) δ 7.51 (dd, *J* = 2, 7 Hz, 1 H, 4-ArH), 7.48 (s, 1 H, 4-ArH), 7.36-7.44 (m, 2 H, 4-ArH), 7.03 (t, *J* = 8 Hz, 1 H, 5-ArH), 6.84 (br s, 1 H, C=CH), 6.66-6.70 (m, 1 H, 5-ArH), 6.66 (dd, *J* = 2, 12 Hz, 1 H, CH=CHCO₂), 6.54 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.37 (t, *J* = 2 Hz, 1 H, 5-ArH), 5.87 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.56 (t, *J* = 7 Hz, 2 H, ArOCH₂), 3.28 (s, 3 H, CO₂CH₃), 1.55-1.65 (m, 2 H, ArOCH₂CH₂), 1.21-1.35 (m, 14 H, 7 × CH₂), and 0.87 (t, *J* = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.65 (C=O), 158.72 (5-ArC), 142.13, 139.06, 136.60, 135.92, 133.26, 131.08, 130.66, 129.13, 129.01, 126.42 (q, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 124.18 (q, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 122.30, 120.76, 115.29, 114.42, 67.66 (ArOCH₂), 51.28 (CO₂CH₃), 31.89, 29.55, 29.31, 25.88, 22.68, and 14.11; IR (film) 2925, 1730 (C=O), 1435, 1325, 1265, and 1165 cm⁻¹; MS (DCI) *m/e* 489 (MH⁺).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-5-(2-decyloxyphenyl)-2,4-pentadienoate (13c): scale = 0.92 mmol, yield = 72%, 12:1 mixture of *Z:E* isomers. ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.57 (m, 2 H, 4-ArH), 7.33-7.37 (m, 2 H, 4-ArH), 7.07-7.13 (m, 2 H, 5-ArH and C=CH), 6.80 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.72 (dd, *J* = 2, 12 Hz, 1 H, CH=CHCO₂), 6.48-6.70 (m, 2 H, 5-ArH), 5.88 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.95 (t, *J* = 7 Hz, 2 H, ArOCH₂), 3.28 (s, 3 H, CO₂CH₃), 1.78 (quint, *J* = 7 Hz, 2 H, ArOCH₂CH₂), 1.21-1.47 (m, 14 H, 7 × CH₂), and 0.87 (t, *J* = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.77 (C=O), 157.29 (5-ArC), 142.93, 139.27, 136.00, 133.11, 131.55, 130.23, 129.21, 128.68, 126.30 (q, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 124.71, 123.89 (q, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 120.43, 119.73, 68.38 (ArOCH₂), 51.18 (CO₂CH₃), 31.90, 29.58, 29.38, 29.33, 29.19, 26.07, 22.67, and 14.11; IR (film) 2925, 2855, 1730 (C=O), 1325, 1250, and 1165 cm⁻¹; MS (DCI) *m/e* 489 (MH⁺).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-5-[4-(2E),(6E)-3,7-dimethyl-octa-2,6-dien-oxy]phenyl)-2,4-pentadienoate (13d): scale = 1.20 mmol, yield = 62%; ¹H NMR (300 MHz, CDCl₃) δ 7.51-7.53 (m, 1 H, 4-ArH), 7.47 (s, 1 H, 4-ArH), 7.38-7.42 (m, 2 H, 4-ArH), 6.79-6.84 (m, 3 H, 2 x 5-ArH and C=CH), 6.62-6.68 (m, 3 H, 2 x 5-ArH and CH=CHCO₂), 5.81 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 5.41 (t, *J* = 7 Hz, 1 H, C=CHCH₂O), 5.03-5.06 (m, 1 H, CH=C(CH₃)₂), 4.45 (d, *J* = 7 Hz, 2 H, ArOCH₂), 3.26 (s, 3 H, CO₂CH₃), 2.02-2.08 (m, 4 H, C=CHCH₂CH₂), and 1.55-1.68 (m, 9 H, 3 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.80 (C=O), 158.77 (5-ArC), 142.64, 141.37, 139.30, 136.04, 134.53, 133.26, 131.83, 131.02 (5-ArC), 129.02, 127.86, 126.40 (q, *J*_{C,f} = 4 Hz, 4-ArC), 124.12 (q, *J*_{C,f} = 4 Hz, 4-ArC), 123.74, 119.73, 119.16, 114.41 (5-ArC), 64.84 (ArOCH₂), 51.22 (CO₂CH₃), 39.50, 26.26, 25.67, 17.67, and 16.64; IR (film) 2925, 1725 (C=O), 1670, 1600, 1510, 1325, 1310, 1250, 1165, and 1125 cm⁻¹; MS (DCI) *m/e* 485 (MH⁺).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoate (13e): scale = 1.40 mmol, yield = 94%; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.53 (m, 4 H, 4-ArH), 6.81 (s, 1 H, C=CH), 6.57-6.67 (m, 3 H, 2 x 5-ArH and CH=CHCO₂), 6.26 (d, *J* = 2 Hz, 1 H, 5-ArH), 5.79 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.91 (t, *J* = 7 Hz, 2 H, CH₂OAr), 3.43 (t, *J* = 7 Hz, 2 H, CH₂OAr), 3.24 (s, 3 H, CO₂CH₃), 1.70-1.79 (m, 2 H, CH₂CH₂OAr), 1.54-1.61 (m, 2 H, CH₂CH₂OAr), 1.24-1.45 (m, 28 H, 14 x CH₂), and 0.83-0.89 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.81 (C=O), 149.23, 148.33, 142.31, 139.58, 136.64, 134.49, 133.46, 131.00 (q, *J*_{C,f} = 38 Hz, 2-ArC), 129.12, 128.08, 126.57 (q, *J*_{C,f} = 4 Hz, 2-ArC), 124.02 (q, *J*_{C,f} = 4 Hz, 2-ArC), 124.00 (q, *J*_{C,f} = 273 Hz, CF₃), 123.78, 119.47, 113.82, 112.79, 69.00 (CH₂O), 68.50 (CH₂O), 51.21 (CO₂CH₃), 31.90, 29.58, 29.32, 29.12, 29.01, 25.94, 25.80, 22.67, and 14.10; IR (KBr) 2925, 2855, 1730 (C=O), 1595, 1510, 1470, 1435, 1325, 1310, 1270, 1240, 1200, 1165, 1130, 1095, 1070, 1000, 800, and 705 cm⁻¹; MS (DCI) *m/e* 645 (MH⁺).

For Methyl (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoate (13f): scale = 1.3 mmol, yield = 82%; ¹H NMR (300 MHz, CDCl₃) δ 7.62 (s, 1 H, ArH), 7.52-7.57 (m, 3 H, ArH), 7.45 (s, 1 H, ArH), 7.36-7.39 (m, 3 H, ArH), 7.02 (s, 1 H, C=CH), 6.74 (dd, *J* = 2, 9 Hz, 1 H, ArH), 6.72 (dd, *J* = 1, 12 Hz,

1 H, CH=CHCO₂), 5.89 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.28 (s, 3 H, CO₂CH₃), 1.72 (s, 4 H, CH₂CH₂), and 1.33 (s, 12 H, 4 × CH₃); IR (KBr) 3010, 2960, 2930, 2865, 1730 (C=O), 1620, 1465, 1435, 1320, 1310, 1240, 1210, 1170, and 1135 cm⁻¹; MS (DCI) *m/e* 492 (MH⁺).

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For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (13g): scale = 0.74 mmol, yield = 90%; ¹H NMR (300 MHz, CDCl₃) δ 7.48 (br d, *J* = 8 Hz, 1 H, 4-ArH), 7.39 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.36 (s, 1 H, 4-ArH), 7.18 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.98 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.82 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.54 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.07 (t, *J* = 8 Hz, 1 H, C=CH), 5.72 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.18 (s, 3 H, CO₂CH₃), 2.63 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.32 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.23 (s, 6 H, 2 × CH₃), and 1.21 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.50 (C=O), 144.76, 142.58, 141.77, 139.15, 138.69, 137.73, 136.97, 132.51, 128.50, 126.52, 126.39, 125.79 (q, *J*_{C,F} = 4 Hz, 4-ArC), 125.61, 123.75 (q, *J*_{C,F} = 4 Hz, 4-ArC), 119.23, 51.08 (CO₂CH₃), 35.12, 35.07, 34.13, 33.94, 31.86, 31.80, and 31.07; IR (film) 2960, 2925, 2860, 1730 (C=O), 1495, 1460, 1435, 1385, 1365, 1325, 1310, 1280, 1165, 1125, 1095, 1070, 825, 800, and 760 cm⁻¹; MS (DCI) *m/e* 471 (MH⁺).

For Methyl (2Z),(4Z)-4-(4-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (13h): scale = 0.96 mmol, yield = 82%; ¹H NMR (300 MHz, CDCl₃) δ 7.16 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.91-6.98 (m, 5 H, 4 × 4-ArH and 1 × 7-ArH), 6.82 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.52 (d, *J* = 13 Hz, 1 H, CH=CHCO₂), 5.99 (t, *J* = 8 Hz, 1 H, C=CH), 5.69 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.24 (s, 3 H, CO₂CH₃), 2.61 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.32 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 × CH₃), and 1.22 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 166.97, 166.57 (d, *J*_{C,F} = 246 Hz, 4-ArC), 144.07, 142.39, 138.09, 137.99, 137.23, 130.71 (d, *J*_{C,F} = 8 Hz, 4-ArC), 126.44, 125.67, 118.84, 114.79 (*J*_{C,F} = 21 Hz, 4-ArC), 51.15 (CO₂CH₃), 35.16, 35.14, 35.09, 34.14, 33.94, 31.89, 31.84 and 31.06; IR (film) 2960, 2925, 2860, 1730 (C=O), 1600, 1510, 1455, 1435, 1360, 1220, 1195, 1170, 1160, 840, and 820 cm⁻¹; MS (DCI) *m/e* 421 (MH⁺).

For Methyl (2Z),(4Z)-4-(3-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (13i): scale = 1.35 mmol, yield = 91%; ^1H NMR (300 MHz, CDCl_3) δ 7.21-7.27 (m, 1 H, 4-ArH), 7.17 (d, $J = 2$ Hz, 1 H, 7-ArH), 7.00 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.80-6.85 (m, 3 H, 2 x 4-ArH and 1 x 7-ArH), 6.71 (apparent dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 6.51 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 6.01 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.71 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.27 (s, 3 H, CO_2CH_3), 2.62 (t, $J = 8$ Hz, 2 H, ArCH_2CH_2), 2.36 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), 1.64 (br s, 4 H, CH_2CH_2), 1.24 (s, 6 H, 2 x CH_3), and 1.22 (s, 6 H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 166.85 (C=O), 162.47 (d, $J^1_{\text{C},\text{F}} = 246$ Hz, 4-ArC), 144.74, 142.54, 142.07, 140.11 (d, $J^3_{\text{C},\text{F}} = 9$ Hz, 4-ArC), 138.36, 137.92, 137.02, 129.38 (d, $J^3_{\text{C},\text{F}} = 9$ Hz, 4-ArC), 126.45 (d, $J^4_{\text{C},\text{F}} = 3$ Hz, 4-ArC), 125.67, 124.77, 119.04, 115.98 ($J^2_{\text{C},\text{F}} = 21$ Hz, 4-ArC), 113.85 ($J^2_{\text{C},\text{F}} = 21$ Hz, 4-ArC), 51.09 (CO_2CH_3), 35.15, 35.09, 34.15, 33.94, 31.87, 31.83, and 31.10; IR (film) 2960, 2925, 2860, 1730 (C=O), 1610, 1580, 1490, 1455, 1435, 1265, 1195, 1170, 825, 790, and 700 cm^{-1} ; MS (DCI) m/e 421 (MH^+).

For Methyl (2Z),(4Z)-4-phenyl-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (13j): scale = 0.69 mmol, yield = 72%; ^1H NMR (300 MHz, CDCl_3) δ 7.19-7.30 (m, 3 H, 4-ArH), 7.16 (d, $J = 8$ Hz, 1 H, 7-ArH), 7.03-7.07 (m, 2 H, 4-ArH), 7.00 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.84 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.55 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 6.00 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.69 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.19 (s, 3 H, CO_2CH_3), 2.62 (t, $J = 8$ Hz, 2 H, ArCH_2CH_2), 2.36 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), 1.64 (br s, 4 H, CH_2CH_2), 1.24 (s, 6 H, 2 x CH_3), and 1.22 (s, 6 H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.15 (C=O), 144.66, 142.55, 142.41, 138.15, 137.83, 129.03, 127.94, 126.97, 126.42, 125.67, 118.74, 51.08 (CO_2CH_3), 35.27, 35.16, 35.10, 34.15, 33.94, 31.89, 31.84, and 30.04; IR (film) 3020, 2960, 2825, 2860, 1730 (C=O), 1625, 1495, 1455, 1435, 1360, 1275, 1190, 1170, 825, 765, and 700 cm^{-1} ; MS (DCI) m/e 403 (MH^+), 371 ($\text{M}^+ - \text{OCH}_3$).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoate (13k): scale = 0.30 mmol, yield = 82%; ^1H NMR (300 MHz, CDCl_3) δ 7.49 (m, 1 H, 4-ArH), 7.41 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.31 (s, 1 H, 4-ArH), 7.23 (m, 1 H, 4-ArH), 6.91 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.86 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.74 (d, $J =$

8 Hz, 1 H, 7-ArH), 6.55 (dd, $J = 1, 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 6.07 (br t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.73 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.78 (s, 3 H, OCH_3), 3.18 (s, 3 H, CO_2CH_3), 2.62 (t, $J = 7$ Hz, 2 H, ArCH_2), 2.32 (q, $J = 7$ Hz, 2 H, ArCH_2CH_2), 2.04 (s, 9 H, adamantyl), and 1.74 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 166.71 ($\text{C}=\text{O}$), 157.18, 141.77, 139.29, 138.72, 138.36, 137.01, 132.56, 132.49, 128.49, 126.77, 126.21, 125.80, 123.72 (d, $J_{\text{C,F}} = 3$ Hz, 4-ArC), 123.70, 119.17, 111.63, 55.03 (ArOCH_3), 51.07 (CO_2CH_3), 40.55, and 37.12; IR (film) 2905, 2850, 1730 ($\text{C}=\text{O}$), 1325, 1235, 1165, and 1125 cm^{-1} ; MS (DCI) m/e 525 (MH^+), 524 (M^+), 523 (M-H^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{35}\text{O}_3\text{F}_3$: C, 73.26; H, 6.72. Found: C, 72.85; H, 6.66.

For Methyl (2Z),(4Z)-4-phenyl-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoate (13l): scale = 0.86 mmol, yield = 51%; ^1H NMR (300 MHz, CDCl_3) δ 7.19-7.32 (m, 3 H, 4-ArH), 7.07-7.10 (m, 2 H, 4-ArH), 6.92 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.87 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.74 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.55 (dd, $J = 12, 1$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 5.99 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.70 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.78 (s, 3 H, ArOCH_3), 3.19 (s, 3 H, CO_2CH_3), 2.62 (t, $J = 7$ Hz, 2 H, ArCH_2), 2.37 (q, $J = 7$ Hz, 2 H, ArCH_2CH_2), 2.04 (s, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 167.14 ($\text{C}=\text{O}$), 157.11, 142.57, 138.33, 138.12, 137.96, 137.87, 132.92, 129.06, 127.96, 126.95, 126.75, 126.23, 118.71, 111.59, 55.08 (OCH_3), 51.08 (CO_2CH_3), 40.57, 37.14, 36.87, 35.06, 31.34, and 29.11; IR (film) 2905, 2850, 1730 ($\text{C}=\text{O}$), 1495, and 1235 cm^{-1} ; MS (DCI) m/e 457 (MH^+), 425 (M-OCH_3), 255, 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{31}\text{H}_{36}\text{O}_3$: C, 81.54; H, 7.95. Found: C, 81.33; H, 7.81.

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoate (13m): scale = 0.46 mmol, yield = 96%; ^1H NMR (300 MHz, CDCl_3) δ 7.51 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.42 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.38 (s, 1 H, 4-ArH), 7.21 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.08 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.64 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.56 (m, 2 H, $\text{CH}=\text{CHCO}_2$ and 7-ArH), 6.08 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.74 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.75 (s, 3 H, OCH_3), 3.20 (s, 3 H, CO_2CH_3), 2.66 (t, $J = 8$ Hz, 2 H, ArCH_2), 2.36 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), 2.06 (s, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ^{13}C

NMR (75 MHz, CDCl_3) δ 166.69 (C=O), 158.75, 141.74, 139.54, 138.86, 138.70, 137.09, 136.35, 132.55, 132.55, 130.34 (d, $J_{\text{C,F}}^2 = 32$ Hz, 4-ArC), 128.54, 126.41, 125.80 (d, $J_{\text{C,F}}^3 = 4$ Hz, 4-ArC), 124.13 (d, $J_{\text{C,F}}^1 = 270$ Hz, CF_3), 123.77, 120.24, 119.35, 111.88, 54.86 (OCH_3), 51.09 (CO_2CH_3), 40.65, 37.14, 36.68, 35.08, 30.98, and 29.12; IR (film) 2905, 2850, 1730 (C=O), 1325, 1250, 1200, 1165, 1125, and 1070 cm^{-1} ; MS (DCI) m/e 525 (MH^+), 523 (M-H^+), 135 ($\text{C}_{10}\text{H}_{15}^+$); Exact mass spectrum Calcd for $\text{C}_{32}\text{H}_{35}\text{O}_3\text{F}_3\text{Na}$ (MNa^+): 547.2436. Found: 547.2424.

10 For Methyl (2Z),(4Z)-4-phenyl-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoate (13n): scale = 2.95 mmol, yield = 96%; ^1H NMR (300 MHz, CDCl_3) δ 7.18-7.31 (m, 3 H, 4-ArH), 7.04-7.08 (m, 3 H, 2 $\times$ 4-ArH and 1 $\times$ 7-ArH), 6.63 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.52-6.57 (m, 2 H, 1 $\times$ 7-ArH and $\text{CH}=\text{CHCO}_2$), 6.00 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.69 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.74 (s, 3 H, OCH_3), 3.19 (CO_2CH_3), 2.63 (t, $J = 8$ Hz, 2 H, ArCH_2), 2.38 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), 2.04 (br s, 9 H, adamantyl), and 1.73 (br s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 167.13 (C=O), 158.69, 142.50, 139.92, 138.23, 137.80, 137.58, 136.18, 129.05, 127.95, 126.99, 126.28, 120.23, 118.81, 111.95, 54.90 (OCH_3), 52.00 (CO_2CH_3), 40.65, 37.14, 36.65, 35.19, 30.90, and 29.10; IR (film) 2905, 2850, 1730 (C=O), 1610, 1495, 1450, 1435, 1410, 1250, 1200, 1170, 1140, 1040, 1025, 760, and 700 cm^{-1} ; MS (DCI) m/e 457 (MH^+).

25 For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[2-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoate (13o): scale = 0.31 mmol, yield = 80%; ^1H NMR (300 MHz, CDCl_3) δ 7.49 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.41 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.37 (s, 1 H, 4-ArH), 7.31 (d, $J = 7$ Hz, 1 H, 4-ArH), 6.92 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.82 (d, $J = 3$ Hz, 1 H, 7-ArH), 6.62 (dd, $J = 3, 8$ Hz, 1 H, 7-ArH), 6.58 (d, $J = 13$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 6.11 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.75 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.74 (s, 3 H, OCH_3), 3.20 (s, 3 H, CO_2CH_3), 2.92 (m, 2 H, ArCH_2), 2.34 (m, 2 H, ArCH_2CH_2), 2.01 (br s, 3 H, adamantyl), 1.90 (m, 6 H, adamantyl), and 1.71 (m, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 166.68 (C=O), 157.58, 149.01, 141.68, 138.98, 138.67, 136.95, 132.62, 131.74, 128.53, 125.69 (d, $J_{\text{C,F}}^3 = 4$ Hz, 4-ArC), 123.84 (d, $J_{\text{C,F}}^3 = 4$ Hz, 4-ArC), 119.44, 113.08, 109.94, 55.07 (OCH_3), 51.12 (CO_2CH_3), 42.07, 37.84, 36.74, 33.19, 32.90, and 29.08; IR (film) 2910, 2850, 1730 (C=O), 1325, 1165,

and 1130 cm^{-1} ; MS (DCI) m/e 525 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{35}\text{O}_3\text{F}_3 \cdot 0.20 \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$: C, 72.67; H, 6.80. Found: C, 72.65; H, 6.68.

5 For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-pentadienoate (13p): scale = 0.55 mmol, yield = 86%; ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.55 (m, 4 H, 4-ArH), 7.02 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.83 (s, 1 H, $\text{C}=\text{CH}$), 6.60-6.67 (m, 2 H, $\text{CH}=\text{CHCO}_2$ and 5-ArH), 6.25 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.83 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.32 (s, 3 H, OCH_3), 3.26 (s, 3 H, CO_2CH_3), 1.98 (s, 9 H, adamantyl), and 1.71 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 166.74 ($\text{C}=\text{O}$), 158.21, 142.10, 139.42, 139.13, 136.35, 135.84, 133.80, 133.38, 130.95 (d, $J^2_{\text{C,F}} = 32$ Hz, 4-ArC), 129.15, 126.58 (d, $J^3_{\text{C,F}} = 4$ Hz, 4-ArC), 126.36, 124.13 (d, $J^3_{\text{C,F}} = 4$ Hz, 4-ArC), 123.99 (q, $J^1_{\text{C,F}} = 271$ Hz, CF_3), 122.96, 120.08, 112.03, 54.23 (ArOCH_3), 51.26 (CO_2CH_3), 40.36, 37.03, 36.96, and 28.98; IR (film) 2905, 2850, 1730 ($\text{C}=\text{O}$), 1325, 1255, 1205, 1165, and 1130 cm^{-1} ; MS (DCI) m/e 497 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{O}_3\text{F}_3$: C, 72.56; H, 6.29. Found: C, 72.43; H, 6.32.

20 For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-*t*-butyldimethylsilyloxyphenyl]-2,4-heptadienoate (13q): scale = 1.29 mmol, yield = 79%; ^1H NMR (300 MHz, CDCl_3) δ 7.50 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.40 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.36 (s, 1 H, 4-ArH), 7.22 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.07 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.61 (dd, $J = 8, 2$ Hz, 1 H, 7-ArH), 6.54 (d, $J = 13$ Hz, $\text{HC}=\text{CHCO}_2$), 6.48 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.06 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.73 (d, $J = 12$ Hz, 1 H, $\text{HC}=\text{CHCO}_2$), 3.73 (s, 3 H, ArOCH_3), 3.19 (s, 3 H, CO_2CH_3), 2.58 (t, $J = 8$ Hz, 2 H, CH_2Ar), 2.31 (q, $J = 7$ Hz, 2 H, ArCH_2CH_2), 2.05 (s, 9 H, adamantyl), 1.73 (s, 6 H, adamantyl), 0.99 (s, 9 H, *t*-butyl), and 0.26 (s, 6 H, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.69 ($\text{C}=\text{O}$), 154.55, 141.67, 139.11, 138.85, 138.65, 137.28, 137.13, 132.55, 130.38 (d, $J^2_{\text{C,F}} = 32$ Hz), 130.16, 128.53, 126.97, 125.75 (d, $J^3_{\text{C,F}} = 4$ Hz), 123.80 (d, $J^3_{\text{C,F}} = 4$ Hz), 120.33, 119.30, 119.05, 51.10 (CO_2CH_3), 40.44, 37.06, 36.53, 34.75, 30.89, 29.03, 26.40, 18.90 ($\text{C}(\text{CH}_3)_3$), and -3.39 ($\text{Si}(\text{CH}_3)_2$); IR (film) 2930, 2906, 2854, 1730 ($\text{C}=\text{O}$), 1324, 1264, 1254, 1166, 1128, 856, and 836 cm^{-1} ; MS (DCI) m/e 625 (MH^+), 623 (M-H^+), 567 (M-t-butyl^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{37}\text{H}_{47}\text{O}_3\text{F}_3$: C, 71.12; H, 7.58. Found: C, 70.80; H, 7.30.

Example 13: General Procedure for Synthesis of 14

A mixture of ester **13** in methanol/tetrahydrofuran/2N sodium hydroxide solution (1:1:1, 0.1 M) was heated at reflux for 1-4 h. The reaction mixture was then allowed to cool to room temperature and 10% hydrochloric acid solution was added until the solution reached pH 1. The resulting cloudy mixture was extracted with methylene chloride (2 to 4 portions), and the organic phase was washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was evaporated from pentane (3 portions) and then dried in vacuo.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-5-(4-decyloxyphenyl)-2,4-pentadienoic acid (**14a**): scale = 0.49 mmol, yield = 100%, 15:1 mixture of 2Z:2E isomers. mp 86-88 °C; UV_{max} (CH₃OH) 300 nm (ϵ = 20,700), 224 nm (ϵ = 10,900), 324 nm (ϵ = 14,800); ¹H NMR (300 MHz, CD₃OD) δ 7.41-7.57 (m, 4 H, 4-ArH), 6.84-6.90 (m, 3 H, 2 x 5-ArH and C=CH), 6.64-6.70 (m, 3 H, 2 x 5-ArH and CH=CHCO₂), 5.88 (d, J = 12 Hz, 1 H, CH=CHCO₂), 3.89 (t, J = 6 Hz, 2 H, ArOCH₂), 1.70 (quint, J = 6 Hz, 2 H, ArOCH₂CH₂), 1.28-1.50 (m, 14 H, 7 x CH₂), and 0.85 (t, J = 6 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 169.90 (C=O), 160.40 (5-ArC), 143.42, 141.17, 136.29, 135.98, 134.69, 132.11 (5-ArC), 129.49, 127.69 (q, $J^3_{C,F}$ = 4 Hz, 4-ArC), 125.00 (q, $J^3_{C,F}$ = 4 Hz, 4-ArC), 121.90, 115.17 (5-ArC), 68.97 (ArOCH₂), 33.05, 30.68, 30.47, 30.44, 30.30, 23.72, and 14.43; IR (KBr) 2500-3500 (br, CO₂H), 2955, 2940, 2920, 2870, 2850, 1700 (C=O), 1600, 1510, 1470, 1450, 1420, 1325, 1310, 1255, 1180, and 1160 cm⁻¹; MS (DCI) m/e 475 (MH⁺). Anal. Calcd for C₂₈H₃₃O₃: C, 70.87; H, 7.01. Found: C, 70.83; H, 7.03.

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For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-5-(3-decyloxyphenyl)-2,4-pentadienoic acid (**14b**): scale = 0.80 mmol, yield = 99%, 18:1 mixture of 2Z:2E isomers. UV_{max} (CH₃OH) 322 nm (ϵ = 19,000), 234 nm (ϵ = 12,300); ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, J = 7 Hz, 1 H, 4-ArH), 7.41-7.51 (m, 3 H, 4-ArH), 7.06 (t, J = 8 Hz, 1 H, 5-ArH), 6.90 (s, 1 H, C=CH), 6.64-6.74 (m, 2 H, 5-ArH and CH=CHCO₂), 6.61 (d, J = 8 Hz, 1 H, 5-ArH), 6.38 (t, J = 2 Hz, 1 H, 5-ArH), 5.94 (d, J = 12 Hz, 1 H, CH=CHCO₂), 3.56 (t, J

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= 7 Hz, 2 H, ArOCH₂), 1.54-1.64 (m, 2 H, ArOCH₂CH₂), 1.21-1.35 (m, 14 H, 7 × CH₂), and 0.88 (t, *J* = 7 Hz, 3 H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 169.95 (C=O), 160.10 (5-ArC), 142.97, 140.95, 138.38, 135.78, 134.66, 130.34, 130.20, 127.78 (q, *J*_{C,f} = 4 Hz, 4-ArC), 125.17 (q, *J*_{C,f} = 4 Hz, 4-ArC), 123.49, 122.87, 116.19, 115.38, 68.66 (ArOCH₂), 33.07, 30.70, 30.66, 30.46, 30.39, 30.18, 27.00, 23.74, and 14.44; IR (film) 2500-3400 (br, CO₂H), 3060, 2925, 2855, 1695 (C=O), 1600, 1575, 1490, 1470, 1435, 1325, 1265, 1230, and 1165 cm⁻¹; MS (DCI) *m/e* 475 (MH⁺). Anal. Calcd for C₂₈H₃₃O₃F₃: C, 70.87; H, 7.01. Found: C, 70.68; H, 6.99.

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For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-5-(2-decyloxyphenyl)-2,4-pentadienoic acid (14c): scale = 0.61 mmol, yield = 100%, 3.5:1 mixture of 2Z:2E isomers. UV_{max} (CH₃OH) 320 nm (*ε* = 2,900), 245 nm (*ε* = 3,000); ¹H NMR (300 MHz, CD₃OD) δ 7.37-7.68 (m, 3 H, 4-ArH), 7.23-7.30 (m, 1 H, 4-ArH), 7.09-7.15 (m, 1 H, 5-ArH), 7.07 (br s, 1 H, C=CH), 6.74-6.99 (m, 1 H, 5-ArH), 6.72 (dd, *J* = 1, 12 Hz, 1 H, CH=CHCO₂), 6.62 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 6.55 (t, *J* = 8 Hz, 1 H, 5-ArH), 5.97 (d, *J* = 12 Hz, 1 H, CH=CHCO₂, 2Z isomer), 5.38 (d, *J* = 15 Hz, 1 H, CH=CHCO₂, 2E isomer), 3.97-4.05 (m, 2 H, ArOCH₂), 1.73-1.87 (m, 2 H, ArOCH₂CH₂), 1.22-1.58 (m, 14 H, 7 × CH₂), and 0.86-0.89 (m, 3 H, CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 169.80 (C=O), 158.72 (5-ArC), 143.43, 141.02, 137.68, 134.48, 132.10, 131.51, 131.44, 131.15, 130.93, 130.32, 129.94, 127.57 (q, *J*_{C,f} = 4 Hz, 4-ArC), 126.41, 124.92 (q, *J*_{C,f} = 4 Hz, 4-ArC), 123.07, 122.14, 120.77, 113.43, 112.94, 69.45 (ArOCH₂), 33.08, 31.34, 30.75, 30.70, 30.50, 30.34, 27.27, 23.75, and 14.45; IR (film) 2500-3500 (br, CO₂H), 2925, 2855, 1695 (C=O), 1595, 1455, 1325, 1290, 1250, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 475 (MH⁺). Anal. Calcd for C₂₈H₃₃O₃: C, 70.87; H, 7.01. Found: C, 70.83; H, 6.91.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-5-[4-(2E),(6E)-3,7-dimethyl-octa-2,6-dien-oxy]phenyl)-2,4-pentadienoic acid (14d): scale = 0.74 mmol, yield = 98%, 11:1 mixture of 2Z:2E isomers. UV_{max} (CH₃OH) 324 nm (*ε* = 12,600), 234 nm (*ε* = 9,200); ¹H NMR (300 MHz, CD₃OD) δ 7.56 (d, *J* = 7 Hz, 1 H, 4-ArH), 7.41-7.50 (m, 3 H, 4-ArH), 6.84-6.88 (m, 3 H, 2 × 5-ArH and ArCH=C), 6.65-6.70 (m, 3 H, 2 × 5-ArH and CH=CHCO₂), 5.88 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 5.37 (dt, *J* = 1, 7 Hz, 1 H, C=CHCH₂O), 5.04-5.07 (m, 1 H, CH=C(CH₃)₂), 4.48 (d, *J* = 7 Hz, 2 H,

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ArOCH₂), 2.04-2.11 (m, 4 H, C=CHCH₂CH₂), and 1.58-1.69 (m, 9 H, 3 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.15 (C=O), 160.10 (5-ArC), 143.43, 141.93, 141.15, 136.33, 135.98, 134.70, 132.58, 132.07 (5-ArC), 130.33, 129.56, 127.68 (q, ³J_{C,F} = 4 Hz, 4-ArC), 125.12 (q, ³J_{C,F} = 4 Hz, 4-ArC), 124.94, 121.88, 121.03, 115.49 (5-ArC), 65.81 (ArOCH₂), 40.54, 27.34, 25.87, 17.73, and 16.61; IR (KBr) 2500-3500 (br, CO₂H), 3035, 2975, 2930, 2890, 1700 (C=O), 1595, 1510, 1440, 1420, 1330, 1310, 1300, 1255, 1180, 1135, and 1095 cm⁻¹; MS (DCI) *m/e* 471 (MH⁺). Anal. Calcd for C₂₈H₂₉O₃F₃: C, 71.47; H, 6.21. Found: C, 71.29; H, 6.16.

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For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid/(2E),(4Z)-4-(3-Trifluoromethylphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid (14e): scale = 1.09 mmol, yield = 73%, 3:2 mixture of 2Z:2E isomers; UV_{max} (CH₃OH) 350 nm (sh, ε = 21,200), 242 (ε = 13,100); ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.72 (m, 4 H, 4-ArH), 6.91 (s, 1 H, C=CH from E-isomer), 6.83 (s, 1 H, C=CH from Z-isomer), 6.59-6.71 (m, 3 H, 2 x 5-ArH and CH=CHCO₂), 6.31 (d, *J* = 2 Hz, 1 H, 5-ArH from Z-isomer), 6.20 (d, *J* = 2 Hz, 1 H, 5-ArH from E-isomer), 5.78 (d, *J* = 12 Hz, 1 H, CH=CHCO₂ from Z-isomer), 5.26 (d, *J* = 15 Hz, 1 H, CH=CHCO₂ from E-isomer), 3.89-3.94 (m, 2 H, CH₂OAr), 3.43 (t, *J* = 7 Hz, 2 H, CH₂OAr from Z-isomer), 3.36 (t, *J* = 7 Hz, 2 H, CH₂OAr from E-isomer), 1.70-1.79 (m, 2 H, CH₂CH₂OAr), 1.51-1.63 (m, 2 H, CH₂CH₂OAr), 1.21-1.47 (m, 28 H, 14 x CH₂), and 0.83-0.88 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 171.80 (C=O from E-isomer), 166.81 (C=O from Z-isomer), 112.56-151.52 (27 peaks from ArC and C=C, both isomers), 68.99 (CH₂OAr), 68.51 (CH₂OAr), 68.31 (CH₂OAr), 31.90, 29.57, 29.35, 29.12, 28.99, 25.94, 25.79, 22.68, and 14.10; IR (KBr) 2300-3300 (br, CO₂H), 2955, 2920, 2850, 1690 (C=O from Z-isomer), 1675 (C=O from E-isomer), 1615, 1590, 1510, 1470, 1430, 1330, 1275, 1235, 1205, 1165, 1140, 1130, 1070, and 1015 cm⁻¹; MS (FAB) *m/e* 630 (M⁺). Anal. Calcd for C₃₈H₅₃O₄F₃: C, 72.35; H, 8.47. Found: C, 72.45; H, 8.48.

For (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid (14f): scale = 1.0, yield = 100%; UV_{max} (CH₃OH) 332 nm (ε = 23,800), 282 nm (ε = 23,100), and 279 nm (ε = 22,800); ¹H NMR (300 MHz, CD₃OD) δ 7.68 (s, 1

H, ArH), 7.58 (s, 1 H, ArH), 7.52 (s, 1 H, ArH), 7.42-7.47 (m, 2 H, ArH), 7.41 (d, $J = 9$ Hz, 1 H, ArH), 7.08 (br s, 1 H, C=CH), 6.80 (dd, $J = 2, 9$ Hz, 1 H, ArH), 6.76 (dd, $J = 1, 12$ Hz, 1 H, CH=CHCO₂), 5.96 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 1.76 (s, 4 H, CH₂CH₂), and 1.35 (br s, 12 H, 4 × CH₃); ¹³C NMR (75 MHz, CD₃OD/CDCl₃) δ 167.92 (C=O), 144.06, 143.62, 141.45, 138.70, 135.56, 134.22, 132.60, 131.61, 130.84, 130.48, 129.50, 128.09, 128.06, 125.53, 124.70, 124.44, 124.17, 123.63, 123.10, 120.44, 34.02 (CH₂CH₂), 33.46, 33.36, and 30.86 (4 × CH₃); IR (KBr) 2400-3300 (br, CO₂H), 3050, 3010, 2960, 2930, 2985, 1695 (C=O), 1610, 1430, 1325, 1310, 1280, 1250, 1225, 1180, and 1135 cm⁻¹; MS (DCI) m/e 479 (MH⁺). Anal. Calcd. for C₃₀H₂₉O₂F₃ · 0.25 H₂O: C, 74.59; H, 6.15. Found: C, 74.56; H, 6.14.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (14g): scale = 0.62 mmol, yield = 40%; UV_{max} (CH₃OH) 252 nm ($\epsilon = 9,800$); ¹H NMR (300 MHz, CD₃OD) δ 7.51 (br d, $J = 8$ Hz, 1 H, 4-ArH), 7.41 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.33 (s, 1 H, 4-ArH), 7.16 (d, $J = 8$ Hz, 1 H, 7-ArH), 7.13 (d, $J = 8$ Hz, 1 H, 4-ArH), 6.99 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.79 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.57 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 6.08 (t, $J = 8$ Hz, 1 H, C=CH), 5.76 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 2.62 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.27 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 1.66 (br s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 × CH₃), and 1.21 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 169.97 (C=O), 145.64, 143.43, 142.79, 140.42, 139.31, 138.88, 138.66, 134.11, 129.70, 127.53 (q, $J_{C,F} = 4$ Hz, 4-ArC), 126.92 (q, $J_{C,F} = 4$ Hz, 4-ArC), 124.67, 121.24, 36.31, 36.05, 35.06, 34.86, 32.54, and 32.31; IR (film) 2500-3500 (br, CO₂H), 3020, 2960, 2930, 2860, 1700 (C=O), 1615, 1455, 1435, 1355, 1325, 1310, 1280, 1250, 1220, 1165, 1130, 1100, 1070, 760, and 705 cm⁻¹; MS (DCI) m/e 457 (MH⁺). Anal. Calcd for C₂₈H₃₁O₂F₃ · 0.15 H₂O: C, 73.22; H, 6.87. Found: C, 73.25; H, 6.90.

For (2Z),(4Z)-4-(4-Fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (14h): scale = 0.77 mmol, yield = 61%; UV_{max} (CH₃OH) 252 nm ($\epsilon = 12,000$); ¹H NMR (300 MHz, CD₃OD) δ 7.16 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.99 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.91-6.97 (m, 4 H, 4-ArH), 6.79 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.50 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 5.99 (t, $J = 8$ Hz, 1 H, C=CH), 5.72 (d, $J = 12$ Hz, 1 H, CH=CHCO₂), 2.60 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.27 (q, $J = 8$ Hz, 2 H,

ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 x CH₃), and 1.22 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.43, 163.23 (d, $J_{C,F}^1 = 246$ Hz, 4-ArC), 145.59, 143.36, 143.07, 139.52, 138.92, 137.71, 132.19 (d, $J_{C,F}^3 = 8$ Hz, 4-ArC), 127.62, 127.47, 126.95, 120.84, 115.54 (d, $J_{C,F}^2 = 21$ Hz, 4-ArC),
 5 36.32, 36.10, 35.06, 34.85, 32.59, and 32.34; IR (film) 2400-3500 (br, CO₂H), 2960, 2925, 2860, 1695 (C=O), 1605, 1510, 1455, 1435, 1360, 1280, 1220, 1160, 840, 825, and 760 cm⁻¹; MS (DCI) *m/e* 407 (MH⁺), 389 (M⁺ - OH). Anal. Calcd for C₂₇H₃₁O₂F: C, 79.77; H, 7.69. Found: C, 79.40; H, 7.51.

10 For (2Z),(4Z)-4-(3-Fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (14i): scale = 1.13 mmol, yield = 74%; UV_{max} (CH₃OH) 270 nm (sh, ε = 7,700), 242 (ε = 9,700); ¹H NMR (300 MHz, CDCl₃) δ 7.16-7.26 (m, 2 H, 1 x 4-ArH and 1 x 7-ArH), 7.00 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.80-6.91 (m, 3 H, 2 x 4-ArH and 1
 15 x 7-ArH), 6.71 (apparent dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 6.59 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.03 (t, *J* = 8 Hz, 1 H, C=CH), 5.71 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 2.62 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.37 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.64 (br s, 4 H, CH₂CH₂), 1.23 (s, 6 H, 2 x CH₃), and 1.21 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 165.20 (C=O), 162.47 (d, $J_{C,F}^1 =$
 20 246 Hz, 4-ArC), 145.14, 144.74, 142.52, 140.01 (d, $J_{C,F}^3 = 8$ Hz, 4-ArC), 137.98, 137.93, 136.49, 129.41 (d, $J_{C,F}^3 = 8$ Hz, 4-ArC), 126.45, 125.71, 124.77, 115.97 (d, $J_{C,F}^2 = 21$ Hz, 4-ArC), 113.91 (d, $J_{C,F}^2 = 21$ Hz, 4-ArC), 35.14, 35.09, 34.14, 33.94, 31.87, 31.83, and 31.19; IR (film) 2400-3500 (br, CO₂H), 2960, 2925, 2860, 1700 (C=O), 1610, 1580, 1490, 1455, 1440, 1360, 1250, 1220,
 25 1190, 885, 825, 785, and 760 cm⁻¹; MS (DCI) *m/e* 407 (MH⁺). Anal. Calcd for C₂₇H₃₁O₂F: C, 79.77; H, 7.69. Found: C, 79.21; H, 7.76.

For (2Z),(4Z)-4-Phenyl-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (14j): scale = 0.45 mmol, yield =
 30 81%; UV_{max} (CH₃OH) 247 nm (sh, ε = 11,700), 220 (ε = 19,000); ¹H NMR (300 MHz, CD₃OD) δ 7.19-7.27 (m, 3 H, 4-ArH), 7.15 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.95-7.00 (m, 3 H, 2 x 4-ArH and 1 x 7-ArH), 6.80 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.52 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 5.99 (t, *J* = 8 Hz, 1 H, C=CH), 5.73 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 2.60 (t, *J* = 8 Hz, 2 H,
 35 ArCH₂), 2.29 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 1.66 (br s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 x CH₃), and 1.21 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 145.56, 143.67, 143.30, 139.63, 139.44, 136.82, 130.27, 128.91, 128.02, 127.56,

127.45, 126.91, 120.71, 36.36, 36.33, 36.21, 35.06, 34.85, 32.62, and 32.34; IR (film) 2400-3500 (br, CO₂H), 3020, 2960, 2925, 2860, 1695 (C=O), 1620, 1495, 1455, 1440, 1360, 1285, 1245, 825, 760, and 700 cm⁻¹; MS (DCI) *m/e* 389 (MH⁺), 371 (M⁺ - OH). Anal. Calcd for C₂₇H₃₂O₂ · 0.2 H₂O: C, 82.69; H, 8.32. Found: C, 82.76; H, 8.27.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid (14k): scale = 0.19 mmol, yield = 75%; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.37 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.32 (m, 1 H, 4-ArH), 7.21 (d, *J* = 8 Hz, 1 H, 4-ArH), 6.91 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.86 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.73 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.63 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.08 (t, *J* = 8 Hz, 1 H, C=CH), 5.72 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.78 (s, 3 H, OCH₃), 2.62 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.33 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.04 (s, 9 H, adamantyl), and 1.74 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 170.89 (C=O), 157.17, 145.10, 138.98, 138.66, 138.36, 136.50, 132.48, 130.35 (d, *J*_{C,F} = 32 Hz, 4-ArC), 128.43, 126.77, 126.24, 125.75 (d, *J*_{C,F} = 4 Hz, 4-ArC), 124.47, 123.79 (d, *J*_{C,F} = 4 Hz, 4-ArC), 120.48 (d, *J*_{C,F} = 271 Hz, CF₃), 118.41, 111.63, 55.03 (OCH₃), 40.56, 37.13, 36.86, 34.77, 31.50, and 29.10; IR (film) 2400-3500 (br, CO₂H), 2905, 2850, 1700 (C=O), 1325, 1235, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 511 (MH⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₁H₃₃O₃F₃: C, 72.92; H, 6.51. Found: C, 72.93; H, 6.58.

For (2Z),(4Z)-4-Phenyl-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid (14l): scale = 0.37 mmol, yield = 60%; ¹H NMR (300 MHz, CDCl₃) δ 7.19-7.33 (m, 3 H, 4-ArH), 7.12 (m, 2 H, 4-ArH), 6.95 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.90 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.75 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.66 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 6.03 (t, *J* = 8 Hz, 1 H, C=CH), 5.72 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.79 (s, 3 H, ArOCH₃), 2.64 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.41 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.07 (s, 9 H, adamantyl), and 1.77 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 171.65 (C=O), 157.12, 145.98, 138.33, 137.85, 137.44, 137.15, 133.01, 128.02, 127.08, 126.79, 126.31, 118.19, 111.62, 55.10 (OCH₃), 40.60, 37.17, 36.90, 34.93, 31.49, and 29.14; IR (KBr) 2400-3600 (br, CO₂H), 2905, 2850, 1695 (C=O), 1495, 1445, 1235, and 700 cm⁻¹; MS (DCI) *m/e* 443 (MH⁺), 255, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₀H₃₄O₃ · 0.11 H₂O: C, 81.05; H, 7.76. Found: C, 80.68; H, 7.78.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid (**14m**): scale = 0.75 mmol, yield = 77%; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.35 (m, 2 H, 4-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.07 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.60-6.60 (m, 2 H, 7-ArH and CH=CHCO₂), 6.55 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.08 (t, *J* = 7 Hz, 1 H, C=CH), 5.72 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.74 (s, 3 H, OCH₃), 2.64 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.36 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.05 (s, 9 H, adamantyl), and 1.74 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 170.95 (C=O), 158.74, 145.01, 139.59, 138.63, 138.54, 136.56, 136.35, 132.46, 130.36 (d, *J*_{C,F} = 32 Hz, 4-ArC), 128.47, 126.39, 125.78, (d, *J*_{C,F} = 4 Hz, 4-ArC), 123.84 (d, *J*_{C,F} = 4 Hz, 4-ArC), 122.28, 120.25, 118.59, 111.92, 54.87 (OCH₃), 40.64, 37.14, 36.67, 34.92, 31.06, and 29.10; IR (KBr) 2400-3600 (br, CO₂H), 2905, 2850, 1700 (C=O), 1325, 1250, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 511 (MH⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₁H₃₃O₃F₃: C, 72.92; H, 6.51. Found: C, 72.90; H, 6.65.

For (2Z),(4Z)-4-Phenyl-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid (**14n**): scale = 1.93 mmol, yield = 65%; UV_{max} (CH₃OH) 284 nm (sh, ε = 8,000), 276 (ε = 9,200), 242 (ε = 14,500); ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.29 (m, 3 H, 4-ArH), 7.04-7.08 (m, 3 H, 2 × 4-ArH and 1 × 7-ArH), 6.60-6.65 (m, 2 H, 1 × 7-ArH and CH=CHCO₂), 6.56 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.01 (t, *J* = 8 Hz, 1 H, C=CH), 5.71 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 3.73 (s, 3 H, OCH₃), 2.63 (t, *J* = 8 Hz, 2 H, ArCH₂), 2.41 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.04 (br s, 9 H, adamantyl), and 1.74 (br s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 170.48 (C=O), 158.71, 145.81, 139.97, 137.76, 137.58, 136.69, 136.20, 129.03, 127.99, 127.11, 126.28, 120.31, 118.07, 112.06, 54.92 (OCH₃), 40.68, 37.15, 36.66, 35.02, 30.98, and 29.12; IR (KBr) 2400-3600 (br, CO₂H), 3055, 3030, 2905, 2850, 1695 (C=O), 1610, 1570, 1495, 1450, 1410, 1290, 1245, 1180, 1160, 1140, 1040, 1025, 810, and 700 cm⁻¹; MS (DCI) *m/e* 443 (MH⁺). Anal. Calcd for C₃₀H₃₄O₃: C, 81.41; H, 7.74. Found: C, 81.03; H, 7.78.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[2-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid (**14o**): scale = 0.21 mmol, yield = 77%; ¹H NMR (300 MHz, CDCl₃) δ 7.45 (m, 1 H, 4-ArH), 7.36 (m, 2 H, 4-ArH), 7.28 (d, *J* = 8 Hz, 1 H, 4-ArH), 6.92 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.82 (d,

$J = 3$ Hz, 1 H, 7-ArH), 6.60-6.67 (m, 2 H, 7-ArH and $\text{CH}=\text{CHCO}_2$), 6.12 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.74 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.74 (s, 3 H, OCH_3), 2.90 (m, 2 H, ArCH_2), 2.35 (m, 2 H, ArCH_2CH_2), 1.89-2.08 (s, 9 H, adamantyl), and 1.62-1.75 (m, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 170.74 ($\text{C}=\text{O}$), 157.57, 149.02, 145.04, 138.58, 136.42, 132.65, 132.53, 131.79, 130.22, 128.47, 125.67 (d, $\beta_{\text{C},\text{f}} = 4$ Hz, 4-ArC), 123.91 (d, $\beta_{\text{C},\text{f}} = 3$ Hz, 4-ArC), 118.63, 113.08, 109.93, 55.07 (OCH_3), 42.18, 42.05, 37.83, 36.74, 32.99, and 29.07; IR (KBr) 2400-3600 (br, CO_2H), 2905, 2850, 1700 ($\text{C}=\text{O}$), 1610, 1325, 1250, 1165, and 1125 cm^{-1} ; MS (DCI) m/e 511 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{31}\text{H}_{33}\text{O}_3\text{F}_3$: C, 72.92; H, 6.51. Found: C, 72.55; H, 6.47.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-pentadienoic acid (14p): scale = 0.37 mmol, yield = 84%; ^1H NMR (300 MHz, CDCl_3) δ 7.50 (s, 1 H, 4-ArH), 7.34-7.46 (m, 3 H, 4-ArH), 7.03 (d, $J = 8$ Hz, 1 H, 5-ArH), 6.84 (s, 1 H, $\text{C}=\text{CH}$), 6.70 (dd, $J = 1, 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 6.64 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.30 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.80 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.32 (s, 3 H, OCH_3), 1.98 (s, 9 H, adamantyl), and 1.71 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 171.15 ($\text{C}=\text{O}$), 158.21, 145.28, 139.42, 139.24, 136.25, 135.48, 133.80, 133.22, 130.95 (d, $\beta_{\text{C},\text{f}} = 32$ Hz, 4-ArC), 129.09, 126.47 (d, $\beta_{\text{C},\text{f}} = 3$ Hz, 4-ArC), 126.37, 124.21 (d, $\beta_{\text{C},\text{f}} = 3$ Hz, 4-ArC), 123.06, 120.42 (q, $\beta_{\text{C},\text{f}} = 271$ Hz, CF_3), 112.16, 54.22 (OCH_3), 40.36, 37.04, 36.98, and 28.98; IR (KBr) 2400-3600 (br, CO_2H), 2910, 2880, 2850, 1690 ($\text{C}=\text{O}$), 1330, 1250, 1240, 1165, and 1120 cm^{-1} ; MS (DCI) m/e 483 (MH^+), 135 ($\text{C}_{10}\text{H}_{15}^+$). Anal. Calcd for $\text{C}_{29}\text{H}_{29}\text{O}_3\text{F}_3$: C, 72.18; H, 6.06. Found: C, 72.19; H, 6.09.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-hydroxyphenyl]-2,4-heptadienoic acid (14q): prepared from **15** using the general procedure above (example 12). The crude product was purified by column chromatography (20:1 silica gel/crude product; elution with 5% methanol/methylene chloride), scale = 0.33 mmol, yield = 55%; ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.35-7.39 (m, 2 H, 4-ArH), 7.19 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.06 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.59-6.65 (m, 2 H, $\text{CH}=\text{CHCO}_2$ and 7-ArH), 6.34 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.04 (t, $J = 7$ Hz, 1 H, $\text{C}=\text{CH}$), 5.75 (d, $J = 12$ Hz, 1 H, $\text{HC}=\text{CHCO}_2$), 2.58 (t, $J = 7$ Hz, 2 H, CH_2Ar), 2.34 (q, $J = 7$ Hz, 2 H,

ArCH₂CH₂), 2.04-2.07 (m, 9 H, adamantyl), and 1.74 (s, 6 H, adamantyl);
¹³C NMR (75 MHz, CDCl₃) δ 171.18 (C=O), 154.28, 145.48, 139.66, 138.58,
 137.84, 136.34, 134.21, 132.46, 130.43 (d, $J^2_{c,f}$ = 32 Hz, 4-ArC), 128.58,
 126.95, 125.69 (d, $J^3_{c,f}$ = 4 Hz, 4-ArC), 124.07 (d, $J^1_{c,f}$ = 271 Hz, CF₃), 123.96
 5 (d, $J^3_{c,f}$ = 3 Hz, 4-ArC), 120.58, 118.51, 116.97, 40.59, 37.05, 36.38, 34.27,
 30.82, and 29.02; IR (KBr) 2500-3600 (br, CO₂H), 2905, 2850, 1680 (C=O),
 1615, 1420, 1325, 1270, 1260, 1225, 1165, 1125, and 1075 cm⁻¹; MS (DCI)
m/e 497 (MH⁺), 496 (M⁺), 495 (M-H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for
 C₃₀H₃₁O₃F₃: C, 72.56; H, 6.29. Found: C, 72.56; H, 6.37.

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For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-
 pentyloxyphenyl]-2,4-heptadienoic acid (**14r**): prepared from **16r**;
 purified by column chromatography (40:1 silica gel/crude product;
 elution with 3% methanol/methylene chloride); scale = 0.55 mmol,
 15 yield = 74%; ¹H NMR (300 MHz, CDCl₃) δ 7.45 (d, J = 7 Hz, 1 H, 4-ArH),
 7.33-7.38 (m, 2 H, 4-ArH), 7.17 (d, J = 8 Hz, 1 H, 4-ArH), 7.06 (d, J = 8 Hz,
 1 H, 7-ArH), 6.57-6.65 (m, 2 H, 7-ArH and HC=CHCO₂), 6.54 (d, J = 2 Hz,
 1 H, 7-ArH), 6.08 (t, J = 8 Hz, 1 H, C=CH), 5.73 (d, J = 12 Hz, 1 H,
 HC=CHCO₂), 3.86 (t, J = 6.5 Hz, 2 H, OCH₂), 2.63 (t, J = 8 Hz, 2 H, CH₂Ar),
 20 2.36 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 2.04-2.07 (m, 9 H, adamantyl), 1.83
 (quint, J = 7 Hz, 2 H, OCH₂CH₂), 1.74 (s, 6 H, adamantyl), 1.45-1.56 (m, 2
 H, O(CH₂)₂CH₂), 1.33-1.42 (m, 2 H, O(CH₂)₃CH₂), and 0.93 (t, J = 7 Hz, 3
 H, O(CH₂)₄CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.84 (C=O), 158.09,
 145.00, 139.49, 138.73, 138.61, 136.57, 136.04, 132.48, 130.36 (d, $J^2_{c,f}$ = 32 Hz,
 4-ArC), 128.46, 126.35, 125.76, 123.80, 119.92, 119.59, 118.49, 112.08, 67.52
 25 (OCH₂), 40.59, 37.17, 36.70, 35.12, 31.09, 30.27, 29.12, 28.65, 22.43, and
 14.08; IR (film) 2400-3300 (br, CO₂H), 2905, 2850, 1700 (C=O), 1325, 1165,
 and 1130 cm⁻¹; MS (DCI) *m/e* 567 (MH⁺), 549 (M-OH)⁺, 431 (M-
 C₁₀H₁₅)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₅H₄₁O₃F₃: C, 74.18; H, 7.29.
 30 Found: C, 73.99; H, 7.39.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-
 (3,5-difluorobenzyloxy)phenyl]-2,4-heptadienoic acid (**14s**): prepared
 from **16s**; purified by column chromatography (20:1 silica gel/crude
 35 product; elution with 3% methanol/methylene chloride); scale = 0.48
 mmol, yield = 86%; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, J = 8 Hz, 1 H,
 4-ArH), 7.32-7.38 (m, 2 H, 4-ArH), 7.17 (d, J = 8 Hz, 1 H, 4-ArH), 7.13 (d, J

= 8 Hz, 1 H, 7-ArH), 7.00 (d, J = 6 Hz, 2 H, HArCH₂), 6.67-6.78 (m, 2 H, HArCH₂ and 7-ArH), 6.62 (d, J = 13 Hz, 1 H, HC=CHCO₂), 6.56 (d, J = 1.5 Hz, 1 H, 7-ArH), 6.05 (t, J = 8 Hz, 1 H, C=CH), 5.73 (d, J = 12 Hz, 1 H, HC=CHCO₂), 4.98 (s, 2 H, OCH₂), 2.63 (t, J = 8 Hz, 2 H, CH₂Ar), 2.35 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 2.04-2.08 (m, 9 H, adamantyl), and 1.72 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 170.71 (C=O), 163.22 (d, $J^1_{C,F}$ = 247 Hz, 3,5-difluorobenzyl), 157.23, 145.02, 139.73, 138.58, 138.34, 136.64, 136.47, 132.43, 128.49, 126.88, 125.76, 123.89, 121.08, 118.57, 112.79, 109.68 (d, $J^2_{C,F}$ = 25 Hz, 3,5-difluorobenzyl), 102.98 (t, $J^2_{C,F}$ = 25 Hz, 3,5-difluorobenzyl), 68.89 (CH₂O), 40.68, 37.04, 36.77, 34.85, 31.02, and 29.02; IR (KBr) 2400-3600 (br, CO₂H), 2905, 2850, 1700 (C=O), 1630, 1600, 1325, 1245, 1165, 1120, 1070 cm⁻¹; MS (DCI) m/e 623 (MH⁺), 622 (M⁺), 621 (M-H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₇H₃₅O₃F₅: C, 71.37; H, 5.67. Found: C, 70.93; H, 5.62.

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For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(4-methoxybenzyloxy)phenyl]-2,4-heptadienoic acid (14t): prepared from 16t; purified by column chromatography (20:1 silica gel/crude product; elution with 3% methanol/methylene chloride); scale = 0.55 mmol, yield = 73%; ¹H NMR (300 MHz, CDCl₃) δ 7.46 (d, J = 8 Hz, 1 H, 4-ArH), 7.32-7.40 (m, 4 H, 2 x 4-ArH and 2 x HArCH₂), 7.17 (d, J = 7.5 Hz, 1 H, 4-ArH), 7.10 (d, J = 8 Hz, 1 H, 7-ArH), 6.91 (dt, J = 9, 2 Hz, 2 H, HArCH₂), 6.59-6.66 (m, 3 H, 2 x 7-ArH and HC=CHCO₂), 6.06 (t, J = 7 Hz, 1 H, C=CH), 5.73 (d, J = 12 Hz, 1 H, HC=CHCO₂), 4.93 (s, 2 H, OCH₂), 3.82 (s, 3 H, OCH₃), 2.64 (t, J = 8 Hz, 2 H, CH₂Ar), 2.36 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 2.07-2.08 (m, 6 H, adamantyl), 1.99 (s, 3 H, adamantyl), and 1.68 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 170.60 (C=O), 159.14, 157.80, 144.99, 139.57, 138.61, 138.56, 136.59, 136.39, 132.47, 130.57, 130.14, 129.71, 129.46, 128.88, 128.48, 126.57, 125.79 (d, $J^3_{C,F}$ = 4 Hz, 4-ArC), 123.85 (d, $J^3_{C,F}$ = 4 Hz, 4-ArC), 122.29, 120.44, 118.50, 113.81, 112.75, 69.73 (OCH₂), 55.29 (OCH₃), 40.56, 37.08, 36.73, 34.91, 31.04, and 29.06; IR (KBr) 2500-3600 (br, CO₂H), 2905, 2850, 1700 (C=O), 1610, 1515, 1325, 1245, 1165, 1130, 1070, 1030, and 805 cm⁻¹; MS (DCI) m/e 617 (MH⁺), 616 (M⁺), 615 (M-H)⁺, 135 (C₁₀H₁₅⁺), 121. Anal. Calcd for C₃₈H₃₉O₄F₃: C, 74.01; H, 6.37. Found: C, 73.77; H, 6.35.

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For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-benzyloxyphenyl]-2,4-heptadienoic acid (**14u**): prepared from **16u**; purified by column chromatography (20:1 silica gel/crude product; elution with 3% methanol/methylene chloride), scale = 0.47 mmol, yield = 98%; ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.48 (m, 8 H, 5 × HArCH₂ and 3 × 4-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.12 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.60-6.67 (m, 3 H, 2 × 7-ArH and HC=CHCO₂), 6.07 (t, *J* = 7 Hz, 1 H, C=CH), 5.73 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 5.01 (s, 2 H, OCH₂), 2.64 (t, *J* = 8 Hz, 2 H, CH₂Ar), 2.36 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.01-2.10 (m, 9 H, adamantyl), and 1.70 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 170.86 (C=O), 157.74, 145.07, 139.62, 138.61, 137.40, 136.60, 136.42, 130.37 (d, *J*_{C,F} = 32 Hz, 4-ArC), 132.46, 128.46, 127.65, 127.25, 126.63, 125.82, 123.83, 120.55, 118.50, 112.76, 70.00 (OCH₂), 40.58, 37.07, 36.75, 34.91, 31.05, and 29.06; IR (KBr) 2400-3600 (CO₂H), 2905, 2850, 1700 (C=O), 1325, 1245, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 587 (MH⁺), 135 (C₁₀H₁₅⁺), 91 (C₇H₇⁺). Anal. Calcd for C₃₇H₃₇O₃F₃: C, 75.75; H, 6.36. Found: C, 75.58; H, 6.53.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(carboxymethoxy)phenyl]-2,4-heptadienoic acid (**14v**): prepared from methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(carbo-*t*-butoxymethoxy)-phenyl]-2,4-heptadienoate (**16v**) according to the general procedure except that the reflux time was increased to 48 h, scale = 0.16 mmol, yield = 90%; ¹H NMR (300 MHz, CDCl₃) δ 10.19 (br s, 2 H, CO₂H), 7.46 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.32-7.37 (m, 2 H, 4-ArH), 7.11-7.15 (m, 2 H, 4-ArH and 7-ArH), 6.70 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.64 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 6.43 (s, 1 H, 7-ArH), 6.07 (t, *J* = 7 Hz, 1 H, C=CH), 5.75 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 4.58 (s, 2 H, OCH₂), 2.64 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.37 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.04-2.08 (m, 9 H, adamantyl), and 1.75 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 174.87 (C=O), 171.77 (C=O), 156.53, 145.33, 139.61, 138.51, 138.29, 136.77, 136.54, 132.47, 130.41 (d, *J*_{C,F} = 32 Hz, 4-ArC), 128.56, 127.04, 125.70, 123.90, 122.25, 121.53, 118.49, 112.49, 64.77 (OCH₂), 40.60, 37.01, 36.74, 34.63, 30.88, and 29.08; IR (KBr) 2400-3600 (br, CO₂H), 2905, 2850, 1730 (C=O), 1705 (C=O), 1435, 1420, 1325, 1245, 1165, 1130, and 1070 cm⁻¹; MS (DCI) *m/e* 555 (MH⁺), 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₂H₃₃F₃O₅: C, 69.30; H, 6.00. Found: C, 69.12; H, 5.98.

Example 14: Procedure for Synthesis of Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-hydroxyphenyl]-2,4-heptadienoate (15)

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A colorless solution of **13q** (2.50 g, 4.00 mmol) in THF (100 mL) was treated dropwise with a 1.1 M solution of tetrabutylammonium fluoride (3.64 mL, 4.00 mmol). After 5 min, the yellow reaction mixture was partitioned between ether and a saturated ammonium chloride solution. The organic phase was washed with brine, dried with anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography (40:1 silica gel/crude product; elution with hexane and then 2:1 methylene chloride/hexane) to give 1.99 g of a yellow oil. The oil was dissolved in pentane (150 mL) and cooled at -30 °C. The precipitate which formed over the course of 18 h was collected by filtration, and dried in vacuo to give 1.57 g (77%) of **15** as a yellow solid; mp 72-4 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.42 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.38 (s, 1 H, 4-ArH), 7.24 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.08 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.62 (dd, *J* = 8, 2 Hz, 1 H, 7-ArH), 6.57 (d, *J* = 12 Hz, HC=CHCO₂), 6.41 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.03 (t, *J* = 8 Hz, 1 H, C=CH), 5.77 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 4.95 (s, 1 H, OH), 3.27 (s, 3 H, CO₂CH₃), 2.62 (t, *J* = 7 Hz, 2 H, CH₂Ar), 2.35 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.06-2.09 (m, 9 H, adamantyl), and 1.77 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 166.86 (C=O), 154.38, 142.16, 139.60, 138.63, 138.21, 136.93, 134.21, 132.52, 130.34 (d, *J*_{C,F} = 32 Hz, 4-ArC), 128.59, 126.89, 125.73 (d, *J*_{C,F} = 4 Hz, 4-ArC), 123.84 (d, *J*_{C,F} = 4 Hz, 4-ArC), 120.55, 119.38, 116.81, 51.25 (CO₂CH₃), 40.59, 37.05, 36.37, 34.36, 30.58, and 29.01; IR (KBr) 3385 (OH), 2905, 2850, 1700 (C=O), 1325, 1315, 1230, 1155, 1125, 1075 cm⁻¹; MS (DCI) *m/e* 511 (MH⁺), 509 (M-H)⁺, 135 (C₁₀H₁₅⁺). Anal. Calcd for C₃₁H₃₃O₃F₃ • C₅H₁₂: C, 73.60; H, 7.19. Found: C, 73.62; H, 7.04.

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Example 15: General Procedure for Synthesis of 16

Procedure A: A solution of phenol **15** (1 equivalent) in acetone (0.2-0.3 M) was treated with the alkyl halide (1-2 equivalents),

potassium iodide (0 to 0.1 equivalents), and powdered, anhydrous potassium carbonate (1 equivalent). The heterogeneous reaction mixture was stirred and heated at reflux for 24 h. The resulting slurry was cooled slightly, and then the acetone was removed under reduced pressure. The residue was partitioned between ether and water. The organic phase was washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography (20:1 to 40:1 ratio silica gel/crude product; elution with 5% ethyl acetate/hexane).

Procedure B: A solution of the phenol **15** (1 equivalent) and the alkyl halide (1-1.5 equivalents) in dimethylformamide (ca. 0.12 M) under a nitrogen atmosphere was treated with sodium hydride (60 % dispersion in oil, 0.98 equivalents). The mixture was stirred for 1-18 h. The reaction mixture was partitioned between water and 2:1 hexane/ethyl acetate. The organic phase was washed with water (5x), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography (20:1 to 40:1 ratio silica gel/crude product; elution with 5-10% ethyl acetate/hexane).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-pentyloxyphenyl]-2,4-heptadienoate (**16r**): via procedure B using pentyl iodide, scale = 0.59 mmol, yield = 58%; ^1H NMR (300 MHz, CDCl_3) δ 7.51 (d, J = 8 Hz, 1 H, 4-ArH), 7.39-7.44 (m, 2 H, 4-ArH), 7.21 (d, J = 8 Hz, 1 H, 4-ArH), 7.09 (d, J = 8 Hz, 1 H, 7-ArH), 6.63 (d, J = 8 Hz, 1 H, 7-ArH), 6.55-6.59 (m, 7-ArH and $\text{HC}=\text{CHCO}_2$), 6.09 (t, J = 8 Hz, 1 H, $\text{C}=\text{CH}$), 5.75 (d, J = 12 Hz, 1 H, $\text{HC}=\text{CHCO}_2$), 3.89 (t, J = 6.5 Hz, 2 H, OCH_2), 3.21 (s, 3 H, CO_2CH_3), 2.66 (t, J = 8 Hz, 2 H, CH_2Ar), 2.37 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 2.06-2.10 (m, 9 H, adamantyl), 1.76-1.90 (m, 8 H, OCH_2CH_2 and 6 x adamantyl), 1.54 (quint, J = 7 Hz, 2 H, $\text{O}(\text{CH}_2)_2\text{CH}_2$), 1.43 (quint, J = 7 Hz, 2 H, $\text{O}(\text{CH}_2)_3\text{CH}_2$), and 0.96 (t, J = 7 Hz, 3 H, $\text{O}(\text{CH}_2)_4\text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 166.71 ($\text{C}=\text{O}$), 158.13, 141.76, 139.45, 138.97, 138.72, 137.08, 136.06, 132.57, 130.34 (d, $J^2_{\text{C},\text{F}}$ = 32 Hz, 4-ArC), 128.55, 126.38, 125.82 (d, $J^3_{\text{C},\text{F}}$ = 4 Hz, 4-ArC), 123.75 (d, $J^3_{\text{C},\text{F}}$ = 4 Hz, 4-ArC), 120.63 (d, $J^1_{\text{C},\text{F}}$ = 257 Hz, CF_3), 119.92, 119.31, 112.07, 67.52 (OCH_2), 51.10 (CO_2CH_3), 40.64, 37.20, 36.73, 35.12, 31.02, 29.20, 29.16, 28.68, 22.45,

and 14.10; IR (film) 2905, 2850, 1730 (C=O), 1325, 1165, and 1125 cm^{-1} ; MS (DCI) m/e 581 (MH^+), 549 (M-OCH_3) $^+$, 445 ($\text{M-C}_{10}\text{H}_{15}$) $^+$, 135 ($\text{C}_{10}\text{H}_{15}$) $^+$. Anal. Calcd for $\text{C}_{36}\text{H}_{43}\text{O}_3\text{F}_3$: C, 74.46; H, 7.46. Found: C, 74.40; H, 7.33.

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For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(3,5-difluorobenzyloxy)phenyl]-2,4-heptadienoate (16s): via procedure B using 3,5-difluorobenzyl bromide, scale = 0.65 mmol, yield = 82%; ^1H NMR (300 MHz, CDCl_3) δ 7.49 (d, J = 8 Hz, 1 H, 4-ArH), 7.40 (t, J = 8 Hz, 1 H, 4-ArH), 7.35 (s, 1 H, 4-ArH), 7.19 (d, J = 8 Hz, 1 H, 4-ArH), 7.13 (d, J = 8 Hz, 1 H, 7-ArH), 6.97-7.00 (m, 2 H, HArCH_2), 6.75 (tt, J = 9, 2 Hz, 1 H, HArCH_2), 6.69 (dd, J = 8, 2 Hz, 1 H, 7-ArH), 6.52-6.56 (m, 2 H, 7-ArH and HC=CHCO_2), 6.05 (t, J = 7.5 Hz, 1 H, C=CH), 5.74 (d, J = 12 Hz, 1 H, HC=CHCO_2), 4.99 (s, 2 H, OCH_2Ar), 3.19 (s, 3 H, OCH_3), 2.64 (t, J = 8 Hz, 2 H, CH_2Ar), 2.33 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 2.04-2.09 (m, 9 H, adamantyl), and 1.72 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 166.67 (C=O), 168.33 (d, $J_{\text{C,F}}^1$ = 248 Hz, 3,5-difluorobenzyl), 157.23, 141.69, 141.49, 139.69, 138.64, 138.59, 137.13, 136.47, 132.50, 128.55, 126.88, 125.79 (d, $J_{\text{C,F}}^3$ = 4 Hz, 4-ArC), 123.81 (d, $J_{\text{C,F}}^3$ = 4 Hz, 4-ArC), 121.06, 119.42, 112.78, 109.60, 109.66 (d, $J_{\text{C,F}}^2$ = 25 Hz, 3,5-difluorobenzyl), 102.99 (t, $J_{\text{C,F}}^2$ = 25 Hz, 3,5-difluorobenzyl), 68.88 (CH_2O), 51.12 (OCH_3), 40.68, 37.03, 36.77, 35.01, 30.94, and 29.01; IR (film) 2905, 2850, 1725 (C=O), 1600, 1325, 1165, 1120, and 1070 cm^{-1} ; MS (DCI) m/e 637 (MH^+), 636 (M^+), 635 (M-H) $^+$, 605 (M-OCH_3) $^+$, 135 ($\text{C}_{10}\text{H}_{15}$) $^+$. Anal. Calcd for $\text{C}_{38}\text{H}_{37}\text{O}_3\text{F}_5$: C, 71.69; H, 5.86. Found: C, 71.53; H, 5.82.

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For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(4-methoxybenzyloxy)phenyl]-2,4-heptadienoate (16t): via procedure A using 4-methoxybenzyl chloride, scale = 0.65 mmol, yield = 84%; ^1H NMR (300 MHz, CDCl_3) δ 7.52 (d, J = 8 Hz, 1 H, 4-ArH), 7.38-7.45 (m, 4 H, 2 $\times$ 4-ArH and 2 $\times$ HArCH_2), 7.21 (d, J = 7.5 Hz, 1 H, 4-ArH), 7.11 (d, J = 8 Hz, 1 H, 7-ArH), 6.93 (d, J = 9 Hz, 2 H, HArCH_2), 6.65-6.69 (m, 2 H, 2 $\times$ 7-ArH), 6.56 (d, J = 12 Hz, 1 H, HC=CHCO_2), 6.09 (t, J = 7 Hz, 1 H, C=CH), 5.67 (d, J = 12 Hz, 1 H, HC=CHCO_2), 4.94 (s, 2 H, OCH_2), 3.83 (s, 3 H, ArOCH_3), 3.20 (s, 3 H, CO_2CH_3), 2.67 (t, J = 8 Hz, 2 H, CH_2Ar), 2.38 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 2.09 (s, 6 H, adamantyl), 2.01 (s, 3 H, adamantyl), and 1.60 (s, 6 H, adamantyl).

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For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-benzyloxyphenyl]-2,4-heptadienoate (16u): via procedure A using benzyl bromide, scale = 0.59 mmol, yield = 92%; via procedure B, scale = 0.08 mmol, yield = 79%; ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.52 (m, 8 H, 5 × HArCH₂ and 3 × 4-ArH), 7.20 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.13 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.66-6.68 (m, 2 H, 2 × 7-ArH), 6.55 (d, *J* = 13 Hz, 1 H, HC=CHCO₂), 6.07 (t, *J* = 7 Hz, 1 H, C=CH), 5.75 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 5.03 (s, 2 H, OCH₂), 3.19 (s, 3 H, OCH₃), 2.66 (t, *J* = 8 Hz, 2 H, CH₂Ar), 2.35 (q, *J* = 8 Hz, 2 H, ArCH₂CH₂), 2.02-2.11 (m, 9 H, adamantyl), and 1.71 (s, 6 H, adamantyl); IR (film) 2905, 2850, 1700 (C=O), 1325, 1245, 1165, 1130, 1070, 1025, 805, and 695 cm⁻¹; MS (DCI) *m/e* 601 (MH⁺), 600 (M⁺), 599 (M-H)⁺, 509 (M-CH₂Ph)⁺, 135 (C₁₀H₁₅⁺).

For Methyl (2Z),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(carbo-*t*-butoxymethoxy)phenyl]-2,4-heptadienoate (16v): prepared via procedure B using *t*-butyl bromoacetate, scale = 1.30 mmol, yield = 62%. ¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.42 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.37 (s, 1 H, 4-ArH), 7.22 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.11 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.68 (dd, *J* = 8, 2 Hz, 1 H, 7-ArH), 6.57 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 6.41 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.07 (t, *J* = 7 Hz, 1 H, C=CH), 5.77 (d, *J* = 12 Hz, 1 H, HC=CHCO₂), 4.43 (s, 2 H, OCH₂), 3.20 (s, 3 H, OCH₃), 2.63 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.35 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.06-2.11 (m, 9 H, adamantyl), 1.72-1.82 (m, 6 H, adamantyl), and 1.48 (s, 9 H, *t*-butyl).

Example 16: General Procedure for Synthesis of 17

A solution of aldehyde **2** (1 equivalent) in anhydrous toluene (0.1 M) at room temperature under argon was treated sequentially with methyl diethylphosphonoacetate (1.5 equivalents) and sodium methoxide (25 wt% in methanol, 1.4 equivalents). The reaction mixture was stirred at room temperature for 12-16 h, and then treated with additional sodium methoxide (25 wt% in methanol, 1 equivalent). The mixture was stirred for 0.5 h and then partitioned between diethyl ether and saturated ammonium chloride solution. The organic layer was washed with saturated sodium chloride

solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification by column chromatography (40:1 ratio of silica gel/crude product; elution with 5% ethyl acetate in hexanes) gave the desired product.

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For Methyl (2E),(4Z)-4-(3-carbomethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-pentadienoate (17a): scale = 0.81 mmol, yield = 75%; UV_{max} (CH₃OH) 326 nm (ϵ = 36,800), 232 nm (ϵ = 20,900); ¹H NMR (300 MHz, CDCl₃) δ 8.06 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.87 (t, J = 2 Hz, 1 H, 4-ArH), 7.67 (d, J = 16 Hz, 1 H, CH=CHCO₂), 7.52 (t, J = 8 Hz, 1 H, 4-ArH), 7.36 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.07 (d, J = 8 Hz, 1 H, 5-ArH), 6.90 (s, 1 H, C=CH), 6.82 (d, J = 2 Hz, 1 H, 5-ArH), 6.72 (dd, J = 2, 8 Hz, 1 H, 5-ArH), 5.80 (d, J = 16 Hz, 1 H, CH=CHCO₂), 3.88 (s, 3 H, CO₂CH₃), 3.70 (s, 3 H, CO₂CH₃), 1.51-1.60 (m, 4 H, CH₂CH₂), 1.17 (s, 6 H, 2 $\times$ CH₃), and 0.92 (s, 6 H, 2 $\times$ CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.60 (C=O), 166.71 (C=O), 149.80, 146.02, 144.79, 139.69, 137.88, 137.23, 134.05, 132.34, 131.28, 130.51, 129.48, 129.04, 128.40, 127.73, 126.63, 119.11, 52.20 (CO₂CH₃), 51.52 (CO₂CH₃), 34.79, 34.22, 33.92, 31.54, and 31.38; IR (film) 2955, 2860, 1720 (C=O), 1615, 1590, 1435, 1310, 1280, 1265, 1205, 1190, 1170, 1120, 1095, 1080, and 980 cm⁻¹; MS (DCI) m/e 433 (MH⁺), 401 (M⁺ - OCH₃).

For Methyl (2E),(4Z)-4-(3-carbomethoxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoate (17b): scale = 1.80 mmol, yield = 99%; ¹H NMR (300 MHz, CDCl₃) δ 8.08 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 7.88 (t, J = 2 Hz, 1 H, 4-ArH), 7.72 (d, J = 15 Hz, 1 H, CH=CHCO₂), 7.53 (d, J = 12 Hz, 2 H, ArH), 7.45-7.51 (m, 2 H, ArH), 7.32-7.37 (m, 2 H, ArH), 7.01 (s, 1 H, C=CH), 6.67 (dd, J = 2, 9 Hz, 1 H, ArH), 5.43 (d, J = 15 Hz, 1 H, CH=CHCO₂), 3.89 (s, 2 H, CO₂CH₃), 3.72 (s, 3 H, CO₂CH₃), 1.71 (s, 4 H, CH₂CH₂), and 1.17-1.23 (m, 15 H, 4 $\times$ CH₃ and CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.64 (C=O), 166.77 (C=O), 149.50, 145.74, 144.99, 142.30, 139.97, 138.77, 137.86, 137.49, 134.28, 133.62, 132.13, 131.35, 131.12, 130.62, 129.37, 129.19, 126.91, 125.44, 124.66, 123.01, 119.41, 52.25 (CO₂CH₃), 51.60 (CO₂CH₃), 34.96, 34.67, 32.44 (4 $\times$ CH₃), and 29.73; IR (film) 2955, 2925, 2860, 1720 (C=O), 1615, 1595, 1460, 1435, 1365, 1305, 1295, 1265, 1210, 1195, 1170, 1120, and 1110 cm⁻¹; MS (DCI) m/e 483 (MH⁺), 451 (MH⁺ - CH₃OH).

For Methyl (2E),(4Z)-4-(3-carbomethoxyphenyl)-5-(3,4-bis(pentyloxyphenyl)-2,4-pentadienoate (17c): scale = 0.32 mmol, yield = 95%; ^1H NMR (300 MHz, CDCl_3) δ 8.03 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 7.87 (t, $J = 2$ Hz, 1 H, 4-ArH), 7.65 (dd, $J = 1, 15.5$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.51 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.36 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 6.86 (d, $J = 1$ Hz, 1 H, $\text{C}=\text{CH}$), 6.60-6.67 (m, 2 H, 2 x 5-ArH), 6.28 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.32 (d, $J = 15$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.91 (t, $J = 6.5$ Hz, 2 H, ArOCH_2), 3.88 (s, 3 H, CO_2CH_3), 3.63 (s, 3 H, CO_2CH_3), 3.40 (t, $J = 6.5$ Hz, 2 H, ArOCH_2), 1.70-1.79 (m, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.54-1.59 (m, 2 H, $\text{ArOCH}_2\text{CH}_2$), 1.24-1.42 (m, 8 H, 2 x CH_2), and 0.85-0.95 (m, 6 H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.65 (C=O), 166.57 (C=O), 148.72, 148.23, 139.38, 137.94, 136.04, 134.21, 131.31, 130.69, 129.46, 128.95, 128.05, 124.54, 118.53, 113.91, 112.59, 68.91 (ArOCH_2), 68.41 (ArOCH_2), 52.21 (CO_2CH_3), 51.49 (CO_2CH_3), 28.75, 28.59, 28.10, 27.95, 22.40, 22.34, and 14.00; IR (film) 2950, 2935, 2870, 1730 (C=O), 1715 (C=O), 1615, 1590, 1510, 1470, 1435, 1395, 1310, 1275, 1260, 1240, 1210, 1190, 1160, 1140, 1120, 1095, 1075, 1015, 985, and 740 cm^{-1} ; MS (DCI) m/e 495 (MH^+), 463 ($\text{M}^+ - \text{OCH}_3$).

For Methyl (2E),(4Z)-4-(3-carbomethoxyphenyl)-5-(3,4-bis(decyloxyphenyl)-2,4-pentadienoate (17d): scale = 0.32 mmol, yield = 75%; ^1H NMR (300 MHz, CDCl_3) δ 8.04 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 7.87 (t, $J = 2$ Hz, 1 H, 4-ArH), 7.65 (d, $J = 15$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.51 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.36 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 6.86 (s, 1 H, $\text{C}=\text{CH}$), 6.59-6.66 (m, 2 H, 2 x 5-ArH), 6.28 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.32 (d, $J = 15$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.90 (t, $J = 6.5$ Hz, 2 H, 5- ArOCH_2), 3.88 (s, 3 H, CO_2CH_3), 3.70 (s, 3 H, CO_2CH_3), 3.40 (t, $J = 6.5$ Hz, 2 H, 5- ArOCH_2), 1.73 (quintet, 2 H, 5- $\text{ArOCH}_2\text{CH}_2$), 1.50-1.65 (m, 2 H, 5- $\text{ArOCH}_2\text{CH}_2$), 1.18-1.43 (m, 28 H, 14 x CH_2), and 0.83-0.89 (m, 6 H, 2 x CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.67 (C=O), 166.57 (C=O), 149.74, 149.64, 148.21, 139.40, 137.94, 136.02, 134.21, 131.30, 130.69, 129.46, 128.95, 128.02, 124.49, 118.51, 113.91, 112.57, 68.91 (ArOCH_2), 68.44 (ArOCH_2), 52.22 (CO_2CH_3), 51.50 (CO_2CH_3), 31.92, 31.89, 29.58, 29.33, 29.06, 28.92, 25.92, 25.79, 22.68, and 14.12; IR (film) 2950, 2920, 2870, 2850, 1720 (C=O), 1615, 1585, 1515, 1470, 1435, 1310, 1280, 1245, 1210, 1195, 1170, 1145, 1120, 1090, 1020, 980, and 740 cm^{-1} ; MS (DCI) m/e 635 (MH^+), 603 ($\text{M}^+ - \text{OCH}_3$).

For Ethyl (2E),(4Z)-4-(3-carboethoxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (17e): scale = 0.98 mmol, yield = 82%; prepared as described in the general procedure except that sodium ethoxide (21 wt% in ethanol) was used in place of sodium methoxide. ¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.77 (s, 1 H, 4-ArH), 7.51 (d, *J* = 16 Hz, 1 H, CH=CHCO₂), 7.38 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 4-ArH), 6.97 (m, 2 H, 7-ArH), 6.81 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.21 (t, *J* = 8 Hz, 1 H, C=CH), 5.28 (d, *J* = 16 Hz, 1 H, CH=CHCO₂), 4.37 (q, *J* = 7 Hz, 2 H, CO₂CH₂CH₃), 4.15 (q, *J* = 7 Hz, 2 H, CO₂CH₂CH₃), 2.63 (t, *J* = 7 Hz, 2 H, ArCH₂CH₂), 2.27 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 1.65 (s, 4 H, CH₂CH₂), 1.39 (t, *J* = 7 Hz, 3 H, CO₂CH₂CH₃), and 1.18-1.25 (m, 15 H, 4 × CH₃ and CO₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.24 (C=O), 166.34 (C=O), 148.02, 144.74, 142.59, 142.21, 139.63, 137.71, 136.77, 133.66, 130.82, 130.25, 128.65, 128.56, 126.50, 126.45, 125.70, 119.24, 61.09 (CO₂CH₂CH₃), 60.27 (CO₂CH₂CH₃), 35.16, 35.10, 34.15, 33.95, 31.91, 31.87, 31.67, 14.35 (CO₂CH₂CH₃), and 14.28 (CO₂CH₂CH₃); IR (film) 2960, 2930, 1720 (C=O), 1625, 1305, 1280, 1260, and 1175 cm⁻¹; MS (DCI) *m/e* 489 (MH⁺), 443 (M-OCH₂CH₃)⁺.

20 Example 17: General Procedure for Synthesis of 18

A mixture of ester 17 in methanol/tetrahydrofuran/2N sodium hydroxide solution (1:1:1, 0.1 M) was heated at reflux for 1-4 h. The reaction mixture was then allowed to cool to room temperature and 10% hydrochloric acid solution was added until the solution reached pH 1. The resulting cloudy mixture was extracted with methylene chloride (2 portions), and the organic phase was washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was evaporated from pentane (3 portions) and then dried in vacuo.

For (2E),(4Z)-4-(3-Carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-pentadienoic acid (18a): scale = 0.50 mmol, yield = 75%; mp 279-282 °C; UV_{max} (CH₃OH) 324 nm (ε = 34,400), 232 nm (ε = 19,100); ¹H NMR (300 MHz, CD₃OD) δ 8.08 (dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 7.84 (t, *J* = 2 Hz, 1 H, 4-ArH), 7.71 (d, *J* = 16 Hz, 1 H, CH=CHCO₂), 7.62 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.41 (dt, *J* = 2, 8 Hz, 1 H, 4-

ArH), 7.15 (d, $J = 8$ Hz, 1 H, 5-ArH), 7.03 (s, 1 H, C=CH), 6.87 (dd, $J = 2, 8$ Hz, 1 H, 5-ArH), 6.81 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.28 (d, $J = 16$ Hz, 1 H, CH=CHCO₂), 1.54-1.60 (m, 4 H, CH₂CH₂), 1.18 (s, 6 H, 2 x CH₃), and 0.98 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.47 (C=O), 169.37 (C=O), 151.21, 147.03, 145.66, 140.98, 139.51, 138.91, 135.24, 133.85, 133.35, 131.89, 130.78, 130.28, 129.44, 129.09, 127.68, 120.49, 35.94, 35.15, 34.87, 31.95, and 31.86; IR (film) 3400 (br, CO₂H), 2960, 2925, 2860, 1685 (C=O), 1615, 1590, 1450, 1410, 1280, and 1215 cm⁻¹; MS (DCI) m/e 405 (MH⁺), 387 (M⁺ - OH). Anal. Calcd. for C₂₆H₂₈O₄ · 0.25 H₂O: C, 76.34; H, 7.02.
10 Found: C, 76.21; H, 6.85.

For (2E),(4Z)-4-(3-Carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid (18b): scale = 1.60 mmol, yield = 99%; UV_{max} (CH₃OH) 342 nm ($\epsilon = 36,700$), 294 nm ($\epsilon = 27,500$), 284 nm ($\epsilon = 25,900$); ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.86 (br t, $J = 8$ Hz, 1 H, 4-ArH), 7.60-7.73 (m, 7 H, 6 x ArH and CH=CHCO₂), 7.42-7.46 (m, 2 H, ArH), 7.37 (s, 1 H, C=CH), 5.23 (d, $J = 15$ Hz, 1 H, CH=CHCO₂), 1.67 (s, 4 H, CH₂CH₂), and 1.28 (br s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 167.29 (C=O), 166.91 (C=O), 148.78, 145.20, 144.56, 139.34, 137.76, 137.21, 133.88, 132.07, 131.65, 131.11, 130.91, 130.17, 129.88, 129.75, 128.95, 126.70, 125.084, 124.81, 124.52, 120.14, 34.41, 34.34, 34.22, and 32.17; IR (KBr) 2400-3400 (br, CO₂H), 3010, 2960, 2920, 2860, 1685 (C=O), 1610, 1575, 1450, 1410, 1365, 1295, and 1215 cm⁻¹; MS (DCI) m/e 455 (MH⁺) and 411 (MH⁺ - CO₂H); Anal. Calcd for
20 C₃₀H₃₀O₄·0.6H₂O: C, 77.42; H, 6.76. Found: C, 77.37; H, 6.93.

For (2E),(4Z)-4-(3-Carboxyphenyl)-5-(3,4-bis(pentyloxy)phenyl)-2,4-pentadienoic acid (18c): scale = 0.16 mmol, yield = 95%; UV_{max} (CH₃OH) 346 nm ($\epsilon = 28,500$), 230 nm ($\epsilon = 18,400$); ¹H NMR (300 MHz, CD₃OD) δ 8.09 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 7.86 (t, $J = 2$ Hz, 1 H, 4-ArH), 7.70 (d, $J = 15.5$ Hz, CH=CHCO₂), 7.63 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.42 (dt, $J = 2, 8$ Hz, 1 H, 4-ArH), 6.99 (s, 1 H, C=CH), 6.73-6.80 (m, 2 H, 5-ArH), 6.30 (d, $J = 2$ Hz, 1 H, 5-ArH), 5.26 (d, $J = 15$ Hz, 1 H, CH=CHCO₂), 3.92 (t, $J = 6.5$ Hz, 2 H, ArOCH₂), 3.37 (t, $J = 6.5$ Hz, 2 H, ArOCH₂), 1.68-1.77 (m, 2 H, ArOCH₂CH₂), 1.50-1.56 (m, 2 H, ArOCH₂CH₂), 1.27-1.46 (m, 8 H, 4 x CH₂), and 0.84-0.98 (m, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.50 (C=O), 169.00 (C=O), 151.33, 151.12, 149.50, 140.68, 139.52, 137.65,
35

135.39, 132.01, 130.84, 130.28, 129.69, 126.35, 119.86, 115.07, 114.06, 70.02 (ArOCH₂), 69.60 (ArOCH₂), 29.99, 29.78, 29.37, 29.19, 23.48, 23.41, and 14.39; IR (film) 2000-3400 (br, CO₂H), 1695 (C=O), 1680 (C=O), 1615, 1580, 1510, 1465, 1430, 1315, 1270, 1240, 1210, and 1140 cm⁻¹; MS (DCI) *m/e* 467 (MH⁺), 449 (M⁺ - OH). Anal. Calcd. for C₂₈H₃₄O₆: C, 72.08; H, 7.34. Found: C, 72.84; H, 7.84.

For (2E),(4Z)-4-(3-Carboxyphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid (18d): scale = 0.21 mmol, yield = 96%; mp 151-154 °C; UV_{max} (CH₃OH) 354 nm (ϵ = 30,700), 242 nm (ϵ = 15,200); ¹H NMR (300 MHz, CDCl₃) δ 8.12 (dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 7.96 (t, *J* = 2 Hz, 1 H, 4-ArH), 7.75 (d, *J* = 15 Hz, CH=CHCO₂), 7.55 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.42 (dt, *J* = 2, 8 Hz, 1 H, 4-ArH), 6.92 (s, 1 H, C=CH), 6.61-6.68 (m, 2 H, 5-ArH), 6.30 (d, *J* = 2 Hz, 1 H, 5-ArH), 5.31 (d, *J* = 15 Hz, 1 H, CH=CHCO₂), 3.91 (t, *J* = 6.5 Hz, 2 H, ArOCH₂), 3.42 (t, *J* = 6.5 Hz, 2 H, ArOCH₂), 1.74 (quintet, 2 H, ArOCH₂CH₂), 1.50-1.65 (m, 2 H, ArOCH₂CH₂), 1.20-1.45 (m, 28 H, 14 × CH₂), and 0.82-0.88 (m, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 172.58 (C=O), 171.44 (C=O), 149.92, 148.25, 137.91, 135.69, 135.00, 131.35, 130.60, 129.62, 127.81, 124.76, 118.00, 114.06, 112.58, 68.91 (ArOCH₂), 68.44 (ArOCH₂), 31.92, 31.89, 29.58, 29.33, 29.06, 28.92, 25.92, 25.79, 22.68, and 14.12; IR (film) 2300-3600 (br, CO₂H), 2925, 2855, 1685 (C=O), 1615, 1585, 1510, 1470, 1450, 1415, 1310, 1270, 1240, 1205, and 1140 cm⁻¹; MS (DCI) *m/e* 607 (MH⁺), 589 (M⁺ - OCH₃). Anal. Calcd. for C₃₈H₅₄O₆: C, 75.21; H, 8.97. Found: C, 75.30; H, 8.96.

For (2E),(4Z)-4-(3-Carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (18e): scale = 0.53 mmol, yield = 39%; ¹H NMR (300 MHz, DMSO-*d*₆) δ 12.63 (br s, 2 H, CO₂H), 7.90 (d, *J* = 7 Hz, 1 H, 4-ArH), 7.57 (s, 1 H, 4-ArH), 7.44 (m, 2 H, CH=CHCO₂ and 4-ArH), 7.13 (d, *J* = 8 Hz, 1 H, 4-ArH), 6.96 (m, 2 H, 7-ArH), 6.76 (d, *J* = 8 Hz, 1 H, 7-ArH), 6.36 (t, *J* = 8 Hz, 1 H, C=CH), 5.05 (d, *J* = 16 Hz, 1 H, CH=CHCO₂), 2.57 (m, 2 H, ArCH₂), 2.15 (m, 2 H, ArCH₂CH₂), 1.57 (s, 4 H, CH₂CH₂), 1.17 (s, 6 H, 2 × CH₃), and 1.13 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 167.36 (C=O), 167.34 (C=O), 147.60, 143.97, 142.24, 141.82, 138.91, 137.67, 136.39, 133.32, 131.03, 129.60, 128.84, 128.42, 126.14, 125.58, 119.21, 34.65, 34.33, 33.72, 33.55, 31.64, and 31.59; IR (KBr) 2400-3600 (br, CO₂H), 2960, 2930, 1690 (C=O), 1620, 1450,

1310, and 1290 cm^{-1} ; MS (DCI) m/e 432 (MH^+), 417 ($\text{M}-\text{CH}_2$) $^+$, 415 ($\text{M}-\text{OH}$) $^+$, 387; Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_4 \cdot 0.2 \text{H}_2\text{O}$: C, 77.12; H, 7.49. Found: C, 76.76; H, 7.43.

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Example 18: General Procedure for Synthesis of 19

A solution of aldehyde **12** (1 equivalent) in anhydrous toluene (0.1 M) at room temperature under argon was treated sequentially with methyl diethylphosphonoacetate (1.5 equivalents) and sodium methoxide (25 wt% in methanol, 1.4 equivalents). The reaction mixture was stirred at room temperature for 12-16 h, and then treated with additional sodium methoxide (25 wt% in methanol, 1 equivalent). The mixture was stirred for 0.5 h and then partitioned between diethyl ether and saturated ammonium chloride solution. The organic layer was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification by column chromatography on silica gel (40:1 ratio of silica gel/crude product; elution with 5% ethyl acetate in hexanes) gave the desired product.

For Methyl (2E),(4Z)-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (**19a**): scale = 0.49 mmol, yield = 86%; ^1H NMR (300 MHz, CDCl_3) δ 7.54 (br d, $J = 8$ Hz, 1 H, 4-ArH), 7.48 (d, $J = 15$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.41 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.24 (s, 1 H, 4-ArH), 7.16 (d, $J = 8$ Hz, 1 H, 4-ArH), 6.94-6.96 (m, 2 H, 7-ArH), 6.78 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.21 (t, $J = 8$ Hz, 1 H, $\text{C}=\text{CH}$), 5.23 (d, $J = 15$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.68 (s, 3 H, CO_2CH_3), 2.61 (t, $J = 8$ Hz, 2 H, ArCH_2), 2.24 (q, $J = 8$ Hz, 2 H, ArCH_2CH_2), 1.63 (br s, 4 H, CH_2CH_2), 1.24 (s, 6 H, $2 \times \text{CH}_3$), and 1.20 (s, 6 H, $2 \times \text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 167.55 ($\text{C}=\text{O}$), 147.98, 144.79, 142.73, 139.12, 137.49, 137.20, 132.63, 128.97, 126.56, 126.48, 125.86 (q, $J_{\text{C},\text{F}} = 4$ Hz, 4-ArC), 125.67, 124.37 (q, $J_{\text{C},\text{F}} = 4$ Hz, 4-ArC), 118.81, 51.54 (CO_2CH_3), 35.10, 35.06, 34.13, 33.95, 31.87, 31.83, and 31.69; IR (film) 2960, 2926, 2860, 1720 ($\text{C}=\text{O}$), 1625, 1435, 1325, 1310, 1295, 1270, 1170, 1130, 1110, 1070, and 705 cm^{-1} ; MS (DCI) m/e 471 (MH^+).

For Methyl (2E),(4Z)-4-(4-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (19b): scale = 0.85 mmol, yield = 84%; ^1H NMR (300 MHz, CDCl_3) δ 7.46 (d, J = 16 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.16 (d, J = 8 Hz, 1 H, 7-ArH), 6.72-7.00 (m, 6 H, 4 $\times$ 4-ArH and 2 $\times$ 7-ArH), 6.15 (t, J = 8 Hz, 1 H, $\text{C}=\text{CH}$), 5.27 (d, J = 16 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.68 (s, 3 H, CO_2CH_3), 2.61 (t, J = 8 Hz, 2 H, ArCH_2), 2.25 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 1.64 (br s, 4 H, CH_2CH_2), 1.24 (s, 6 H, 2 $\times$ CH_3), and 1.22 (s, 6 H, 2 $\times$ CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.74, 148.66, 144.72, 142.61, 142.29, 139.54, 137.69, 130.78 (d, $\beta_{\text{c,f}}$ = 8 Hz, 4-ArC), 126.50, 125.78, 118.56, 115.31 (d, $\beta_{\text{c,f}}$ = 21 Hz, 4-ArC), 51.47 (CO_2CH_3), 35.11, 35.08, 35.00, 34.13, 33.94, 31.90, 31.85 and 31.66; IR (film) 2960, 2925, 2860, 1720 ($\text{C}=\text{O}$), 1625, 1510, 1460, 1435, 1305, 1270, 1225, 1190, 1170, 845, and 825 cm^{-1} ; MS (DCI) m/e 421 (MH^+).

For Methyl (2E),(4Z)-4-(3-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (19c): scale = 1.09 mmol, yield = 81%; ^1H NMR (300 MHz, CDCl_3) δ 7.45 (d, J = 15 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.21-7.28 (m, 1 H, 4-ArH), 7.17 (d, J = 2 Hz, 1 H, 7-ArH), 6.92-6.99 (m, 2 H, 1 $\times$ 4-ArH and 1 $\times$ 7-ArH), 6.79 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 6.61 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 6.49 (dq, J = 2, 8 Hz, 1 H, 4-ArH), 6.15 (t, J = 8 Hz, 1 H, $\text{C}=\text{CH}$), 5.29 (d, J = 15 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.71 (s, 3 H, CO_2CH_3), 2.62 (t, J = 8 Hz, 2 H, ArCH_2), 2.26 (q, J = 8 Hz, 2 H, ArCH_2CH_2), 1.64 (br s, 4 H, CH_2CH_2), 1.24 (s, 6 H, 2 $\times$ CH_3), and 1.20 (s, 6 H, 2 $\times$ CH_3); ^{13}C NMR (75 MHz, CDCl_3) δ 167.69 ($\text{C}=\text{O}$), 148.09, 144.76, 142.66, 142.22, 139.35, 138.56 (d, $\beta_{\text{c,f}}$ = 9 Hz, 4-ArC), 137.59, 129.90 (d, $\beta_{\text{c,f}}$ = 9 Hz, 4-ArC), 126.49, 125.75, 124.86, 118.66, 116.13 (d, $\beta_{\text{c,f}}$ = 21 Hz, 4-ArC), 114.33 (d, $\beta_{\text{c,f}}$ = 21 Hz, 4-ArC), 51.49 (CO_2CH_3), 35.08, 34.98, 34.13, 33.95, 31.84, and 31.68; IR (film) 2960, 2925, 2860, 1720 ($\text{C}=\text{O}$), 1625, 1610, 1580, 1435, 1305, 1265, 1190, and 1170 cm^{-1} ; MS (DCI) m/e 421 (MH^+).

For Methyl (2E),(4Z)-4-phenyl-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoate (19d): scale = 0.63 mmol, yield = 91%; ^1H NMR (300 MHz, CDCl_3) δ 7.48 (d, J = 15 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.23-7.32 (m, 3 H, 4-ArH), 7.16 (d, J = 8 Hz, 1 H, 7-ArH), 6.96 (d, J = 2 Hz, 1 H, 7-ArH), 6.84-6.88 (m, 2 H, 4-ArH), 6.79 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 6.15 (t, J = 8 Hz, 1 H, $\text{C}=\text{CH}$), 5.33 (d, J = 15 Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.69 (s, 3 H, CO_2CH_3), 2.61 (t, J = 8 Hz, 2 H, ArCH_2), 2.27 (q,

$J = 8$ Hz, 2 H, ArCH_2CH_2), 1.64 (br s, 4 H, CH_2CH_2), 1.24 (s, 6 H, $2 \times \text{CH}_3$), and 1.21 (s, 6 H, $2 \times \text{CH}_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 167.87 (C=O), 148.78, 144.68, 142.51, 141.87, 140.53, 137.83, 136.32, 129.11, 128.34, 127.32, 126.46, 125.74, 118.51, 51.40 (CO_2CH_3), 35.15, 35.10, 34.13, 33.93, 31.90, 31.85, and 31.59; IR (film) 2960, 2925, 2860, 1720 (C=O), 1620, 1495, 1455, 1435, 1305, 1265, 1190, 1170, 1105, 980, 825, and 700 cm^{-1} ; MS (DCI) m/e 403 (MH^+).

For Methyl (2E),(4Z)-4-(3-trifluoromethylphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoate (19e): scale = 0.30 mmol, yield = 81%; ^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.50 (d, $J = 16$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.43 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.14 (s, 1 H, 4-ArH), 7.04 (d, $J = 8$ Hz, 1 H, 4-ArH), 6.87 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.82 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.73 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.21 (t, $J = 8$ Hz, 1 H, C=CH), 5.23 (d, $J = 16$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.78 (s, 3 H, ArOCH_3), 3.69 (s, 3 H, CO_2CH_3), 2.62 (t, $J = 7$ Hz, 2 H, ArCH_2), 2.23 (q, $J = 7$ Hz, 2 H, ArCH_2CH_2), 2.02 (s, 9 H, adamantyl), and 1.73 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 167.54 (C=O), 157.24, 148.05, 142.85, 139.13, 138.32, 137.24, 132.66, 132.16, 130.91 (d, $J^2_{\text{C},\text{F}} = 32$ Hz, 4-ArC), 128.94, 126.89, 126.29, 125.79 (d, $J^3_{\text{C},\text{F}} = 4$ Hz, 4-ArC), 124.32 (d, $J^3_{\text{C},\text{F}} = 4$ Hz, 4-ArC), 118.76, 111.62, 55.01 (ArOCH_3), 51.52 (CO_2CH_3), 40.57, 37.09, 36.86, 34.76, 32.00, and 29.07; IR (film) 2905, 2850, 1720 (C=O), 1325, 1235, 1170, and 1130 cm^{-1} ; MS (DCI) m/e 525 (MH^+), 255, 135 ($\text{C}_{10}\text{H}_{15}^+$); Anal. Calcd for $\text{C}_{32}\text{H}_{35}\text{O}_3\text{F}_3$: C, 73.26; H, 6.72. Found: C, 73.58; H, 6.70.

For Methyl (2E),(4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoate (19f): scale = 0.46 mmol, yield = 66%; ^1H NMR (300 MHz, CDCl_3) δ 7.55 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.49 (d, $J = 16$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 7.42 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.24 (s, 1 H, 4-ArH), 7.07 (d, $J = 8$ Hz, 1 H, 4-ArH), 6.95 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.59 (dd, $J = 8, 2$ Hz, 1 H, 7-ArH), 6.50 (d, $J = 1$ Hz, 1 H, 7-ArH), 6.21 (t, $J = 8$ Hz, 1 H, C=CH), 5.24 (d, $J = 16$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 3.73 (s, 3 H, ArOCH_3), 3.69 (s, 3 H, CO_2CH_3), 2.64 (t, $J = 7$ Hz, 2 H, ArCH_2), 2.26 (q, $J = 7$ Hz, 2 H, ArCH_2CH_2), 2.05 (s, 9 H, adamantyl), and 1.74 (s, 6 H, adamantyl); ^{13}C NMR (75 MHz, CDCl_3) δ 167.53 (C=O), 158.75, 147.90, 142.48, 139.23, 137.20, 136.45, 132.72, 130.90 (d, $J^2_{\text{C},\text{F}} = 32$ Hz, 4-ArC),

128.97, 126.42, 125.84 (d, $J_{C,F} = 4$ Hz, 4-ArC), 124.35 (d, $J_{C,F} = 4$ Hz, 4-ArC), 120.31, 118.93, 111.89, 54.84 (ArOCH₃), 51.54 (CO₂CH₃), 40.63, 37.13, 36.68, 34.92, 31.58, and 29.10; IR (film) 2905, 2850, 1720 (C=O), 1325, 1310, 1170, 1130, and 1070 cm⁻¹; MS (DCI) m/e 525 (MH⁺), 493 (M-OCH₃)⁺, 135 (C₁₀H₁₅)⁺; Anal. Calcd for C₃₂H₃₅O₃F₃: C, 73.26; H, 6.72. Found: C, 73.09; H, 6.50.

Example 19: General Procedure for Synthesis of 20

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A mixture of ester **19** in methanol/tetrahydrofuran/2N sodium hydroxide solution (1:1:1, 0.1 M) was heated at reflux for 1-4 h. The reaction mixture was then allowed to cool to room temperature and 10% hydrochloric acid solution was added until the solution reached pH 1. The resulting cloudy mixture was extracted with methylene chloride (2 portions), and the organic phase was washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was evaporated from pentane (3 portions) and then dried in vacuo.

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For (2E),(4Z)-4-(3-Trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (**20a**): scale = 0.39 mmol, yield = 94%; UV_{max} (CH₃OH) 260 nm ($\epsilon = 23,200$); ¹H NMR (300 MHz, CD₃OD) δ 7.61 (br d, $J = 8$ Hz, 1 H, 4-ArH), 7.51 (d, $J = 15$ Hz, 1 H, CH=CHCO₂), 7.48 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.18 (d, $J = 8$ Hz, 1 H, 4-ArH), 7.16 (s, 1 H, 4-ArH), 6.97 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.83 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.76 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.31 (t, $J = 8$ Hz, 1 H, C=CH), 5.08 (d, $J = 15$ Hz, 1 H, CH=CHCO₂), 2.65 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.20 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 x CH₃), and 1.20 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.45 (C=O), 149.55, 145.61, 144.14, 143.58, 140.63, 139.03, 138.89, 134.26, 130.40, 127.84, 127.61, 126.97 (q, $J_{C,F} = 4$ Hz, 2-ArC), 125.28 (q, $J_{C,F} = 4$ Hz, 2-ArC), 120.23, 36.30, 35.87, 35.06, 34.88, 33.17, and 32.33; IR (film) 2400-3600 (br, CO₂H), 2960, 2930, 2860, 1690 (C=O), 1620, 1460, 1415, 1365, 1325, 1310, 1275, 1205, 1165, 1130, and 1070 cm⁻¹; MS (DCI) m/e 457 (MH⁺). Anal. Calcd. for C₂₈H₃₁O₂F₃: C, 73.66; H, 6.84. Found: C, 73.41; H, 6.84.

For (2E),(4Z)-4-(4-Fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (20b): scale = 0.66 mmol, yield = 88%; UV_{max} (CH₃OH) 264 nm (ϵ = 24,300); ¹H NMR (300 MHz, CD₃OD) δ 7.47 (d, J = 16 Hz, 1 H, CH=CHCO₂), 7.18 (d, J = 8 Hz, 1 H, 7-ArH), 6.96-7.08 (m, 3 H, ArH), 6.76 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 6.62-6.69 (m, 2 H, ArH), 6.22 (t, J = 8 Hz, 1 H, C=CH), 5.13 (d, J = 16 Hz, 1 H, CH=CHCO₂), 2.63 (t, J = 8 Hz, 2 H, ArCH₂), 2.21 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.26 (s, 6 H, 2 x CH₃), and 1.20 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.69, 163.45 (d, $J^1_{C,F}$ = 246 Hz, 4-ArC), 150.22, 145.58, 143.59, 141.13, 139.21, 133.76, 132.19 (d, $J^3_{C,F}$ = 8 Hz, 4-ArC), 127.88, 127.55, 126.85, 120.84, 116.14 (d, $J^2_{C,F}$ = 21 Hz, 4-ArC), 36.32, 35.92, 35.06, 34.88, 33.19, 32.38, and 32.36; IR (film) 2400-3600 (br, CO₂H), 2960, 2925, 2860, 1690 (C=O), 1615, 1510, 1495, 1460, 1415, 1155, 985, 840, and 825 cm⁻¹; MS (DCI) m/e 407 (MH⁺). Anal. Calcd. for C₂₇H₃₁O₂F·0.1 H₂O: C, 79.41; H, 7.70. Found: C, 79.27; H, 7.67.

For (2E),(4Z)-4-(3-Fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (20c): scale = 0.65 mmol, yield = 48%; UV_{max} (CH₃OH) 262 nm (ϵ = 24,900); ¹H NMR (300 MHz, CD₃OD) δ 7.47 (d, J = 15 Hz, 1 H, CH=CHCO₂), 7.25-7.33 (m, 1 H, 4-ArH), 7.18 (d, J = 2 Hz, 1 H, 7-ArH), 6.97-7.04 (m, 2 H, 1 x 4-ArH and 1 x 7-ArH), 6.76 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 6.51 (dt, J = 2, 8 Hz, 1 H, 4-ArH), 6.30 (dq, J = 2, 8 Hz, 1 H, 4-ArH), 6.24 (t, J = 8 Hz, 1 H, C=CH), 5.12 (d, J = 15 Hz, 1 H, CH=CHCO₂), 2.64 (t, J = 8 Hz, 2 H, ArCH₂), 2.22 (q, J = 8 Hz, 2 H, ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.26 (s, 6 H, 2 x CH₃), and 1.20 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 170.53 (C=O), 148.75, 145.00, 143.58, 141.00, 140.15, 139.09 (d, $J^3_{C,F}$ = 9 Hz, 4-ArC), 131.18 (d, $J^3_{C,F}$ = 9 Hz, 4-ArC), 127.87, 127.52, 127.10, 126.25, 120.01, 117.05 (d, $J^2_{C,F}$ = 21 Hz, 4-ArC), 115.17 (d, $J^2_{C,F}$ = 21 Hz, 4-ArC), 36.31, 35.88, 35.06, 34.89, 33.22, and 32.34; IR (film) 2300-3600 (br, CO₂H), 2960, 2925, 2860, 1685 (C=O), 1605, 1580, 1490, 1455, 1425, 1385, 1360, 1320, 1310, 1265, 1250, 1200, 915, 880, 825, 795, and 695 cm⁻¹; MS (DCI) m/e 407 (MH⁺). Anal. Calcd. for C₂₇H₃₁O₂F: C, 79.77; H, 7.69. Found: C, 79.74; H, 7.63.

For (2E),(4Z)-4-Phenyl-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid (20d): scale = 0.63 mmol, yield = 91%; UV_{max} (CH₃OH) 264 nm (ϵ = 22,000); ¹H NMR (300 MHz, CD₃OD)

δ 7.48 (d, $J = 15$ Hz, 1 H, CH=CHCO₂), 7.27-7.33 (m, 3 H, 4-ArH), 7.17 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.96 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.70-6.78 (m, 3 H, 2 $\times$ 4-ArH and 1 $\times$ 7-ArH), 6.20 (t, $J = 8$ Hz, 1 H, C=CH), 5.15 (d, $J = 15$ Hz, 1 H, CH=CHCO₂), 2.62 (t, $J = 8$ Hz, 2 H, ArCH₂), 2.22 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 1.67 (br s, 4 H, CH₂CH₂), 1.25 (s, 6 H, 2 $\times$ CH₃), and 1.20 (s, 6 H, 2 $\times$ CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 150.42, 145.54, 145.46, 143.46, 143.13, 142.17, 139.26, 137.77, 130.27, 129.40, 128.41, 127.78, 127.50, 127.06, 119.93, 36.34, 36.02, 35.06, 34.87, 33.14, and 32.36; IR (KBr) 2400-3300 (br, CO₂H), 3020, 2955, 2925, 2865, 1690 (C=O), 1615, 1600, 1495, 1460, 1440, 1415, 1385, 1360, 1310, 1300, 1285, 1275, 1250, 1235, 1200, 990, 820, and 695 cm⁻¹; MS (DCI) m/e 389 (MH⁺), 371 (M⁺ - OH). Anal. Calcd. for C₂₇H₃₂O₂: C, 83.46; H, 8.30. Found: C, 83.51; H, 8.58.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid (20e): scale = 0.19 mmol, yield = 87%; ¹H NMR (300 MHz, CDCl₃) δ 7.57 (m, 2 H, 4-ArH and CH=CHCO₂), 7.44 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.15 (s, 1 H, 4-ArH), 7.05 (d, $J = 8$ Hz, 1 H, 4-ArH), 6.87 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.82 (dd, $J = 2, 8$ Hz, 1 H, 7-ArH), 6.73 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.27 (t, $J = 8$ Hz, 1 H, C=CH), 5.23 (d, $J = 16$ Hz, 1 H, CH=CHCO₂), 3.79 (s, 3 H, ArOCH₃), 2.63 (t, $J = 7$ Hz, 2 H, ArCH₂), 2.25 (q, $J = 7$ Hz, 2 H, ArCH₂CH₂), 2.03 (s, 9 H, adamantyl), and 1.73 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 172.20 (C=O), 157.27, 150.14, 144.20, 139.11, 138.36, 136.95, 132.63, 132.05, 130.97 (d, $J_{C,F} = 32$ Hz, 4-ArC), 129.02, 126.87, 126.28, 125.80, 124.42, 118.14, 111.64, 55.01 (OCH₃), 40.57, 37.10, 36.87, 34.69, 32.08, and 20.07; IR (KBr) 2400-3700 (br, CO₂H), 2905, 2850, 1690, 1615, 1325, 1235, 1165, and 1130 cm⁻¹; MS (DCI) m/e 511 (MH⁺), 493 (M-OH)⁺, 465, 255, 135 (C₁₀H₁₅)⁺; Anal. Calcd for C₃₁H₃₃O₃F₃: C, 72.92; H, 6.51. Found: C, 72.50; H, 6.68.

For (2Z),(4Z)-4-(3-Trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid (20f): scale = 0.24 mmol, yield = 69%; ¹H NMR (300 MHz, CDCl₃) δ 7.55 (m, 2 H, 4-ArH and CH=CHCO₂), 7.43 (t, $J = 8$ Hz, 1 H, 4-ArH), 7.24 (d, $J = 1$ Hz, 1 H, 4-ArH), 7.07 (d, $J = 8$ Hz, 1 H, 4-ArH), 6.95 (d, $J = 8$ Hz, 1 H, 7-ArH), 6.59 (dd, $J = 8, 2$ Hz, 1 H, 7-ArH), 6.50 (d, $J = 2$ Hz, 1 H, 7-ArH), 6.26 (t, $J = 8$ Hz, 1 H, C=CH), 5.23 (d, $J = 16$ Hz, 1 H, CH=CHCO₂), 3.73 (s, 3 H, ArOCH₃), 2.64

(t, $J = 7$ Hz, 2 H, ArCH₂), 2.28 (q, $J = 8$ Hz, 2 H, ArCH₂CH₂), 2.05 (s, 9 H, adamantyl), and 1.74 (s, 6 H, adamantyl); ¹³C NMR (75 MHz, CDCl₃) δ 172.34 (C=O), 158.77, 150.00, 143.82, 139.22, 139.18, 136.89, 136.51, 132.69, 130.98 (d, $J_{C,F}^2 = 32$ Hz, 4-ArC), 129.04, 126.45, 125.80, 124.46, 122.14, 120.29, 118.35, 111.88, 54.85 (OCH₃), 40.63, 37.13, 36.69, 34.84, 31.66, and 29.10; IR (KBr) 2400-3600 (br, CO₂H), 2905, 2850, 1690 (C=O), 1615, 1325, 1165, and 1130 cm⁻¹; MS (DCI) m/e 511 (MH⁺), 493 (M-OH)⁺, 135 (C₁₀H₁₅)⁺; Anal. Calcd for C₃₁H₃₃O₃F₃: C, 72.92; H, 6.51. Found: C, 72.79; H, 6.60.

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Example 20: Synthesis of 3-(t-Butyldiphenylsiloxymethyl)-bromobenzene 22

A stirred solution of 3-bromobenzyl alcohol (21) (10.0 g, 53.5 mmol), 4-dimethylaminopyridine (0.33 g, 2.7 mmol), and t-butylchlorodiphenylsilane (17.6 g, 64.2 mmol) in anhydrous CH₂Cl₂ (240 mL) was cooled to 0 °C under argon. Triethylamine (8.1 g, 80.2 mmol) was added dropwise via syringe and the reaction mixture was allowed to warm to room temperature over 3.5 h. The reaction solution was washed with water, and the aqueous portion was extracted again with CH₂Cl₂. The organic layers were combined, washed sequentially with 1 N HCl solution, water, and saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to afford 25.3 g of **22** as a clear, pale yellow oil. Purification by column chromatography (20:1 ratio silica gel/crude product; elution with 5% to 7.5% ethyl acetate/hexanes) yielded 21.2 g (93%) of **22** as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.63-7.65 (m, 4 H, ArH), 7.35-7.48 (m, 8 H, ArH), 7.18-7.28 (m, 2 H, ArH), 4.72 (s, 2 H, CH₂OSi), and 1.05 (s, 9 H, SiC(CH₃)₃).

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Example 21: Synthesis of 3-(t-Butyldiphenylsiloxymethyl)benzyl alcohol 23

Magnesium turnings (1.45 g, 59.5 mmol) were weighed into a flask which was then flame-dried under vacuum. An argon atmosphere was introduced, and anhydrous THF (30 mL) and dibromoethane (approx. 0.1 mL) were added. The mixture was stirred

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at room temperature. Approximately 25 mL of a solution of **22** (21.1 g, 49.6 mmol) in anhydrous THF (120 mL) was added via cannula.

Within 10 min, the solution became dark yellow-brown. The remainder of the solution of **22** was then added via cannula, and the entire reaction solution was heated at reflux for 2 h. The solution was allowed to cool to room temperature, and p-formaldehyde (2.98 g, 99.2 mmol) was added. The reaction mixture was stirred at room temperature for 19 h and then poured into a separatory funnel containing saturated ammonium chloride solution. The aqueous mixture was extracted twice with diethyl ether. The organic layers were combined, washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 19.1 g of a clear, yellow liquid. Purification by column chromatography (10:1 ratio silica gel/crude product; gradient elution with 10% to 30% ethyl acetate/hexanes) provided 11.9 g (64%) of **23** as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.69-7.73 (m, 4 H, ArH), 7.25-7.46 (m, 10 H, ArH), 4.79 (s, 2 H, CH_2OSi), 4.68 (s, 2 H, CH_2OH), and 1.11 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$); ^{13}C NMR (75 MHz, CDCl_3) δ 141.32, 140.67, 135.48, 133.35, 129.61, 128.41, 127.62, 125.46, 125.29, 124.54, 65.32 (CH_2OSi , CH_2OH), 26.75 ($\text{SiC}(\text{CH}_3)_3$), and 19.22 ($\text{SiC}(\text{CH}_3)_3$); IR (film) 3340 (br, OH), 2940, 2860, 1475, 1430, 1150, and 1110 cm^{-1} ; MS (FAB) m/e 399 ($\text{M} + \text{Na}$) $^+$.

Example 22: Synthesis of 3-(t-Butyldiphenylsiloxymethyl)benzyl chloride 24

Methanesulfonyl chloride (3.96 g, 34.6 mmol) was added dropwise to a stirred solution of **23** (11.8 g, 31.4 mmol), LiCl (1.33 g, 31.4 mmol), and s-collidine (4.19 g, 34.6 mmol) in anhydrous DMF (120 mL) at 0 $^\circ\text{C}$ under argon. The reaction mixture was allowed to warm to room temperature over 2 h, and was then poured into water and extracted twice with diethyl ether. The organic layers were combined and washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 11.8 g (95%) of **24** as a clear, dark yellow liquid. The chloride was used without purification in the next reaction. ^1H NMR (300 MHz, CDCl_3) δ 7.72-7.76 (m, 4 H, ArH), 7.31-7.48 (m, 10 H, ArH), 4.82 (s, 2 H, CH_2OSi),

4.62 (s, 2 H, CH₂Cl), and 1.15 (s, 9 H, SiC(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 141.71, 137.35, 135.58, 135.51, 133.39, 129.74, 129.60, 128.64, 127.74, 127.08, 126.20, 126.06, 65.24 (CH₂OSi), 46.34 (CH₂Cl), 26.84 (SiC(CH₃)₃), and 19.32 (SiC(CH₃)₃); MS (DCI) *m/e* 395 (MH⁺).

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Example 23: Synthesis of [3-(*t*-Butyldiphenylsiloxymethyl)-phenyl]acetonitrile 25

Sodium cyanide (1.57 g, 32.0 mmol) and tetrabutylammonium iodide (0.11 g, 0.30 mmol) were added to a stirred solution of **24** (11.8 g, 29.9 mmol) in anhydrous DMF (90 mL) at room temperature under argon. The reaction mixture was heated to 80 °C for 2 h. The solution was allowed to cool to room temperature and was poured into saturated ammonium chloride solution and extracted twice with diethyl ether. The organic layers were combined, washed with saturated sodium chloride, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 11.0 g of a clear, brown oil. Purification by column chromatography (20:1 ratio silica gel/crude product; gradient elution with 1% to 10% ethyl acetate/hexanes) provided 8.39 g (73%) of **25** as a pale yellow, clear oil. ¹H NMR (300 MHz, CDCl₃) δ 7.64-7.67 (m, 4 H, ArH), 7.19-7.41 (m, 10 H, ArH), 4.74 (s, 2 H, CH₂OSi), 3.70 (s, 2 H, CH₂CN), and 1.08 (s, 9 H, SiC(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 142.24, 135.57, 133.31, 129.81, 129.04, 127.78, 126.41, 125.69, 125.54, 117.87 (CN), 65.13 (CH₂OSi), 26.85 (SiC(CH₃)₃), 23.65 (CH₂CN), and 19.31 (SiC(CH₃)₃); IR (film) 2960, 2930, 2890, 2860, 2250 (CN), 1470, 1430, 1150, 1110, and 1080 cm⁻¹; MS (DCI) *m/e* 386 (MH⁺).

Example 24: Synthesis of (4*E*)-2-[3-(*t*-Butyldiphenylsiloxymethyl)-phenyl]-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-hexenonitrile 26

A solution of diisopropylamine (0.23 g, 2.25 mmol) in anhydrous THF (2 mL) was cooled to 0 °C under argon, and treated with *n*-BuLi (1.4 M in hexanes, 1.46 mL, 2.05 mmol) dropwise via syringe. The solution was stirred for 30 min, and was cooled to -78 °C. A solution of **25** (0.73 g, 2.05 mmol) in anhydrous THF (4 mL) was

added via cannula. The resulting orange solution was stirred for 30 min, and then added via cannula to a solution of **36** (0.92 g, 2.86 mmol) in anhydrous THF (1.5 mL) cooled to -78 °C. The flask was rinsed with anhydrous THF (1 mL). The reaction mixture was allowed to warm to room temperature over 4 h, and was poured into a separatory funnel containing saturated ammonium chloride solution and diethyl ether. The layers were agitated and separated, and the organic layer was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to afford 1.55 g of a clear, yellow oil. Purification by column chromatography (30:1 ratio silica gel/crude product; gradient elution with 1% to 5% ethyl acetate/hexanes) provided 0.77 g (60%) of **26** as a clear, dark yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.66-7.69 (m, 4 H, ArH), 7.07-7.44 (m, 13 H, ArH), 5.71 (t, *J* = 6 Hz, 1 H, CH=C), 4.77 (s, 2 H, CH₂OSi), 3.86 (t, *J* = 6 Hz, 1 H, CHCN), 2.71-2.86 (m, 2 H, CH₂CHCN), 1.92 (s, 3 H, C=CCH₃), 1.67 (s, 4 H, CH₂CH₂), 1.27 (s, 6 H, 2 × CH₃), 1.27 (s, 6 H, 2 × CH₃), and 1.09 (s, 9 H, SiC(CH₃)₃); ¹³C NMR (75 MHz, CDCl₃) δ 143.88, 142.03, 135.44, 135.30, 133.20, 129.66, 128.80, 127.65, 126.27, 125.87, 125.60, 124.80, 123.67, 123.09, 120.74, 120.53 (CN), 65.07 (CH₂OSi), 37.55 (CHCN), 35.03, 34.92, 34.17, 33.95, 31.75, 31.69, 27.82 (SiC(CH₃)₃), 19.20 (SiC(CH₃)₃), and 16.01; IR (film) 2960, 2930, 2860, 2240 (CN), 1460, 1430, 1110, and 1080 cm⁻¹; MS (DCI) *m/e* 626 (MH⁺).

Example 25: Synthesis of (4E)-2-[3-(*t*-Butyldiphenylsiloxymethyl)-phenyl]-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-hexenal **27**

Diisobutylaluminum hydride (1.0 M in hexanes, 1.54 mL, 1.54 mmol) was added dropwise to a solution of **26** (0.74 g, 1.18 mmol) in anhydrous diethyl ether (22 mL) at 0 °C under argon. The reaction mixture was allowed to warm to room temperature over 2.5 h. The reaction was quenched with ethyl acetate (2.5 mL) and 1 N H₂SO₄ solution (5 mL) and stirring was continued for 10 min. The mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was extracted again with diethyl ether. The organic layers were combined, washed sequentially with 1 N NaOH solution and saturated sodium chloride solution, and concentrated in vacuo to

give 0.72 g (97%) of **27** as a dark yellow oil. ^1H NMR showed the presence of trace impurities, but the compound decomposed on silica gel. The material was used without purification in the next reaction. ^1H NMR (300 MHz, CDCl_3) δ 9.73 (s, 1 H, CHO), 7.61-7.77 (m, 4 H, ArH), 7.03-7.42 (m, 13 H, ArH), 5.62 (t, $J = 9$ Hz, 1 H, $\text{CH}=\text{C}$), 4.78 (s, 2 H, CH_2OSi), 3.66 (t, $J = 6$ Hz, 1 H, CHCHO), 2.92-3.01 (m, 1 H, $1 \times \text{CH}_2\text{CH}$), 2.55-2.67 (m, 1 H, $1 \times \text{CH}_2\text{CH}$), 1.95 (s, 3 H, $\text{C}=\text{CCH}_3$), 1.66 (s, 4 H, CH_2CH_2), 1.28 (s, 12 H, $4 \times \text{CH}_3$), and 1.07 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$).

10 **Example 26: Synthesis of Methyl (2Z),(6E)-4-[3-(t-butylidiphenylsiloxy-methyl)phenyl]-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,6-octadienoate 28**

Potassium bis(trimethylsilyl) amide (0.5 M in toluene, 2.28 mL, 1.14 mmol) was added to a stirred solution of 18-crown-6 (1.51 g, 5.72 mmol), bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate (0.36 g, 1.14 mmol), and **27** (0.72 g, 1.14 mmol) in anhydrous THF (16.5 mL) at -78°C under argon. The reaction mixture was maintained at -78°C for 1 h, and was then allowed to warm to room temperature over 3 h. The solution was poured into a separatory funnel containing saturated ammonium chloride solution and was extracted twice with diethyl ether. The organic layers were combined, washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to afford 0.85 g of a bright yellow oil. Purification by column chromatography (40:1 ratio silica gel/crude product; gradient elution from 1% to 5% ethyl acetate/hexanes) yielded 0.42 g (53%) of **28** as a dark yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.67-7.72 (m, 4 H, ArH), 7.18-7.42 (m, 12 H, ArH), 7.06 (dd, $J = 2, 8$ Hz, 1 H, ArH), 6.33 (t, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 5.80 (d, $J = 12$ Hz, 1 H, $\text{CH}=\text{CHCO}_2$), 5.67 (t, $J = 9$ Hz, 1 H, $\text{CH}=\text{CCH}_3$), 4.90-4.98 (m, 1 H, $\text{CHCH}=\text{CH}$), 4.78 (s, 2 H, CH_2OSi), 3.70 (s, 3 H, CO_2CH_3), 2.58-2.64 (m, 2 H, CH_2CH), 1.98 (s, 3 H, $\text{CH}=\text{CCH}_3$), 1.68 (s, 4 H, CH_2CH_2), 1.27 (s, 12 H, $4 \times \text{CH}_3$), and 1.10 (s, 9 H, $\text{SiC}(\text{CH}_3)_3$).

35 **Example 27: Synthesis of Methyl (2Z),(6E)-4-[3-(hydroxymethyl)phenyl]-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,6-octadienoate 29**

A solution of **28** (0.70 g, 1.02 mmol) in 3% concentrated HCl in methanol was heated slightly to dissolve the starting material and then was stirred at room temperature for 4.5 h. The reaction mixture was poured into water and extracted twice with diethyl ether. The organic layers were combined, washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to provide 0.73 g of a yellow liquid. Purification by column chromatography (30:1 ratio silica gel/crude product; gradient elution with 5% to 20% ethyl acetate/hexanes) yielded 0.34 g (74%) of **29** as a clear yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.20-7.34 (m, 6 H, ArH), 7.04 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.38 (t, *J* = 12 Hz, 1 H, CH=CHCO₂), 5.81 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 5.64 (t, *J* = 9 Hz, 1 H, CH=CCH₃), 4.90-4.99 (m, 1 H, CHCH=CH), 4.68 (d, *J* = 6 Hz, 2 H, CH₂OH), 3.71 (s, 3 H, CO₂CH₃), 2.64 (t, *J* = 6 Hz, 2 H, CH₂CH), 1.97 (s, 3 H, CH=CCH₃), 1.66 (s, 4 H, CH₂CH₂), and 1.26 (s, 12 H, 4 × CH₃).

Example 28: Synthesis of Methyl (2Z),(6E)-4-[3-formylphenyl]-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,6-octadienoate 30

MnO₂ (0.40 g, 4.6 mmol) was added to a solution of **29** (0.41 g, 0.92 mmol) in CH₂Cl₂ (4 mL) and the slurry was stirred in a stoppered flask at room temperature. Additional portions of MnO₂ (0.40 g, 4.6 mmol each time) were added to the reaction mixture after 15 h, 17 h, 21.5 h, and 23.5 h. Additional CH₂Cl₂ (5 mL) was added to the mixture after 15 h. After 39 h, the slurry was filtered through a 1 inch pad of Celite and the filtrate was concentrated to give 0.33 g (83%) of **30** as a clear yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 9.98 (s, 1 H, CHO), 7.82 (s, 1 H, 4-ArH), 7.72 (d, *J* = 9 Hz, 1 H, 4-ArH), 7.58 (d, *J* = 9 Hz, 1 H, 4-ArH), 7.46 (t, *J* = 8 Hz, 1 H, 4-ArH), 7.18 (d, *J* = 6 Hz, 1 H, 7-ArH), 7.19 (s, 1 H, 7-ArH), 7.02 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 6.37 (t, *J* = 10.5 Hz, 1 H, CH=CHCO₂), 5.84 (d, *J* = 12 Hz, 1 H, CH=CHCO₂), 5.59 (t, *J* = 7.5 Hz, 1 H, CH=CCH₃), 5.00 (q, *J* = 7.5 Hz, 1 H, CHCH=CH), 3.69 (s, 3 H, CO₂CH₃), 2.65 (t, *J* = 9 Hz, 2 H, CH₂CH), 1.94 (s, 3 H, CH=CCH₃), 1.64 (s, 4 H, CH₂CH₂), and 1.23 (s, 12 H, 4 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 192.36 (C=O), 151.29, 144.44, 134.24, 129.26, 128.42, 128.32, 126.23, 123.74, 123.47, 123.07, 119.43, 51.25 (CO₂CH₃), 43.45, 35.15 and 35.03 (CH₂CH₂),

34.25, 34.01, 31.81, 30.94, and 16.11; IR (film) 2960, 2925, 2860, 1720 (ester C=O), 1700 (CH=O), 1455, 1435, 1215, 1195, and 1175 cm^{-1} ; MS (DCI) m/e 445 (MH^+).

5 **Example 29: Synthesis of Methyl (2Z),(6E)-4-[3-carbomethoxyphenyl]-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,6-octadienoate**
31

MnO₂ (0.64 g, 7.4 mmol) was added to a solution of **30** (0.33 g,
10 0.74 mmol), sodium cyanide (0.20 g, 4.0 mmol), and glacial acetic acid (approx. 0.02 mL) in anhydrous methanol (12 mL) and the slurry was stirred in a stoppered flask at room temperature. Additional MnO₂ (0.64 g, 7.4 mmol) was added to the mixture after 4 h. After 20 h, the
15 reaction mixture was filtered through a 1 inch pad of Celite and the filtrate was concentrated to give a beige solid. The solid was diluted with water and diethyl ether and poured into a separatory funnel. The layers were agitated and separated, and the aqueous portion was extracted again with diethyl ether. The organic layers were combined,
20 washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated to yield 0.32 g (91%) of **31** as a yellow oil. The diester was used in the next reaction without purification. ¹H NMR (300 MHz, CDCl₃) δ 7.98 (s, 1 H, 4-ArH), 7.88 (d, J = 8 Hz, 1 H, 4-ArH), 7.50 (d, J = 8 Hz, 1 H, 4-ArH), 7.36 (t, J = 7.5 Hz, 1 H, 4-ArH), 7.18 (d, J = 6 Hz, 1 H, 7-ArH), 7.17 (s, 1 H, 7-ArH), 7.02 (dd, J = 2,
25 8 Hz, 1 H, 7-ArH), 6.38 (t, J = 11 Hz, 1 H, CH=CHCO₂), 5.82 (d, J = 12 Hz, 1 H, CH=CHCO₂), 5.60 (t, J = 6 Hz, 1 H, CH=CCH₃), 4.96 (q, J = 10.5 Hz, 1 H, CHCH=CH), 3.89 (s, 3 H, ArCO₂CH₃), 3.69 (s, 3 H, CO₂CH₃), 2.64 (t, J = 7.5 Hz, 2 H, CH₂CH), 1.95 (s, 3 H, CH=CCH₃), 1.64 (s, 4 H, CH₂CH₂), and 1.24 (s, 12 H, 4 $\times$ CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 167.10 (C=O), 166.46
30 (C=O), 151.61, 144.40, 143.55, 143.43, 140.75, 136.83, 132.70, 130.43, 128.62, 128.45, 127.86, 126.18, 123.76, 123.72, 123.08, 119.17, 52.11 (CO₂CH₃), 51.21 (CO₂CH₃), 43.60, 35.21 and 35.18 (CH₂CH₂), 35.05, 34.24, 34.00, 31.80 (4 $\times$ CH₃), 31.93, 29.71, 16.10, and 15.27; IR (film) 2955, 2925, 2860, 1725 (C=O), 1435, 1280, 1230, 1195, and 1175 cm^{-1} ; MS (DCI) m/e 475 (MH^+).

35

Example 30: Synthesis of (2Z),(6E)-4-[3-Carboxyphenyl]-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,6-octadienoic acid **32**

A solution of **31** (0.32 g, 0.67 mmol) and bis(tributyltin) oxide (1.61 g, 2.7 mmol) in anhydrous toluene (18 mL) was stirred at reflux under argon for 111 h. The reaction mixture was allowed to cool to room temperature and was concentrated to remove toluene. The remaining solution was treated with 0.5 N HCl solution (30 mL) and was extracted with ethyl acetate (3 x 40 mL). The organic layers were combined and extracted with 1 N NaOH solution (3 x 65 mL). The aqueous layers were combined and acidified with 1 N HCl solution to pH 3. The acidified aqueous solution was then extracted with CH₂Cl₂ (3 x 250 mL). The organic layers were combined and concentrated to give 0.24 g of a yellow solid. Purification by reverse-phase column chromatography on C₁₈ silica gel (100:1 ratio of silica gel/crude product; elution with 10% H₂O/methanol to 100% methanol) yielded 0.12 g (40%) of **32** as an off-white solid. mp 145 - 148 °C; UV_{max} (CH₃OH) 249 nm (ϵ = 16,500), 237 nm (ϵ = 22,500); ¹H NMR (300 MHz, CD₃OD) δ 8.00 (s, 1 H, 4-ArH), 7.88 (d, J = 8 Hz, 1 H, 4-ArH), 7.58 (d, J = 8 Hz, 1 H, 4-ArH), 7.42 (t, J = 7 Hz, 1 H, 4-ArH), 7.11-7.18 (m, 2 H, 7-ArH), 6.99 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 6.47 (t, J = 11 Hz, 1 H, CH=CHCO₂), 5.86 (d, J = 12 Hz, 1 H, CH=CHCO₂), 5.56 (t, J = 6 Hz, 1 H, CH=CCH₃), 4.97 (m, 1 H, CHCH=CH, obscured under CH₃OH), 2.65 (t, J = 8 Hz, 2 H, CH₂CH), 1.94 (s, 3 H, CH=CCH₃), 1.66 (s, 4 H, CH₂CH₂), and 1.23 (s, 12 H, 4 x CH₃); ¹³C NMR (75 MHz, CD₃OD) δ 169.58 (C=O), 152.51, 145.36, 145.19, 144.33, 142.38, 138.29, 133.72, 133.60, 133.50, 130.02, 129.88, 129.73, 129.00, 127.24, 127.18, 124.96, 124.84, 124.80, 124.12, 120.74, 45.08, 36.36, 36.24, 36.05, 35.31, 35.15, 34.91, 32.30, 32.21, 16.31, and 14.09; IR (KBr) 3600-2400 (br, CO₂H), 2960, 2925, 2860, 1695 (C=O), 1640, 1455, 1420, 1280, and 1245 cm⁻¹; MS (DCI) m/e 447 (MH⁺); Anal. Calcd for C₂₉H₃₄O₄·0.5 H₂O: C, 76.42; H, 7.74. Found: C, 76.52; H, 7.76.

Example 31: Synthesis of Ethyl (2E)-3-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-butenate 34

A solution of 2-acetyl-5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalene (**33**, 4.60 g, 20.0 mmol) and methyl diethylphosphonoacetate (7.33 g, 34.9 mmol) in anhydrous toluene (80 mL) was treated dropwise via syringe with sodium methoxide (25 wt%

in methanol, 5.5 mL, 24.0 mmol) at room temperature under argon. The reaction mixture was stirred for 14 h and then poured into a separatory funnel containing diethyl ether and saturated ammonium chloride solution. The layers were agitated and separated, and the organic layer was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to afford 6.5 g of a pale yellow oil. Purification by column chromatography (20:1 ratio silica gel/crude product; elution with 10% ethyl acetate/hexanes) gave 4.10 g (72%) of **34** as a clear, colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, *J* = 2 Hz, 1 H, ArH), 7.30 (d, *J* = 7 Hz, 1 H, ArH), 7.25 (dd, *J* = 2, 8 Hz, 1 H, ArH), 6.15 (br s, 1 H, C=CH), 3.75 (s, 3 H, CO₂CH₃), 2.58 (s, 3 H, CH₃C=C), 1.67 (s, 4 H, CH₂CH₂), 1.26 (s, 6 H, 2 × CH₃), and 1.28 (s, 6 H, 2 × CH₃).

Example 32: Synthesis of (2E)-3-(5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-butenol 35

A solution of ester **34** (4.10 g, 14.3 mmol) in anhydrous diethyl ether (40 mL) was added via cannula over 10 min to a slurry of lithium aluminum hydride (0.33 g, 8.6 mmol) in diethyl ether (100 mL) at 0 °C under argon. After 2 h, additional lithium aluminum hydride (0.13 g, 3.4 mmol) was added, and the mixture was stirred for 5 h. The reaction was quenched by sequential addition of H₂O (0.46 mL), 15% aqueous sodium hydroxide (0.46 mL), and H₂O (1.38 mL). The resulting slurry was filtered and the filtrate was concentrated in vacuo to give 3.8 g of a colorless oil. Purification by column chromatography (30:1 ratio silica gel/crude product; elution with 10% to 15% ethyl acetate/hexanes) provided 3.51 g (95%) of **35** as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.35 (d, *J* = 2 Hz, 1 H, ArH), 7.28 (d, *J* = 8 Hz, 1 H, ArH), 7.18 (dd, *J* = 2, 8 Hz, 1 H, ArH), 5.95 (t, *J* = 5 Hz, 1 H, C=CH), 4.35 (t, *J* = 5 Hz, 2 H, CH₂OH), 2.10 (s, 3 H, CH₃C=C), 1.65 (s, 4 H, CH₂CH₂), 1.30 (s, 6 H, 2 × CH₃), and 1.28 (s, 6 H, 2 × CH₃).

Example 33: Synthesis of (2E)-3-(5,6,7,8-Tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-butenyl bromide 36

A stirred solution of phosphorous tribromide (0.31 g, 1.16 mmol) and pyridine (0.057 g, 0.72 mmol) in petroleum ether (18 mL) was cooled to -10 °C under argon. The mixture was treated with a solution of **35** (0.94 g, 3.62 mmol) in anhydrous diethyl ether (18 mL).
5 The reaction mixture was allowed to warm to room temperature over 2.5 h. The solution was then diluted with diethyl ether and washed twice with water. The aqueous layers were combined and back-extracted with another portion of diethyl ether. The organic layers were combined, washed with saturated sodium chloride solution,
10 dried over anhydrous magnesium sulfate, filtered, and concentrated to give 1.00 g (86%) of **36** as an off-white solid. The bromide was used without purification in the next reaction. ¹H NMR (300 MHz, CDCl₃) δ 7.33 (d, 1 H, ArH), 7.28 (d, 1 H, ArH), 7.18 (dd, *J* = 12 Hz, 1 H, ArH), 6.05 (t, *J* = 9 Hz, 1 H, C=CH), 4.12 (d, *J* = 9 Hz, 2 H, CH₂Br), 2.13 (s, 3 H, CH=CCH₃), 1.68 (s, 4 H, CH₂CH₂), 1.26 (s, 6 H, 2 × CH₃), and 1.24 (s, 6 H, 2 × CH₃).
15

Example 34: Synthesis of (Z)-2-(3-Trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenyl acetate 37

20 A solution of (Z)-2-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2-pentenol **5x** (0.99 g, 2.4 mmol) in anhydrous pyridine (25 mL) at room temperature under argon was treated with 4-dimethylaminopyridine (0.01 g) and acetic anhydride (0.32 g, 3.1 mmol). The reaction mixture was stirred for 2 h
25 and then partitioned between diethyl ether (100 mL) and 1 N HCl solution (50 mL). The ether layer was washed further with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 1.09 g (100%) of the product as a
30 colorless oil. The acetate was used without purification in the next reaction. ¹H NMR (300 MHz, CDCl₃) δ 7.50 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.36-7.41 (m, 2 H, 2-ArH), 7.17 (d, *J* = 8 Hz, 1 H, 2-ArH), 7.11 (d, *J* = 8 Hz, 1 H, 5-ArH), 6.98 (d, *J* = 2 Hz, 1 H, 5-ArH), 6.82 (dd, *J* = 2, 8 Hz, 1 H, 5-ArH), 5.89 (t, *J* = 7.5 Hz, 1 H, C=CH), 4.73 (s, 2 H, CH₂OAc), 2.61 (t, *J* = 7
35 Hz, 2 H, ArCH₂), 2.24 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 1.99 (s, 3 H, CH₃C=O), 1.64 (s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 × CH₃), and 1.22 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 170.66 (C=O), 144.70, 142.52, 138.81,

137.91, 134.89, 133.09, 131.95, 128.67, 126.48, 126.45, 125.73, 125.36, 125.31, 124.02, 68.68 (CH₂OAc), 35.33, 35.14, 35.09, 34.12, 31.87, 31.81, 30.67, and 20.89; IR (film) 2960, 2925, 2860, 1745 (C=O), 1325, 1225, 1165, and 1130 cm⁻¹; MS (DCI) *m/e* 399 (M⁺ - OAc).

5

Example 35: Synthesis of Methyl (Z)-2-carbomethoxy-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-heptenoate 38

10 Dimethyl malonate (1.44 g, 10.9 mmol) was added dropwise to a
slurry of sodium hydride (80% dispersion in oil, 0.31 g, 10.5 mmol) in
anhydrous THF (20 mL) at room temperature under argon. The
reaction mixture was stirred for 15 min and then treated with a
15 solution of (Z)-2-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-
tetramethyl-2-naphthalenyl)-2-pentenyl acetate (37) (1.09 g, 2.38 mmol),
triphenylphosphine (0.062 g, 0.24 mmol), and
tetrakis(triphenylphosphine)palladium(0) (0.137 g, 0.12 mmol) in THF
(4 mL). The resulting mixture was heated at reflux for 4 h. The yellow
solution was allowed to cool to room temperature and was partitioned
20 between diethyl ether and saturated ammonium chloride solution.
The organic phase was washed with saturated sodium chloride
solution, dried over anhydrous magnesium sulfate, filtered, and
concentrated to afford 1.68 g of crude product. Purification was
achieved by column chromatography (30:1 ratio of silica gel/crude
25 product; elution with 2% to 4% ethyl acetate in hexanes, 25 mL
fractions). Fractions 8-21 (R_f = 0.25, 10% ethyl acetate/hexanes) were
pooled and concentrated to give 0.65 g of a colorless oil. NMR showed
the presence of 10% other isomers. Fractions 22-30 (R_f = 0.25, 10% ethyl
acetate/hexanes) were pooled and concentrated to provide 0.41 g of a
30 colorless oil. NMR showed >98% of one isomer, methyl (Z)-2-
carbomethoxy-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-
tetramethyl-2-naphthalenyl)-4-heptenoate **38**. The combined yield of
the reaction was 84%. ¹H NMR (300 MHz, CDCl₃) δ 7.33 -7.51 (m, 3 H,
4-ArH), 7.10-7.23 (m, 2 H, 1 x 4-ArH and 1 x 7-ArH), 6.95 (d, *J* = 2 Hz, 1
35 H, 7-ArH), 6.79 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 5.65 (t, *J* = 7 Hz, 1 H, C=CH),
3.64 (s, 6 H, 2 x CO₂CH₃), 3.31 (t, *J* = 8 Hz, 1 H, HC(CO₂Me)₂), 2.92 (d, *J* = 8
Hz, 2 H, CH₂CH(CO₂Me)₂), 2.53 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.13 (q, *J* = 7

Hz, 2 H, ArCH₂CH₂), 1.63 (s, 4 H, CH₂CH₂), 1.23 (s, 6 H, 2 × CH₃), and 1.21 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 169.17 (C=O), 144.69, 142.41, 140.17, 138.07, 136.01, 132.02, 131.17, 128.76, 126.41, 126.32, 125.60, 125.25, 123.86, 52.45 (CO₂CH₃), 50.60 (C(CO₂Me)₂), 38.16, 35.65, 35.15, 35.09, 34.12, 33.92, 31.87, 31.80, and 30.80; IR (film) 2960, 2925, 2860, 1755 (C=O), 1740 (C=O), 1435, 1325, 1310, 1275, 1235, 1160, 1130, and 1070 cm⁻¹; MS (DCI) *m/e* 531(MH⁺), 499 (M⁺ - CH₃O).

Example 36: Synthesis of (Z)-2-Carboxy-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-heptenoic acid
39

A solution of methyl (Z)-2-carbomethoxy-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-heptenoate (38) (0.15 g, 0.28 mmol) in 1:1:1 methanol/THF/2N sodium hydroxide solution (4.5 mL) was heated at reflux for 4 h. The reaction mixture was allowed to cool to room temperature and was treated with 10% hydrochloric acid solution (10 mL). The aqueous solution was extracted with diethyl ether (2 × 50 mL), and the organic layers were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 0.13 g (92%) of a white foam. ¹H NMR (300 MHz, CDCl₃) δ 7.48 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.37 (d, *J* = 8 Hz, 1 H, 4-ArH), 7.32 (br s, 1 H, 4-ArH), 7.09-7.20 (m, 2 H, 1 × 4-ArH and 1 × 7-ArH), 6.94 (d, *J* = 2 Hz, 1 H, 7-ArH), 6.77 (dd, *J* = 2, 8 Hz, 1 H, 7-ArH), 5.68 (t, *J* = 7.5 Hz, 1 H, C=CH), 3.36 (t, *J* = 8 Hz, 1 H, CH(CO₂Me)₂), 2.94 (d, *J* = 8 Hz, 2 H, CH₂CH(CO₂Me)₂), 2.53 (t, *J* = 7 Hz, 2 H, ArCH₂), 2.14 (q, *J* = 7 Hz, 2 H, ArCH₂CH₂), 1.63 (s, 4 H, CH₂CH₂), 1.22 (s, 6 H, 2 × CH₃), and 1.20 (s, 6 H, 2 × CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 173.50 (C=O), 144.72, 142.46, 139.80, 138.06, 135.35, 132.10, 131.72, 128.83, 126.37, 125.73, 125.22, 124.06, 50.14 (C(CO₂Me)₂), 37.97, 35.49, 35.15, 35.09, 34.10, 33.92, 31.86, 31.80, and 30.86; IR (KBr) 2400-3600 (br), 1720 (C=O), 1460, 1440, 1410, 1325, 1310, 1165, 1130, and 1070 cm⁻¹; MS (FAB) *m/e* 525 (M⁺ + Na); Anal. Calcd for C₂₉H₃₃O₄F₃·0.25 H₂O: C, 68.69; H, 6.66. Found: C, 68.73; H, 6.68.

Example 37: Synthesis of (Z)-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-heptenoic acid 40

A solution of (Z)-2-carboxy-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-heptenoic acid **39** (0.108 g, 0.21 mmol) in anhydrous acetonitrile (2 mL) was treated with copper(I) oxide (0.003 g, 0.02 mmol). The mixture was heated at reflux for 7 h, and then additional copper(I) oxide (0.003 g, 0.02 mmol) was added and heating was continued for 14 h further. The reaction mixture was then allowed to cool to room temperature and was concentrated in vacuo. The residue was treated with water (5 mL) and 10% aqueous hydrochloric acid solution (5 mL). The aqueous mixture was extracted with diethyl ether (2 x 50 mL), and then organic layers were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated to give 0.10 g of crude product. Column chromatography (60:1 ratio silica gel/crude product; elution with 30% ethyl acetate/hexanes) gave 0.057 g (58%) of the product as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, J = 8 Hz, 1 H, 4-ArH), 7.37 (d, J = 8 Hz, 1 H, 4-ArH), 7.32 (br s, 1 H, 4-ArH), 7.16 (d, J = 8 Hz, 1 H, 4-ArH), 7.08 (d, J = 8 Hz, 1 H, 7-ArH), 6.97 (d, J = 2 Hz, 1 H, 7-ArH), 6.80 (dd, J = 2, 8 Hz, 1 H, 7-ArH), 5.61 (t, J = 7.5 Hz, 1 H, C=CH), 2.64 (t, J = 7.5 Hz, 2 H, CH₂CO₂), 2.56 (t, J = 7.5 Hz, 2 H, ArCH₂), 2.33 (t, J = 7.5 Hz, 2 H, C=CCH₂CH₂CO₂), 2.15 (q, J = 7.5 Hz, 2 H, ArCH₂CH₂), 1.65 (s, 4 H, CH₂CH₂), 1.24 (s, 6 H, 2 x CH₃), and 1.22 (s, 6 H, 2 x CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 178.61 (C=O), 144.63, 142.39, 140.94, 138.24, 138.13, 131.86, 129.01, 128.68, 126.54, 126.40, 125.85, 125.73, 125.05, 123.63, 35.73, 35.17, 35.11, 34.12, 33.93, 33.85, 32.80, 31.88, 31.82, and 30.85; IR (film) 3600-2400 (br), 2960, 2925, 2860, 1710 (C=O), 1495, 1455, 1440, 1410, 1325, 1310, 1275, 1165, 1130, and 1070 cm⁻¹; MS (FAB) m/e 481 (MH⁺); Anal. Calcd for C₂₈H₃₃O₂F₃·0.25 H₂O: C, 72.62; H, 7.29. Found: C, 72.51; H, 7.16.

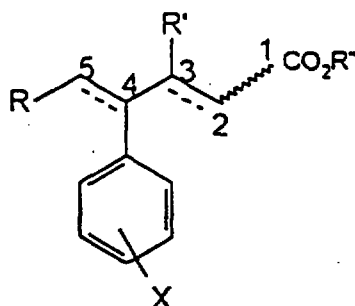
Reasonable variations, such as those which would occur to a skilled artisan can be made herein without departing from the scope of the invention.

CLAIMS

We claim:



- 5 1. A compound of Formula I:

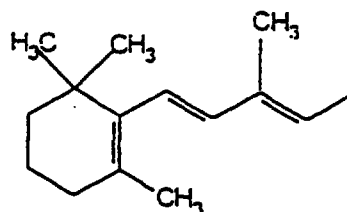


(I)

- 15 wherein the bonds between C₂ and C₃ and/or between C₄ and C₅ are unsaturated;

X = COOH, H, F, Cl, Br, I, COOR'', CONH₂, COR''', CHO, CH₂OH, CH₂OR''', OH, OR''', CF₃, C₁₋₆ alkyl, C₁₋₆ alkenyl, C₁₋₆ haloalkyl, NO₂, P(O)(OH)₂, SO₂H, or SO₃H;

- 20 R = substituted or unsubstituted alkyl, aryl, arylalkyl, alkenyl, or arylalkenyl groups, with the proviso that each of these groups must have 6 or more carbons (preferably 6 to 30) and R cannot be



25

R' = H or C₁₋₆ alkyl;

R'' = H, C₁₋₆ alkyl, C(R³)₂OC(O)R⁴, CH₂CH₂NR⁵R⁶, CH₂CH₂CH₂NR⁵R⁶, CH₂C(O)N(R⁶)₂, or other groups yielding physiologically hydrolyzable esters;

30

R''' = C₁₋₆ alkyl;

R³ = H, CH₃, C₂H₅, CH₃CH₂CH₂ (with R³'s being the same or different);

R⁴ = C₆₋₁₂ aryl, C₁₋₇ linear, branched or cyclic alkyl, or C₁₋₇ linear, branched or cyclic alkoxy;

- 35 R⁵ = R⁶, or when linked with R⁶, is a C₃-C₆ cycloalkyl or a -CH₂CH₂OCH₂CH₂- group; and

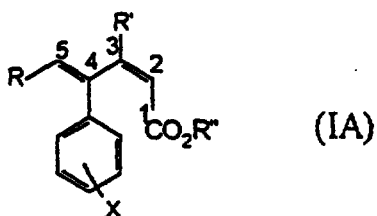
R⁶ = C₁₋₃ alkyl;

and pharmaceutically-acceptable salts thereof.

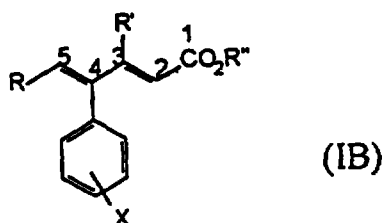


2. The compounds of claim 1 having a structure selected from the group consisting of structure types IA, IB, IC, and ID:

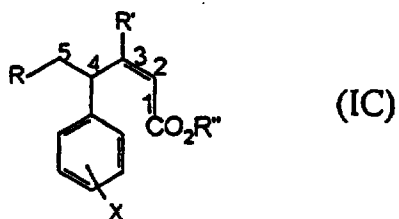
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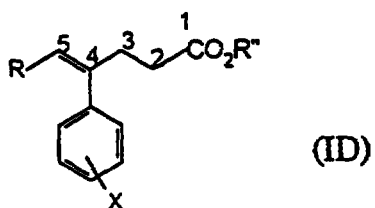
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3. The compound of claim 2 conforming to structure IA.



4. The compound of claim 3 selected from the group consisting of:

- 5 (2Z), (4Z)-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-carboxyphenyl)-5-(4-decyloxyphenyl)-2,4-pentadienoic acid;
- 10 (2Z), (4Z)-4-(3-carboxyphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;
- (2Z), (4Z), (6E)-4-(3-carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4,6-octatrienoic acid;
- 15 (2Z), (4Z)-4-(3-carboxyphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid;
- (2Z), (4Z)-4-(3-carboxyphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid;
- 20 (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(4-decyloxyphenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(3-decyloxyphenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(2-decyloxyphenyl)-2,4-pentadienoic acid;
- 25 (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-[4-(2E), (6E)-3, 7-dimethylocta-2,6-dienoxy]phenyl-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid;
- 30 (2E), (4Z)-4-(3-trifluoromethylphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;
- 35 (2Z), (4Z)-4-(4-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;



- (2Z), (4Z)-4-(3-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;
- (2Z), (4Z)-4-phenyl-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;
- 5 (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid;
- (2Z), (4Z)-4-phenyl-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid;
- 10 (2Z), (4Z)-4-phenyl-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[2-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid;
- 15 (2Z), (4Z)-4-(3-trifluoromethylphenyl)-5-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-pentadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-hydroxyphenyl]-2,4-heptadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-pentyloxyphenyl]-2,4-heptadienoic acid;
- 20 (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(4-methoxybenzyloxy)phenyl]-2,4-heptadienoic acid;
- (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-benzyloxy)phenyl]-2,4-heptadienoic acid;
- 25 (2Z), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-(carboxymethoxy)phenyl]-2,4-heptadienoic acid; and
- (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid;
- 30 5. The compound of claim 2 conforming to structure IB.
6. The compound of claim 5 selected from the group consisting of:
- (2E), (4Z)-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid;
- 35 (2E), (4Z)-4-(3-carboxyphenyl)-5-(3,4-bis(pentyloxy)phenyl)-2,4-pentadienoic acid;



(2E), (4Z)-4-(3-carboxyphenyl)-5-(3,4-bisdecyloxyphenyl)-2,4-pentadienoic acid;

(2E), (4Z)-4-(3-carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;

5 (2E), (4Z)-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;

(2E), (4Z)-4-(4-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;

10 (2E), (4Z)-4-(3-fluorophenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;

(2E), (4Z)-4-phenyl-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,4-heptadienoic acid;

(2E), (4Z)-4-(3-trifluoromethylphenyl)-7-[3-(1-adamantyl)-4-methoxyphenyl]-2,4-heptadienoic acid; and

15 (2E), (4Z)-4-(3-trifluoromethylphenyl)-7-[4-(1-adamantyl)-3-methoxyphenyl]-2,4-heptadienoic acid;

7. The compound of claim 2 conforming to structure IC.

20 8. The compound of claim 7 selected from the group consisting of:

(2E), (6E)-4-(3-carboxyphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-2,6-octadienoic acid, and

25 (2E)-4-[3-carboxyphenyl]-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-hepta-2-enoic acid.

9. The compound of claim 2 conforming to structure ID.

30 10. (Z)-4-(3-trifluoromethylphenyl)-7-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-4-heptenoic acid.

11. A potassium, sodium, triethanolamine, tris(hydroxymethyl)aminomethane, N-methylglucamine, or L-lysine monosalt of a compound of any one of claims 1 to 10 in which
35 R" = H.



12. A potassium, sodium, triethanolamine, tris(hydroxymethyl)aminomethane, N-methylglucamine, or L-lysine bissalt of a compound of claim 1 in which $R'' = H$ and $X = COOH$.

5 13. The dipotassium salt of (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid.

10 14. The disodium salt of (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid.

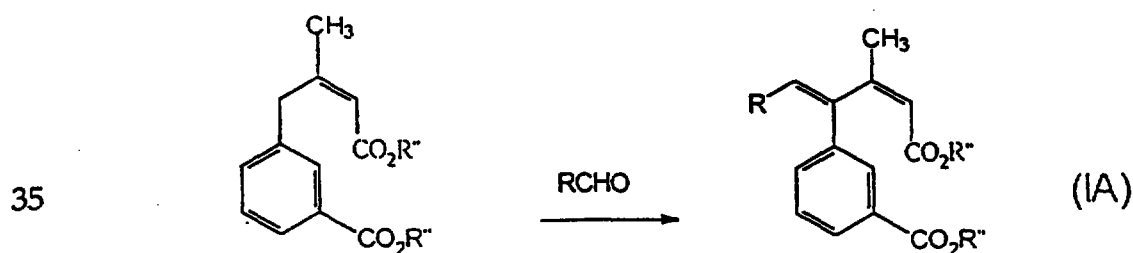
15 15. The bis(triethanolamine) salt of (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid.

20 16. The bis-[tris(hydroxymethyl)aminomethane] salt of (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid.

17. The bis-(N-methylglucamine) salt of (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid.

25 18. The bis-(L-lysine) salt of (2Z), (4Z)-3-methyl-4-(3-carboxyphenyl)-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-anthracenyl)-2,4-pentadienoic acid.

30 19. The method of making a compound of structure type IA comprising the step:





20. A pharmaceutical composition containing an anti-inflammatory effective amount of at least one compound of any one of claims 1 to 18 and a suitable amount of at least one pharmaceutically acceptable carrier.
- 5 21. The composition of claim 20 wherein the compound is present in an amount of about 0.005 to about 10.0 wt%.
22. The composition of claim 21 in a topical dosage form.
23. The composition of claim 21 in an oral dosage form.
24. A compound according to any one of claims 1 to 18 or
10 when made by the method of claim 19, or a composition according to any one of claims 20 to 23, for use as a medicament.
25. A compound according to any one of claims 1 to 18 or when made by the method of claim 19, or a composition
15 according to any one of claims 20 to 23, for use as an anti-inflammatory agent.
26. Use of a compound according to any one of claims 1 to 18 or when made by the method of claim 19, or a composition according to any one of claims 20 to 23, for the manufacture
20 of a medicament for use as an anti-inflammatory agent.

ABSTRACT"ALICYCLIC PHOSPHOLIPASE A₂ INHIBITORS"

Certain novel alicyclic compounds are effective phospholipase A₂ (PLA₂) inhibitors.