Synthesis of Spiro[5.4]decenones and Their Transformation into Bicyclo[4.4]deca-1,4-dien-3-ones by Domino "Elimination–Double-Wagner–Meerwein-Rearrangement" Reactions

Gopal Bose, Ehsan Ullah, and Peter Langer*[a]

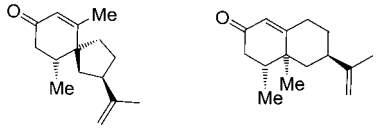
Abstract: The [3+3] cyclization of 1,3-bis-silyl enol ethers with 1,1-diacylcyclopentanes allows a convenient synthesis of spiro[5.4]decenones. Treatment of these compounds with trifluoroacetic acid (TFA) afforded a great variety of bicyclo[4.4.0]deca-1,4-dien-3-ones containing an angular alkyl group. This core structure occurs in a number of pharmacologically relevant natural products.

Keywords: cyclization · domino reactions · rearrangement · silyl enol ethers · spiro compounds

Introduction

1,3-Bis-silyl enol ethers can be regarded as electroneutral 1,3-dicarbonyl dianion equivalents (masked dianions).[1,2] They represent useful synthetic building blocks in Lewis acid mediated transformations. In cyclization reactions, 1,3-bis-silyl enol ethers can react as 1,3-dinucleophiles or, similarly to the well-known Danishefsky diene,[3] as functionalized 1,3-butadienes. Chan and co-workers have reported $TiCl_4$-mediated [3+3] cyclizations of 1,3-bis-silyl enol ethers with 3-silyloxyalk-2-en-1-ones and with ketals of β-ketoaldehydes, β-ketoesters, and β-ketocarboxylic chlorides to give benzene derivatives.[4] In addition, the synthesis of aromatic products by cyclization of free 1,3-dicarbonyl compounds with 1,3-dielectrophiles has been reported.[5,6]

We have recently reported the $TiCl_4$-mediated cyclization of 1,3-bis-silyl enol ethers with 1,1-diacetylcyclopentane to give spiro[5.4]decenones.[7] Treatment of these compounds with trifluoroacetic acid (TFA) resulted in a domino rearrangement[8] and formation of bicyclo[4.4.0]deca-1,4-dien-3-ones containing an angular methyl group. This type of rearrangement has been previously reported by Hagenbruch and Hünig[9a] and by others.[9b–g] The bicyclo[4.4.0]decane core structure is present in a variety of natural products, such as steroids and the eudesmane and eremophilane sesquiterpenes (for example, nootkaton; Scheme 1).[10,11] The spiro[5.4]decane skeleton also occurs in nature. This includes the spirovetivane sesquiterpenes (for example, solavetivone; Scheme 1), which are biosynthetically derived from the eudesmanes.[10] The biosynthetic pathways for the interconversion of eudesmane, eremophilane, and the spirovetivane sesquiterpenes involve Wagner–Meerwein rearrangements.[12–14]



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Scheme 1. Spiro[5.4]decanes and bicyclo[4.4.0]decanes in nature.

We have significantly extended the preparative scope of the methodology, with regard to our preliminary communication.[7] We have successfully developed regioselective cyclizations of unsymmetrical 1,1-diacylcyclopentanes, such as 1-acetyl-1-formylcyclopentane, and also studied cyclizations of 2,2-diacetylindane, 1,1-diacetylcyclopent-3-ene, and 3,3-dimethylpentane-2,4-dione. In addition, the mechanism of the domino process was studied.

Results and Discussion

Our starting point was the development of conditions for the cyclization of 3,3-dimethylpentane-2,4-dione (**2**) with 1,3-bis-silyl enol ether **1a**. Treatment of a CH_2Cl_2 solution of the starting materials with $TiCl_4$ (2 equiv) resulted in the formation of 3-hydroxycyclohex-5-en-1-one **3a** (Scheme 2). The product was formed by cyclization and subsequent extrusion of water. The use of other Lewis acids, such as $BF_3{\cdot}OEt_2$, Me_3SiOTf, or $ZnCl_2$, was unsuccessful. Optimal yields were obtained when the reaction was carried out at −78→20 °C.

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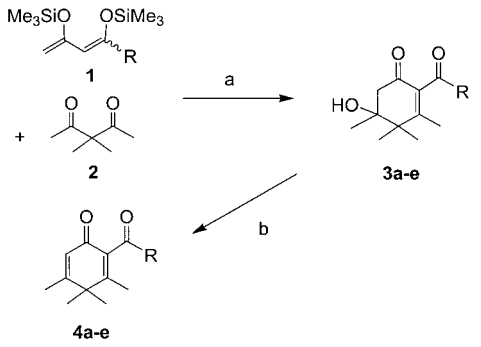


Scheme 2. Cyclization of 1,3-bis-silyl enol ethers with 3,3-dimethylpentane-2,4-dione: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å molecular sieves (MS), −78→20 °C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

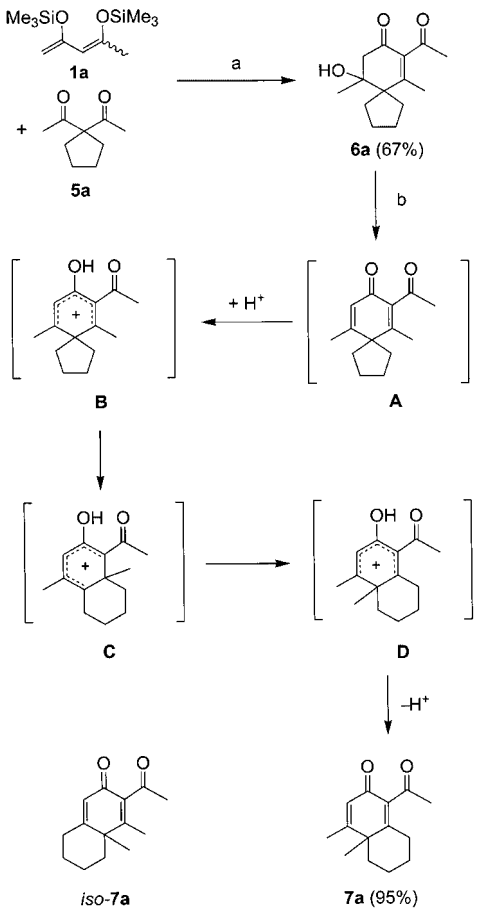
The use of molecular sieves (4 Å) proved to be mandatory. Treatment of a CH_2Cl_2 solution of **3a** with TFA afforded, after optimization of the reaction conditions, the cyclohexa-2,5-dien-1-one **4a** in 88% yield. A number of related products (**3b–e** and **4b–e**) were prepared by variation of the 1,3-bis-silyl enol ether (Table 1).

Table 1. Products and yields.

3,4	R	% 3[a]	% 4[a]
a	Me	47	88
b	OMe	61	95
c	OEt	63	96
d	O*i*Pr	56	90
e	$O(CH_2)_2Me$	61	92

[a] Yield of isolated products.

The $TiCl_4$-mediated cyclization of **1a** with 1,1-diacetylcyclopentane (**5a**), prepared by K_2CO_3-mediated cyclization of acetylacetone with 1,4-dibromobutane,[9,15] afforded the hydroxyspiro[5.4]decenone **6a** in good yield (Scheme 3). The following parameters proved to be important during the optimization of this reaction: a) the choice of the Lewis acid, b) the temperature (−78→20 °C), and c) the presence of molecular sieves (4 Å). Stirring of a TFA/CH_2Cl_2 solution of **6a** for 72 h afforded the bicyclo[4.4.0]deca-1,4-dien-3-one **7a** in high yield. The formation of **7a** can be explained as follows (Scheme 3): acid-mediated elimination of water gave the spiroannulated cyclohexa-2,5-dien-1-one **A**, which was protonated to give intermediate **B**. Ring enlargement by [1,2] rearrangement gave intermediate **C**. Rearrangement of the methyl group gave intermediate **D** and subsequent ex-

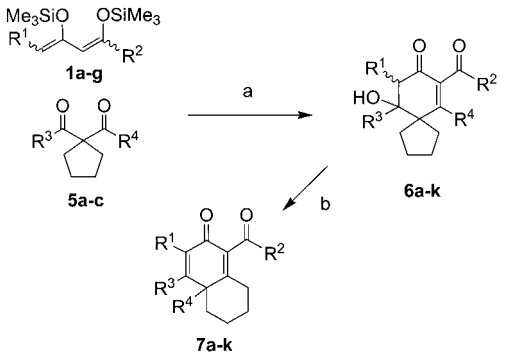


Scheme 3. Cyclization of 1,3-bis-silyl enol ether **1a** with 1,1-diacetylcyclopentane: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å MS, −78→20 °C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

trusion of a proton afforded **7a**. The rearrangement proceeded with very good regioselectivity. The formation of the regioisomer *iso*-**7a** was not observed. The regioselectivity of the ring enlargement (**B**→**C**) can be explained by the fact that carbon atom C-5 of the delocalized carbocation **B** is more electron-poor than carbon atom C-3, due to the proximity of two electron-withdrawing carbonyl groups.

The preparative scope of our methodology was studied. The reaction of **5a** with ester-derived 1,3-bis-silyl enol ethers **1b–e** gave the spiro compounds **6b–e**, which were successfully transformed into the bicyclo[4.4.0]deca-1,4-dien-3-ones **7b–e** (Scheme 4, Table 2). The cyclization of **5a** with 1,3-bis-silyl enol ethers **1f** and **1g**, which contain either a methyl or an ethyl group at the terminal carbon atom, afforded the spiro compounds **6f** and **6g**, respectively. Treatment of these compounds with TFA resulted in formation of the bicyclo[4.4.0]decadienones **7f** and **7g** containing a methyl and an ethyl substituent, respectively. Variation of the 1,1-diacylcyclopentane was studied next. The reaction of **1b–d** with novel 1,1-dipropionylcyclopentane (**5b**), prepared by cyclization of heptane-3,5-dione with 1,4-dibromobutane, resulted in formation of spiro compounds **6h–j**, which were successfully transformed into **7h–j**. The cyclization of 1,3-bis-silyl enol ether **1c** with (unsymmetrical) 1-acetyl-1-benzoylcyclopentane (**5c**)[15d] gave the spiro[5.4]decenone **6k**.

Abstract in German: *Die [3+3] Cyclisierung von 1,3-Bis-Silylenolethern mit 1,1-Diacylcyclopentanen ermöglicht eine effiziente Synthese von Spiro[5.4]decenonen. Durch Behandlung dieser Verbindungen mit Trifluoressigsäure (TFA) konnte eine große Bandbreite von Bicyclo[4.4.0]deca-1,4-dien-3-onen mit angularer Alkylgruppe hergestellt werden. Dieses Gerüstsystem tritt in einer Reihe pharmakologisch relevanter Naturstoffe auf.*



Scheme 4. Synthesis of **6a–k** and **7a–k**: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å MS, −78→20 °C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

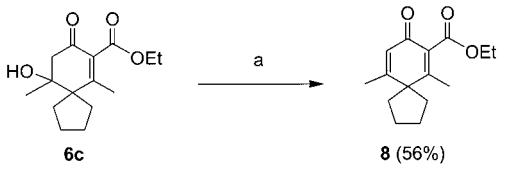
Table 2. Products and yields.

6,**7**	R^1	R^2	R^3	R^4	% **6**[a]	% **7**[a]
a	H	Me	Me	Me	67	95
b	H	OMe	Me	Me	72	98
c	H	OEt	Me	Me	78	96
d	H	O*i*Pr	Me	Me	66	97
e	H	$O(CH_2)_2OMe$	Me	Me	53	97
f	Me	OMe	Me	Me	23[b]	92
g	Et	OEt	Me	Me	41[b]	88
h	H	OMe	Et	Et	58	83
i	H	OEt	Et	Et	53	85
j	H	O*i*Pr	Et	Et	38	89
k	H	OEt	Me	Ph	20	91

[a] Yields of isolated products. [b] Diastereomeric mixture.

The TFA-mediated rearrangement of **6k** selectively afforded the bicyclo[4.4.0]decadienone **7k**.

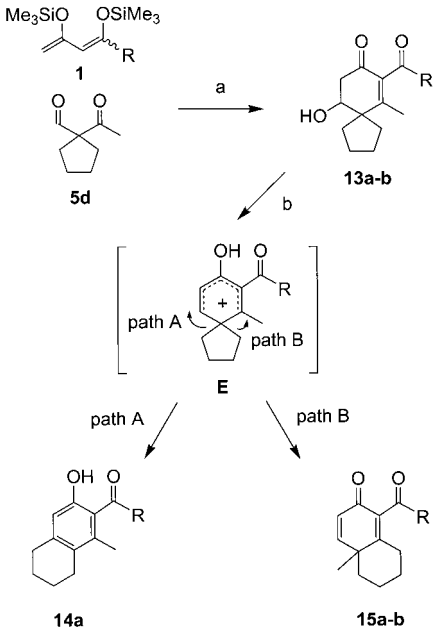
Treatment of hydroxyspiro[5.4]decenone **6c** with TFA for only 3 h (rather than for 72 h) afforded the spiro[5.4]decadienone **8** in 56% yield (Scheme 5). This experiment supports the intermediacy of spiro[5.4]decadienone **A** in the mechanism suggested (Scheme 3). The formation of a carbocation by extrusion of water and subsequent ring enlargement (without protonation of the carbonyl group) appears to be less likely.



Scheme 5. Synthesis of **8**: a) TFA, CH_2Cl_2, 3 h.

Cyclization reactions of 1-acetyl-1-formylcyclopentane (**5d**) were studied next. The synthesis of novel compound **5d** was accomplished as follows (see the Experimental Section). The cyclization of ethyl acetoacetate with 1,4-dibromobutane afforded ethyl 1-acetylcyclopentane-1-carboxylate (**9**). The keto group of **9** was protected by transformation into a ketal (**10**). The ester group was reduced to an alcohol (**11**), the acetal was hydrolyzed, and the alcohol (**12**) was transformed into an aldehyde by application of the Swern oxidation. This straightforward synthesis of **5d** is related to the procedure reported for the preparation of 1-acetyl-1-formylcyclopropane.[16]

The cyclization of 1,3-bis-silyl enol ether **1c** with 1-acetyl-1-formylcyclopentane (**5d**) gave the spiro compound **13a**, which was formed by regioselective attack of the terminal carbon atom of **1c** onto the aldehyde group (Scheme 6,



Scheme 6. Synthesis of **13a**, **13b**, **14a**, **15a**, and **15b**: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å MS, −78→20 °C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

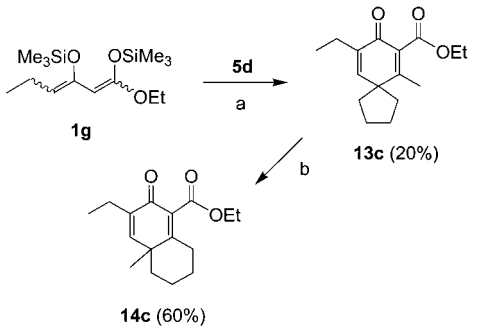
Table 3. Products and yields.

13, **14**, **15**	R	% **13**[a]	% **14**[a]	% **15**[a]
a	OEt	20	43	22
b	Me	27	0	52

[a] Yields of isolated products.

Table 3). Treatment of **13a** with TFA afforded a separable mixture of the expected bicyclo[4.4.0]decadienone **14a** (43%, mechanism path B) and of the tetraline **15a** (22%, mechanism path A). The formation of **15a** can be explained by elimination of water and protonation to give intermediate **E** and subsequent ring enlargement and aromatization. The regioselectivity of the ring enlargement can be explained by the higher reactivity of the secondary carbocation located at C-3 (with respect to the tertiary carbocation located at C-5). The product **15a** is formed by a rapid ring enlargement (mechanism path A) and irreversible formation of a stable aromatic product. The cyclization of **5d** with 1,3-bis-silyl enol ether **1a** afforded **13b**. Treatment of the latter with TFA resulted in exclusive formation of the tetraline **15b** in 52% yield (mechanism path A).

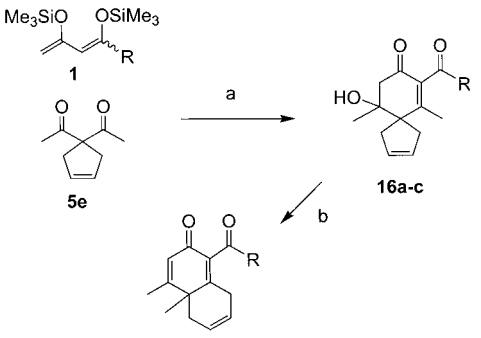
The reaction of **5d** with **1g** afforded the spiro compound **13c** (Scheme 7). Treatment of the latter with TFA exclusively afforded the bicyclo[4.4.0]decadienone **14c** in 60% yield (mechanism path B). The formation of an aromatic product



Scheme 7. Synthesis of **13c** and **14c**: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å MS, −78→20°C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

15 by mechanism path A is disfavored, due to the presence of the ethyl group at carbon atom C-2 and steric repulsion during the ring enlargement.

Cyclization reactions of 1,1-diacetylcyclopent-3-ene (**5e**) were studied next. Direct base-mediated cyclization of acetylacetone with 1,4-dichlorobut-2-ene has been reported to give mixtures of regioisomeric products.[17] Therefore, we have developed a new synthesis of **5e**. The reaction of acetylacetone with allyl bromide afforded the known 3,3-diallylacetylacetone, which was subsequently transformed into **5e** by ring-closing metathesis (RCM) with the Grubbs catalyst and Ti(O*i*Pr)$_4$ (Fürstner conditions).[18] The reaction of 1,3-bis-silyl enol ethers **1b–d** with **5e** afforded the spiro compounds **16a–c** (Scheme 8, Table 4). Treatment of **16a–c** with TFA afforded the bicyclo[4.4.0]deca-1,4,6-trien-3-ones **17a–c**. The formation of the latter can be explained by a double Wagner–Meerwein rearrangement, as described for



Scheme 8. Synthesis of **16a–c** and **17a–c**: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å MS, −78→20°C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

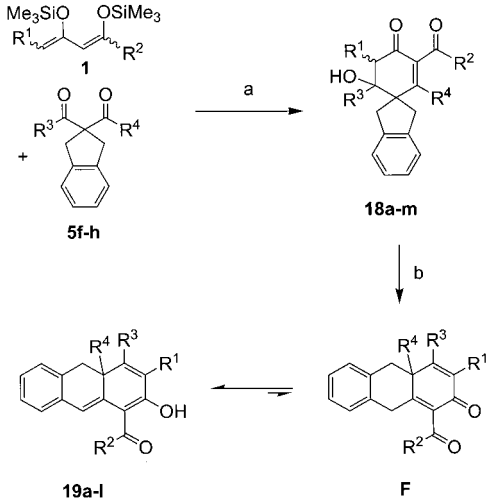
Table 4. Products and yields.

16, **17**	R	% **16**[a]	% **17**[a]
a	OMe	83	76
b	OEt	64	76
c	O*i*Pr	59	73

[a] Yields of isolated products.

7. Despite the acidic conditions, no migration of the double bond was observed during the reaction.

The reaction of 1,3-bis-silyl enol ethers with 2,2-diacetylindane (**5f**), prepared by base-mediated cyclization of acetylacetone with 1,2-bis(bromomethyl)benzene,[19] was studied next (Scheme 9, Table 5). The cyclization of 1,3-bis-silyl enol



Scheme 9. Synthesis of **18a–m** and **19a–l**: a) 1. $TiCl_4$ (2.0 equiv), CH_2Cl_2, 4 Å MS, −78→20°C; 2. H^+, H_2O; b) TFA, CH_2Cl_2, 72 h.

Table 5. Products and yields.

18, **19**	R^1	R^2	R^3	R^4	% **18**[a]	% **19**[a]
a	H	Me	Me	Me	82	82
b	H	OMe	Me	Me	86	79
c	H	OEt	Me	Me	86	86
d	H	O*i*Pr	Me	Me	82	76
e	H	$O(CH_2)_2OMe$	Me	Me	61	85
f	Et	OEt	Me	Me	31[b]	–[c]
g	H	OMe	Me	Ph	23	73
h	H	OMe	Ph	Me	21	84
i	H	OEt	Me	Ph	22	84
j	H	OEt	Ph	Me	17	83
k	H	O*i*Bu	Me	Ph	21	83
l	H	O*i*Bu	Ph	Me	15	73
m	H	O*i*Pr	Et	Et	43	–[c]

[a] Yields of isolated products. [b] Diastereomeric mixture. [c] The product could not be isolated in pure form.

ether **1a** with **5f** afforded the benzo-annulated spiro[5.4]decenone **18a** in good yield. Treatment of **18a** with TFA afforded the tricyclic product **19a**, which can be regarded as a 9,9a-dihydroanthracene. Due to conjugation of the enol moiety with the aryl group, this compound resides in the enol tautomeric form. The reaction of 1,3-bis-silyl enol ethers **1b–e** with **5f** afforded the spiro[5.4]decenones **18b–e**, which were transformed into the 9,9a-dihydroanthracenes **19b–e**. The reaction of **1g** with **5f** afforded **18f**. Treatment of the latter resulted in the formation of the ethyl-substituted 9,9a-dihydroanthracene **19f**; however, this could not be isolated in pure form. The reaction of 1,3-bis-silyl enol ether **1b** with novel 2-acetyl-2-benzoylindane (**5g**) afforded a separable mixture of the regioisomeric spiro[5.4]decenones **18g** (23%) and **18h** (21%). These products were transformed

into the corresponding 9,9a-dihydroanthracenes **19g** and **19h**, respectively. The reaction of ethoxy- and isobutoxy-substituted 1,3-bis-silyl enol ethers with **5g** afforded separable mixtures of the regioisomers **18i** and **18j** and of the regioisomers **18k** and **18l**, respectively. These products were transformed into the 9,9a-dihydroanthracenes **19i–l**. The cyclization of **1d** with novel 2,2-dipropionylindane (**5h**) afforded **18m**. Treatment of the latter with TFA afforded **19m**; however, this could not be isolated in pure form.

Conclusion

The [3+3] cyclization of 1,3-bis-silyl enol ethers with 1,1-diacylcyclopentanes allows a convenient synthesis of spiro[5.4]decenones. Treatment of these compounds with TFA afforded a great variety of bicyclo[4.4.0]deca-1,4-dien-3-ones containing an angular alkyl group.

Experimental Section

General: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For the ^{1}H and ^{13}C NMR spectra (^{1}H NMR: 300, 600 MHz; ^{13}C NMR: 75, 150 MHz), the deuterated solvents indicated were used. Mass spectrometry (MS) data were obtained by using the electron ionization (70 eV), chemical ionization (CI, H_2O), or electrospray ionization (ESI) techniques. For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

Typical procedure for the preparation of 3-hydroxycyclohex-5-en-1-ones of 3: $TiCl_4$ (0.22 mL, 2.00 mmol) was added dropwise to a stirred CH_2Cl_2 solution (100 mL) of 3,3-dimethylpentane-2,4-dione (**2**; 0.133 g, 1.04 mmol) and 1,3-bis(trimethylsilyloxy)-1,3-butadiene **1a** (0.330 g, 1.35 mmol) at −78 °C under an argon atmosphere in the presence of molecular sieves (4 Å; 1.0 g). The temperature of the reaction mixture was allowed to rise to 20 °C over 6 h. The solution was stirred for an additional 6 h at 20 °C. The reaction mixture was filtered and the filtrate was poured into an aqueous solution of HCl (10%, 100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were dried (Na_2SO_4) and filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate 3:2) to give **3a** as a colorless oil (0.102 g, 47%).

2-Acetyl-5-hydroxy-3,4,4,5-tetramethylcyclohex-2-enone (3a): From 1-methyl-1,3-bis(trimethysilyloxy)buta-1,3-diene (**1a**; 0.330 g, 1.35 mmol), 3,3-dimethylpentane-2,4-dione (**2**; 0.133 g, 1.04 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **3a** was obtained as a colorless oil (0.102 g, 47%). R_f=0.08 (hexane/ethyl acetate 7:3); ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.65 (s, 2H; CH_2), 2.33 (s, 3H; CH_3), 2.05 (br, 1H; OH), 1.89 (s, 3H; CH_3), 1.30 (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.20 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=205.19, 195.06, 163.03, 138.77 (C), 75.09 (C−OH), 49.06 (CH_2), 44.51 (C), 31.81, 24.51, 22.24, 20.61, 16.95 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3424 (br), 2986 (m), 1719 (s), 1663 (s), 1621 (m), 1384 (m), 1243 (s), 129 (s), 1092 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=240.5 (7) [M^+], 211.3 (10), 195.3 (34), 179.3 (14), 151.5 (30), 136.2 (100), 108.5 (22), 43.1 (14).

4-Hydroxy-2,3,3,4-tetramethyl-6-oxocyclohex-1-ene carboxylic acid methyl ester (3b): From 1-methoxy-1,3-bis(trimethysilyloxy)buta-1,3-diene (**1b**; 0.386 g, 1.48 mmol), 3,3-dimethylpentane-2,4-dione (**2**; 0.152 g, 1.18 mmol), and $TiCl_4$ (0.24 mL, 2.18 mmol), **3b** was obtained as a colorless solid (0.164 g, 61%). M.p. 114–115 °C; R_f=0.12 (hexane/ethyl acetate 7:3); ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.78 (s, 3H; OCH_3), 2.62 (s, 2H; CH_2), 2.15 (s, 1H; OH), 1.90 (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.22 (s, 3H; CH_3), 1.16 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 193.18, 167.47, 164.33, 132.34 (C), 74.96 (C−OH), 52.05 (OCH_3), 48.83 (CH_2), 44.49 (C), 24.40, 22.09, 20.66, 17.68 ppm (CH_3); IR (KBr): $\tilde{\nu}$= 3411 (br), 2987 (m), 1728 (s), 1661 (s), 1618 (m), 1436 (m), 1340 (m), 1225 (s), 1091 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=226.3 (5) [M^+], 211.1 (11), 194.2 (35), 179.2 (16), 151.5 (29), 136.1 (100), 107.2 (20), 43.0 (16); elemental analysis calcd (%) for $C_{12}H_{18}O_4$: C 63.70, H 8.31; found: C 63.64, H 8.39.

4-Hydroxy-2,3,3,4-tetramethyl-6-oxocyclohex-1-ene carboxylic acid ethyl ester (3c): From 1-ethoxy-1,3-bis(trimethysilyloxy)buta-1,3-diene (**1c**; 0.375 g, 1.37 mmol), 3,3-dimethylpentane-2,4-dione (**2**; 0.135 g, 1.05 mmol), and $TiCl_4$ (0.23 mL, 2.09 mmol), **3c** was obtained as a colorless solid (0.159 g, 63%). M.p. 116–117 °C; R_f=0.12 (hexane/ethyl acetate 7:3); ^{1}H NMR (200 MHz, $CDCl_3$): δ=4.31 (d, 2H, J=7.2 Hz; OCH_2), 2.64 (s, 2H; CH_2), 2.27 (s, 1H; OH), 1.95 (s, 3H; CH_3), 1.33 (t, 3H, J= 7.2 Hz; CH_3), 1.31 (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.21 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=193.44, 167.19, 164.08, 132.39 (C), 74.99 (C−OH), 61.29 (OCH_2), 48.71 (CH_2), 44.35 (C), 24.34, 22.10, 20.59, 17.66, 14.11 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3424 (br), 2986 (m), 1719 (s), 1663 (s), 1621 (m), 1384 (m), 1243 (s), 129 (s), 1092 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=240.5 (7) [M^+], 211.3 (10), 195.3 (34), 179.3 (14), 151.5 (30), 136.2 (100), 108.5 (22), 43.1 (14); elemental analysis calcd (%) for $C_{13}H_{20}O_4$: C 64.98, H 8.39; found: C 64.80, H 8.24.

4-Hydroxy-2,3,3,4-tetramethyl-6-oxocyclohex-1-ene carboxylic acid isopropyl ester (3d): From 1-isopropyloxy-1,3-bis(trimethysilyloxy)buta-1,3-diene (**1d**; 0.380 g, 1.32 mmol), 3,3-dimethylpentane-2,4-dione (**2**; 0.130 g, 1.01 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **3d** was obtained as a colorless solid (0.144 g, 56%). M.p. 68–69 °C; R_f=0.11 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.15 (sep, 1H, J=6.2 Hz; OCH), 2.62 (s, 2H; CH_2), 2.30 (s, 1H; OH), 1.93 (s, 3H; CH_3), 1.31 (s, 3H; CH_3), 1.25 (d, 6H, J=6.2 Hz; CH_3), 1.22 (s, 3H; CH_3), 1.16 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.41, 166.75, 163.45, 132.58 (C), 75.01 (C−OH), 68.93 (OCH), 48.75 (CH_2), 44.30 (C), 24.33, 22.13, 21.70 (2C), 20.60, 17.45 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3415 (br), 2982 (m), 1723 (s), 1658 (s), 1619 (m), 1461 (m), 1356 (s), 1226 (s), 1096 cm^{-1} (s); MS (EI, 70 eV): m/z (%)=254.6 (17) [M^+], 211.4 (77), 195.3 (69), 169.2 (65), 151.8 (44), 136.3 (100), 108.5 (24), 43.1 (52); elemental analysis calcd (%) for $C_{14}H_{22}O_4$ (254.33): C 66.11, H 6.81; found: C 65.93, H 9.38.

4-Hydroxy-2,3,3,4-tetramethyl-6-oxocyclohex-1-ene carboxylic acid 2-methoxyethyl ester (3e): From 1-(2-methoxy)ethoxy-1,3-bis(trimethysilyloxy)buta-1,3-diene (**1e**; 0.401 g, 1.32 mmol), 3,3-dimethylpentane-2,4-dione (**2**; 0.135 g, 1.05 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **3e** was obtained as a colorless solid (0.164 g, 61%). M.p. 78–88 °C; R_f=0.11 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.39 (t, 2H, J=4.8 Hz; OCH_2), 3.64 (t, 2H, J=4.8 Hz; OCH_2), 3.38 (s, 3H; OCH_3), 2.61 (s, 2H; CH_2), 2.29 (s, 1H; OH), 1.96 (s, 3H; CH_3), 1.29 (s, 3H; CH_3), 1.26 (s, 3H; CH_3), 1.19 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=193.31, 167.07, 164.57, 132.08 (C), 74.92 (C−OH), 70.22, 63.92 (OCH_2), 58.75 (OCH_3), 48.72 (CH_2), 44.42 (C), 24.33, 22.02, 20.62, 17.66 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3402 (br), 2987 (m), 1727 (s), 1660 (s), 1619 (m), 1456 (m), 1382 (s), 1245 (s), 1091 cm^{-1} (s); MS (EI, 70 eV): m/z (%)=270.5 (18) [M^+], 211.3 (40), 194.5 (79), 179.2 (41), 151.8 (68), 136.6 (100), 108.5 (32), 43.1 (37); elemental analysis calcd (%) for $C_{14}H_{22}O_5$ (270.33): C 62.20, H 8.20; found: C 62.35, H 8.59.

Typical procedure for the preparation of cyclohexa-2,5-dien-1-ones of 4: TFA (0.4 mL, 5.2 mmol) was added dropwise to a stirred CH_2Cl_2 solution (0.4 mL) of **3a** (0.065 g, 0.31 mmol) at 20 °C. The solution was stirred for 72 h until all starting material disappeared (TLC control). The solvent and TFA were removed in vacuo and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate 7:3) to give **4a** as a colorless oil (0.052 g, 88%).

2-Acetyl-3,4,4,5-tetramethylcyclohexa-2,5-dienone (4a): From **3a** (0.065 g, 0.31 mmol), **4a** was obtained as a colorless oil (0.052 g, 88%). R_f=0.23 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.12 (d, 1H, J=1.2 Hz; =CH), 2.37 (s, 3H; CH_3), 2.05 (d, 3H, J=1.2 Hz; CH_3), 1.96 (s, 3H; CH_3), 1.29 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=205.32, 183.14, 165.71, 160.60, 139.12 (C), 126.40 (CH), 42.96 (C), 31.72, 24.51 (2C), 19.93, 16.17 ppm (CH_3); IR (KBr): $\tilde{\nu}$=1734 (s), 1664 (s), 1623 (s), 1386 (m), 1250 (s), 1048 (m), 888 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=192.2 (2) [M^+], 177.1 (100), 162.1 (5), 149.1 (11), 135.1 (9), 121.1 (8), 91.1 (7), 43.1 (13). The exact molecular mass for $C_{12}H_{16}O_2$: m/z=192.1150±2 mD was confirmed by HRMS (EI, 70 eV).

2,3,3,4-Tetramethyl-6-oxocyclohexa-1,4-dienecarboxylic acid methyl ester (4b): From **3b** (0.075 g, 0.33 mmol), **4b** was obtained as a colorless oil (0.065 g, 95%). R_f=0.18 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.07 (d, 1H, J=1.2 Hz; =CH), 3.79 (s, 3H; OCH_3), 1.99 (d, 3H, J=1.2 Hz; CH_3), 1.97 (s, 3H; CH_3), 1.23 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=181.43, 167.55, 165.32, 161.73, 132.72 (C), 125.92 (CH), 52.05 (CH_3), 42.69 (C), 24.33 (2C), 19.80, 16.82 ppm (CH_3); IR (KBr): $\tilde{\nu}$=1739 (s), 1662 (s), 1627 (s), 1390 (m), 1250 (s), 1048 (m), 870 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=208.2 (100) [M^+], 193.1, 177.1, 149.1, 121.1, 91.1. The exact molecular mass for $C_{12}H_{16}O_3$: m/z=208.1099±2 mD was confirmed by HRMS (EI, 70 eV).

2,3,3,4-Tetramethyl-6-oxocyclohexa-1,4-dienecarboxylic acid ethyl ester (4c): From **3c** (0.070 g, 0.29 mmol), **4c** was obtained as a colorless oil (0.062 g, 96%). R_f=0.22 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.11 (d, 1H, J=1.3 Hz; =CH), 4.32 (d, 2H, J=7.1 Hz; OCH_2), 2.03 (d, 3H, J=1.3 Hz; CH_3), 2.01 (s, 3H; CH_3), 1.32 (t, 3H, J=7.1 Hz; CH_3), 1.28 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=181.59, 167.18, 165.27, 161.30, 132.99 (C), 126.07 (CH), 61.18 (OCH_2), 42.69 (C), 24.40 (2C), 19.86, 16.71, 14.11 ppm (CH_3); IR (neat): $\tilde{\nu}$=2982 (w), 1733 (s), 1665 (s), 1632 (s), 1389 (m), 1244 (s), 1048 (s), 878 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=222.2 (98) [M^+], 207.2 (34), 177.1 (100), 149.1 (87), 135.1 (45), 121.1 (65), 105.5 (41), 91.1 (35). The exact molecular mass for $C_{13}H_{18}O_3$: m/z=222.1256±2 mD was confirmed by HRMS (EI, 70 eV).

2,3,3,4-Tetramethyl-6-oxocyclohex-1,4-dienecarboxylic acid isopropyl ester (4d): From **3d** (0.066 g, 0.26 mmol), **4d** was obtained as a colorless oil (0.055 g, 90%). R_f=0.23 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.12 (d, 1H, J=1.2 Hz; =CH), 5.23 (sep, 1H, J=6.3 Hz; OCH), 2.05 (d, 3H, J=1.2 Hz; CH_3), 2.04 (s, 3H; CH_3), 1.32 (d, 6H, J=6.3 Hz; CH_3), 1.27 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=181.43, 166.56, 165.14, 160.69, 132.99 (C), 125.91 (CH), 68.57 (OCH), 42.49 (C), 24.23 (2C), 21.55 (2C), 19.65, 16.32 ppm (CH_3); IR (neat): $\tilde{\nu}$=2982 (w), 1731 (s), 1667 (s), 1627 (s), 1386 (m), 1249 (s), 1039 cm^{-1} (s); MS (EI, 70 eV): m/z (%)=236.0 (42) [M^+], 220.9 (10), 177.1 (100), 149.1 (56), 135.1 (44), 121.1 (29), 91.0 (31), 43.1 (87). The exact molecular mass for $C_{14}H_{20}O_3$: m/z=236.1412±2 mD was confirmed by HRMS (EI, 70 eV).

2,3,3,4-Tetramethyl-6-oxocyclohex-1,4-dienecarboxylic acid 2-methoxyethyl ester (4e): From **3e** (0.080 g, 0.29 mmol), **4e** was obtained as a colorless oil (0.068 g, 92%). R_f=0.18 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.13 (d, 1H, J=1.2 Hz; =CH), 4.44 (m, 2H; OCH_2), 3.67 (m, 2H; OCH_2), 3.39 (s, 3H; OCH_3), 1.31 (s, 6H; CH_3), 1.05 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=181.31, 167.10, 165.08, 161.53, 132.77 (C), 126.05 (CH), 70.26, 63.84 (OCH_2), 58.76 (OCH_3), 42.68 (C), 24.36 (2C), 19.80, 16.69 ppm (CH_3); IR (KBr): $\tilde{\nu}$=1734 (s), 1664 (s), 1623 (s), 1386 (m), 1250 (s), 1048 (m), 888 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=252.0 (26) [M^+], 237.0 (12), 195.0 (27), 177.0 (100), 148.3 (29), 58.5 (44), 28.1 (29). The exact molecular mass for $C_{14}H_{20}O_4$: m/z=252.1362±2 mD was confirmed by HRMS (EI, 70 eV).

Typical procedure for the preparation of spiro[5.4]decenones 6, 13, 16, and 18: $TiCl_4$ (0.22 mL, 2.00 mmol) was added dropwise to a stirred CH_2Cl_2 solution (100 mL) of 1,1-diacetylcyclopentane (**5a**; 0.160 g, 1.04 mmol) and 1,3-bis(trimethylsilyloxy)-1,3-butadiene (**1a**; 0.380 g, 1.54 mmol) at −78°C under an argon atmosphere in the presence of molecular sieves (4 Å; 1.0 g). The temperature of the reaction mixture was allowed to rise to 20°C over 6 h. The solution was stirred for additional 6 h at 20°C. The reaction mixture was filtered and the filtrate was poured into an aqueous solution of HCl (10%, 100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were dried (Na_2SO_4) and filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate 7:3) to give **6a** as colorless crystals (0.164 g, 67%).

7-Acetyl-10-hydroxy-6,10-dimethylspiro[5,4]dec-6-en-8-one (6a): From 1-methyl-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1a**; 0.380 g, 1.54 mmol), 1,1-diacetylcyclopentane (**5a**; 0.160 g, 1.04 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6a** was obtained as colorless crystals (0.164 g, 67%). M.p. 80–81°C; R_f=0.11 (hexane/ethyl acetate 7:3); ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.60 (br, 2H; CH_2), 2.30 (br, 1H; OH), 2.25 (s, 3H; CH_3), 1.86 (s, 3H; CH_3), 1.73 (br, 8H; CH_2), 1.21 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=205.44, 195.65, 163.68, 137.63 (C), 75.40 (C−OH), 56.26 (C), 49.95, 32.93 (2C, CH_2), 31.75 (CH_3), 28.22 (2C, CH_2), 24.89, 17.04 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3414 (s), 2959 (m), 1704 (s), 1652 (s), 1603 (m), 1383 (m), 1344 (m), 1191 cm^{-1} (m); MS (EI; 70 eV): m/z (%)=236.2 (26) [M^+], 218.0 (64), 193.1 (60), 149.1 (100), 43.0 (89); elemental analysis calcd (%) for $C_{14}H_{20}O_3$: C 71.15, H 8.53; found: C 71.31, H 8.53.

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid methyl ester (6b): From 1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.390 g, 1.5 mmol), 1,1-diacetylcyclopentane (**5a**; 0.156 g, 1.0 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6b** was obtained as colorless crystals (0.184 g, 72%). M.p. 106–107°C; R_f=0.23 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.82 (s, 3H; OCH_3), 2.65 (br, 2H; CH_2), 2.22 (br, 1H; OH), 1.99 (br, 2H; CH_2), 1.98 (s, 3H; CH_3), 1.76 (br, 6H; CH_2), 1.27 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.83, 167.66, 164.91, 131.25 (C), 75.34 (C−OH), 56.13 (C), 52.20 (OCH_3), 49.64, 32.98 (2C), 28.23 (2C, CH_2), 24.86, 17.88 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3431 (s), 2961 (s), 1730 (s), 1663 (s), 1620 (s), 1344 (m), 1385 (s), 1231 (s), 1203 (s), 863 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=252.3 (4) [M^+], 220.2 (16), 162.1 (100), 134.1 (52), 91.1 (54), 43.0 (72); elemental analysis calcd (%) for $C_{14}H_{20}O_4$: C 66.64, H 7.99; found: C 66.58, H 8.23.

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid ethyl ester (6c): From 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.415 g, 1.5 mmol), 1,1-diacetylcyclopentane (**5a**; 0.154 g, 1.0 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6c** was obtained as colorless crystals (0.208 g, 78%). M.p. 107–108°C; R_f=0.35 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.29 (q, 2H, J=7.2 Hz; OCH_2), 2.64 (br, 2H; CH_2), 2.16 (br, 2H; CH_2), 1.98 (s, 3H; CH_3), 1.88 (br, 1H; OH), 1.76 (br, 6H; CH_2), 1.32 (t, 3H, J=7.2 Hz; CH_3), 1.26 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.15, 167.54, 164.61, 131.72 (C), 75.68 (C−OH), 61.53 (OCH_2), 56.35 (C), 49.95, 33.54 (2C), 28.50 (2C, CH_2), 25.11, 17.98, 14.40 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3410 (s), 2966 (s), 1724 (s), 1663 (s), 1619 (s), 1470 (m), 1385 (s), 1342 (s), 1237 (s), 1205 (s), 1089 (s), 1026 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=266.3 (9) [M^+], 220.2 (52), 162.2 (100), 134.1 (33); elemental analysis calcd (%) for $C_{15}H_{22}O_4$: C 67.64, H 8.32; found: C 67.38, H 8.45.

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid isopropyl ester (6d): From 1-isopropoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1d**; 0.430 g, 1.5 mmol) and 1,1-diacetylcyclopentane (**5a**; 0.154 g, 1.0 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6d** was obtained as a colorless oil (0.185 g, 66%). R_f=0.17 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.18 (sep, 1H, J=6.3 Hz; OCH), 2.63 (br, 2H; CH_2), 2.37 (br, 2H; CH_2), 1.97 (s, 3H; CH_3), 1.95 (br, 1H; OH), 1.75 (br, 6H; CH_2), 1.32 (s, 3H; CH_3), 1.28 ppm (d, 6H, J=6.3 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.97, 166.88, 163.89, 131.55 (C), 75.29 (C−OH), 68.84 (OCH), 56.01 (C), 49.66, 32.77 (2C), 28.19 (2C, CH_2), 24.75, 21.67 (2C), 17.47 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3460 (br), 2977 (s), 1728 (s), 1671 (s), 1619 (m), 1379 (m), 1248 (s), 1108 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=280.3 (5) [M^+], 237.2 (22), 220.2 (20), 195.2 (12), 178.2 (11), 162.1 (100), 134.1 (17), 43.0 (16); elemental analysis calcd (%) for $C_{16}H_{24}O_4$: C 68.54, H 8.62; found: C 67.38 H 8.97. The exact molecular mass for $C_{16}H_{24}O_4$: m/z=280.1675±2 mD was confirmed by HRMS (EI, 70 eV).

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid 2-methoxyethyl ester (6e): From 1-(2-methoxy)ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1e**; 0.455 g, 1.5 mmol), 1,1-diacetylcyclopentane (**5a**; 0.154 g, 1.0 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6e** was obtained as a colorless oil (0.156 g, 53%). R_f=0.21 (hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.37 (t, 2H, J=6.0 Hz; OCH_2), 3.62 (t, 2H, J=6.0 Hz; OCH_2), 3.36 (s, 3H; OCH_3), 2.62 (br, 2H; CH_2), 2.09 (br, 2H; CH_2), 2.00 (s, 3H; CH_3), 1.95 (br, 1H; OH), 1.73 (br, 6H; CH_2), 1.22 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.76, 167.16, 164.91, 134.13 (C), 75.38 (C−OH), 70.23, 63.90 (OCH_2), 58.76 (OCH_3), 56.12 (C), 49.26, 32.82 (2C), 28.25 (2C, CH_2), 24.81, 17.71 ppm (CH_3); IR (neat): $\tilde{\nu}$=3462 (br), 2973 (s), 1733 (s), 1666 (s), 1621 (m), 1382 (s), 1253 (s), 1108 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=295.6 (8) [M^+], 219.7 (77), 177.9 (46), 162.0 (100), 133.9 (76), 90.9 (28), 43.1 (28). The exact molecular mass for $C_{16}H_{24}O_5$: m/z=296.1624±2 mD was confirmed by HRMS (EI, 70 eV).

10-Hydroxy-6,9,10-trimethyl-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid methyl ester (6f) (major isomer): From 1-methoxy-1,3-bis(trimethylsi-

lyloxy)penta-1,3-diene (**1f**; 0.410 g, 1.5 mmol), 1,1-diacetylcyclopentane (**5a**; 0.157 g, 1.0 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6f** was obtained as a colorless oil (0.061 g, 23%). R_f=0.23 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.36 (s, 3H; OCH_3), 2.88 (q, 1H, J=6.9 Hz; CH), 2.08 (s, 3H; CH_3), 1.96–1.92 (m, 3H; OH, CH_2), 1.41–1.21 (m, 6H; CH_2), 1.20 (d, 3H, J=7.2 Hz; CH_3), 1.08 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=196.32, 168.60, 163.67, 131.13 (C), 75.38 (C–OH), 57.23 (C), 52.42 (OCH_3), 49.48 (CH), 33.37 (2C), 28.60 (2C, CH_2), 17.71, 16.88, 14.09 ppm (CH_3); IR (neat): $\tilde{\nu}$=3462 (br), 2973 (s), 1733 (s), 1666 (s), 1621 (m), 1382 (s), 1253 (s), 1108 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=266.5 (2) [M^+], 234.4 (15), 192.3 (23), 162.2 (100), 134.2 (60), 91.2 (28), 43.0 (58). The exact molecular mass for $C_{15}H_{22}O_4$: m/z=266.1519±2 mD was confirmed by HRMS (EI, 70 eV).

9-Ethyl-10-hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid ethyl ester (6g): From 1-ethoxy-1,3-bis(trimethylsilyloxy)hexa-1,3-diene (**1g**; 0.380 g, 1.56 mmol), 1,1-diacetylcyclopentane (**5a**; 0.160 g, 1.04 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6g** was obtained as a colorless oil (0.100 g, 41%). R_f=0.23 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.27 (q, 2H, J=7.2 Hz; OCH_2), 2.60–2.40 (m, 1H; CH), 2.10 (br, 1H; OH), 1.94 (s, 3H; CH_3), 1.92–1.40 (m, 10H; CH_2), 1.31 (t, 3H, J=7.2 Hz; CH_3), 1.08 (t, 3H, J=7.5 Hz; CH_3), 1.06 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=196.43, 167.44, 162.37, 131.58 (C), 61.13 (CH), 57.44 (C), 57.10 (CH_2), 33.36, 31.89, 28.72, 27.20, 19.55, 17.42, 16.44, 14.63, 14.10, 11.01 ppm; IR (neat): $\tilde{\nu}$=3515 (s), 2976 (s), 2875 (m), 1732 (s), 1670 (s), 1622 (m), 1457 (m), 1382 (m), 1257 (m), 1210 (m), 1112 (s), 1023 cm^{-1} (m); MS (EI; 70 eV): m/z (%)=294.5 (6) [M^+], 265.5 (76), 219.3 (45), 162.2 (100), 134.2 (75), 43.0 (52). The exact molecular mass for $C_{17}H_{26}O_4$: m/z=294.1831±2 mD was confirmed by HRMS (EI, 70 eV).

6,10-Diethyl-10-hydroxy-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid methyl ester (6h): From 1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.180 g, 0.69 mmol), 1,1-dipropionylcyclopentane (**5b**; 0.097 g, 0.53 mmol), and $TiCl_4$ (0.12 mL, 1.09 mmol), **6h** was obtained as a colorless oil (0.086 g, 58%). R_f=0.22 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 3H; OCH_3), 2.63 (br, 2H; CH_2), 2.30–2.22 (br, 2H; CH_2), 2.12 (br, 1H; OH), 1.93–1.53 (br, 10H; CH_2), 1.13 (t, 3H, J=7.5 Hz; CH_3), 0.87 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.20, 170.99, 167.75, 131.39 (C), 75.33 (C–OH), 57.53 (C), 52.08 (OCH_3), 44.08, 40.62 (CH_2), 29.63 (2C), 27.20 (2C), 24.62 (CH_2), 14.48, 7.38 ppm (CH_3); IR (neat): $\tilde{\nu}$=3496 (br), 2971 (s), 2875 (m), 1735 (s), 1666 (s), 1606 (w), 1436 (m), 1342 (m), 1228 (m), 1082 cm^{-1} (m); MS (EI; 70 eV): m/z (%)=280.4 (10) [M^+], 248.4 (50), 192.2 (62), 176.3 (100), 147.6 (41), 120.5 (48), 91.1 (41), 29.0 (44). The exact molecular mass for $C_{16}H_{24}O_4$: m/z=280.1675±2 mD was confirmed by HRMS (EI, 70 eV).

6,10-Diethyl-10-hydroxy-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid ethyl ester (6i): From 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.415 g, 1.60 mmol), 1,1-dipropionylcyclopentane (**5b**; 0.193 g, 1.06 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6i** was obtained as a colorless oil (0.167 g, 56%). R_f=0.28 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.30 (dq, 2H, J=7.2, 1.5 Hz; OCH_2), 2.67 (br, 2H; CH_2), 2.40–2.30 (br, 4H; CH_2), 2.04 (br, 1H; OH), 1.94–1.59 (br, 8H; CH_2), 1.31 (t, 3H, J=7.2 Hz; CH_3), 1.17 (t, 3H, J=7.5 Hz; CH_3), 0.91 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.20, 170.99, 167.75, 131.39 (C), 75.33 (C–OH), 57.53 (C), 52.08 (OCH_3), 44.08, 40.62 (CH_2), 29.63 (2C), 27.20 (2C), 24.62 (CH_2), 14.48, 7.38 ppm (CH_3); IR (neat): $\tilde{\nu}$=3496 (br), 2971 (s), 2875 (m), 1735 (s), 1666 (s), 1606 (w), 1436 (m), 1342 (m), 1228 (m), 1082 cm^{-1} (m); MS (EI; 70 eV): m/z (%)=294.2 (10) [M^+], 248.2 (25), 219.0 (16), 192.1 (26), 176.1 (100), 91.0 (14), 29.0 (35). The exact molecular mass for $C_{17}H_{26}O_4$: m/z=294.1813±2 mD was confirmed by HRMS (EI, 70 eV).

6,10-Diethyl-10-hydroxy-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid isopropyl ester (6j): From 1-isopropoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1d**; 0.475 g, 1.65 mmol), 1,1-dipropionylcyclopentane (**5b**; 0.200 g, 1.10 mmol), and $TiCl_4$ (0.24 mL, 2.20 mmol), **6j** was obtained as a colorless solid (0.179 g, 53%). M.p. 96–97 °C; R_f=0.34 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.18 (sep, 1H, J=6.3 Hz; OCH), 2.65 (br, 2H; CH_2), 2.36–1.56 (m, 13H; OH, CH_2), 1.30 (d, 6H, J=6.3 Hz; CH_3), 1.19 (t, 3H, J=7.5 Hz; CH_3), 0.88 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.39, 169.99, 167.06, 132.11 (C), 75.33 (C–OH), 68.95 (OCH), 57.72 (C), 45.19, 28.07, 36.48 (2C), 28.48, 27.36, 24.64 (CH_2), 21.85 (2C), 14.72, 7.63 ppm (CH_3); IR (neat): $\tilde{\nu}$=3462 (br), 2975 (s), 1725 (s), 1698 (s), 1667 (s), 1612 (m), 1450 (m), 1102 (s), 827 cm^{-1} (m); MS (EI; 70 eV): m/z (%)=308.1 (10) [M^+], 265.2 (19), 248.1 (22), 192.1 (22), 176.1 (100), 43.1 (14); elemental analysis calcd (%) for $C_{18}H_{28}O_4$: C 70.10, H 9.19; found: C 69.92, H 9.68.

10-Hydroxy-10-methyl-8-oxo-6-phenylspiro[4,5]dec-6-ene-7-carboxylic acid ethyl ester (6k): From 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.415 g, 1.50 mmol), 1-acetyl-1-benzoylcyclopentane (**5c**; 0.216 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **6k** was obtained as a colorless oil (0.125 g, 38%). R_f=0.28 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.38–7.18 (m, 5H; ArH), 3.85 (q, 2H, J=7.2 Hz; OCH_2), 2.90–2.70 (m, 4H; CH_2), 2.07 (br, 1H; OH), 1.98–1.86 (m, 4H; CH_2), 1.55–1.42 (m, 2H; CH_2), 1.39 (s, 3H; CH_3), 0.81 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.63, 166.16 (2C), 136.50, 132.25 (C), 128.03 (2C), 127.83, 127.55 (2C, CH), 75.72 (C–OH), 60.88 (OCH_2), 57.17 (C), 50.07, 33.15 (2C), 27.25, 27.03 (CH_2), 24.83, 13.58 ppm (CH_3); IR (neat): $\tilde{\nu}$=3542 (m), 2953 (m), 1727 (s), 1677 (s), 1612 (m), 1341 (m), 1234 (s), 704 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=328.4 (6) [M^+], 282.8 (33), 224.6 (100), 104.8 (40), 43.1 (76), 28.1 (53). The exact molecular mass for $C_{20}H_{24}O_4$: m/z=328.1675±2 mD was confirmed by HRMS (EI, 70 eV).

10-Hydroxy-6-methyl-8-oxospiro[4.5]dec-6-en-7-carboxylic acid ethyl ester (13a): From 1-acetyl-1-formylcyclopentane (**5d**; 0.200 g, 1.42 mmol), 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (0.585 g, 2.13 mmol), and $TiCl_4$ (0.31 mL, 2.84 mmol), **13a** was obtained as a yellow oil (0.068 g, 20%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.30 (q, 2H, J=7.2 Hz; OCH_2), 3.49 (br, 1H, J=6.9 Hz; CHOH), 2.79 (dd, 1H, J=16.8, 3.7 Hz; CH_2), 2.63 (dd, 1H, J=16.8, 7.2 Hz; CH_2), 2.04 (s, 1H; OH), 1.96 (s, 3H; CH_3), 1.81–1.77 (m, 8H; CH_2), 1.32 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.0, 167.12, 162.55, 132.54 (C), 72.85 (CH), 61.30 (CH_2), 52.57 (C), 43.04, 35.36, 32.48, 27.36, 27.01 (CH_2), 17.69, 14.16 ppm (CH_3); IR (neat): $\tilde{\nu}$=3430 (br), 2959 (m), 1729.2 (s), 1666 (s), 1614 (m), 1378 (m), 1239 (m), 1090 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=252.0 (7) [M^++1], 206.0 (19), 161.9 (83), 134.1 (30), 82.1 (33), 68.0 (67), 43.1 (53), 28.1 (100); elemental analysis calcd (%) for $C_{14}H_{19}O_4$: C 66.93, H 7.5; found: C 66.05, H 8.53.

7-Acetyl-10-hydroxy-10-methylspiro[5,4]dec-6-en-8-one (13b): From 1-acetyl-1-formylcyclopentane (**5d**; 0.150 g, 1.07 mmol), 2,4-bis-trimethylsilyloxypenta-1,3-diene (0.391 g, 1.60 mmol), and $TiCl_4$ (0.23 mL, 2.14 mmol), **13b** was obtained as a yellow oil (0.064 g, 27%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.96 (br, 1H; C*H*OH), 2.78 (dd, 1H, J=16.5, 3.6 Hz; CH_2), 2.61 (dd, 1H, J=16.8, 6.9 Hz; CH_2), 2.32 (s, 3H; CH_3), 2.09–2.01 (m, 3H; CH_2, OH), 1.90 (s, 3H; CH_3), 1.85–1.75 ppm (m, 6H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$); δ=205.48, 195.08, 161.81, 138.68 (C), 72.74 (CH), 52.72 (C), 43.25, 33.41, 32.65 (CH_2), 31.77 (CH_3), 27.30, 26.81 (CH_2), 17.05 ppm (CH_3); IR (neat): $\tilde{\nu}$=3461 (br), 2960 (m), 1703 (s), 1664 (s), 1355 (s), 1215 (m), 1074 cm^{-1} (m); MS (EI, 70 eV): m/z (%): 223.0 (9) [M^++1], 222.0 (51) [M^+], 181.0 (100), 163 (38), 149.1 (81), 122 (40), 43.1 (97), 29.0 (7); elemental analysis calcd (%) for $C_{13}H_{18}O_3$: C 70.27, H 8.62; found: C 69.00, H 8.10.

9-Ethyl-10-methyl-8-oxospiro[5,4,0]deca-6,9-diene-7-carboxylic acid (13c): From 1-acetyl-1-formylcyclopentane (**5d**; 0.150 g, 1.07 mmol), 1,3-bis(trimethylsilyloxy)buta-1,3-diene (0.485 g, 1.60 mmol), and $TiCl_4$ (0.23 mL, 2.14 mmol), **13c** was obtained as a colorless oil (56 mg, 20%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=6.47 (s, 1H; =CH), 4.33 (q, 2H, J=7.2 Hz; OCH_2), 2.54–2.42 (m, 1H; CH_2), 2.38–2.37 (m, 3H; CH_2), 2.05–1.95 (m, 1H; CH_2), 1.87–1.81 (m, 1H; CH_2), 1.73–1.67 (m, 2H; CH_2), 1.43–1.35 (m, 2H; CH_2), 1.34 (t, 3H, J=7.2 Hz; CH_3), 1.28 (s, 3H; CH_3), 1.07 ppm (t, 3H, J=7.5 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=182.98, 167.35, 162.83 (C), 151.30 (CH), 137.64, 130.67 (C) 61.14 (CH_2), 40.02 (C), 38.72, 29.40, 27.59 (CH_2) 23.16 (CH_3), 21.75, 20.70 (CH_2), 14.18, 12.36 ppm (CH_3); IR (neat): $\tilde{\nu}$=3440 (br), 2960 (m); 1730 (s), 1670 (s), 1365 (s), 1237 (m), 1092 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=262.1 (25) [M^+], 217.1 (29), 201.1 (55), 189.1 (100), 161.1 (21), 29.0 (10). The exact molecular mass for $C_{16}H_{22}O_3$: m/z=262.1570±2 mD was confirmed by HRMS (EI, 70 eV).

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]deca-2,6-diene-7-carboxylic acid methyl ester (16a): From 1-(1-acetylcyclopent-3-enyl)ethanone (**5e**; 0.155 g, 1.02 mmol), 1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.400 g, 1.53 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **16a** was ob-

tained as a colorless solid (0.211 g, 83%). M.p. 123–124°C; R_f=0.22 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.76 (br, 1H; =CH), 5.70 (br, 1H; =CH), 3.81 (s, 3H; OCH_3), 2.74–2.64 (m, 6H; CH_2), 2.38 (br, 1H; OH), 1.88 (s, 3H; CH_3), 1.23 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.61, 167.13, 163.45, 130.57 (C), 129.80, 128.39 (CH), 75.22 (C–OH), 52.34 (OCH_3), 49.13 (CH_2), 42.70 (C), 38.73, 31.03 (CH_2), 24.75, 17.74 ppm (CH_3); IR (neat): $\tilde{\nu}$=3442 (br), 2977 (m), 1784 (m), 1734 (s), 1653 (s), 1609 (m), 1435 (m), 1246 (s), 1159 (s), 875 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=250.1 (3) [M^+], 232.1 (18), 218.1 (53), 200.0 (24), 185.1 (23), 160.0 (100), 132.0 (91), 91.0 (23), 43.1 (31); elemental analysis calcd (%) for $C_{14}H_{18}O_4$: C 67.18, H 7.24; found: C 67.00, H 7.22. The exact molecular mass for $C_{14}H_{18}O_4$: m/z=250.1205±2 mD was confirmed by HRMS (EI, 70 eV).

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-2,6-diene-7-carboxylic acid ethyl ester (16b): From 1-(1-acetylcyclopent-3-enyl)ethanone (**5e**; 0.149 g, 0.98 mmol), 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.400 g, 1.47 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **16b** was obtained as a colorless solid (0.165 g, 64%). M.p. 89–90°C; R_f=0.26 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.75 (br, 1H; =CH), 5.70 (br, 1H; =CH), 4.29 (q, 2H, J=7.2 Hz; OCH_2), 2.74–2.32 (m, 7H; CH_2, OH), 1.95 (s, 3H; CH_3), 1.31 (t, 3H, J=7.2 Hz; CH_3), 1.24 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.73, 167.13, 163.16, 130.57 (C), 129.87, 128.39 (CH), 75.27 (C–OH), 61.24 (OCH_2), 54.59 (C), 48.71, 39.49, 38.21 (CH_2), 24.38, 17.38, 14.08 ppm (CH_3); IR (neat): $\tilde{\nu}$=3442 (br), 2977 (m), 1784 (m), 1734 (s), 1653 (s), 1609 (m), 1435 (m), 1246 (s), 1159 (s), 875 cm^{-1} (w); MS (EI, 70 eV): m/z (%)= 264.2 (3) [M^+], 246.1 (14), 218.1 (51), 200.1 (21), 185.1 (19), 160.1 (100), 132.0 (89), 91.0 (21), 43.1 (33); elemental analysis calcd (%) for $C_{15}H_{20}O_4$: C 68.16, H 7.63; found: C 68.62, H 7.38.

10-Hydroxy-6,10-dimethyl-8-oxo-spiro[4,5]dec-2,6-diene-7-carboxylic acid isospropyl ester (16c): From 1-(1-acetylcyclopent-3-enyl)ethanone (**5e**; 0.200 g, 1.31 mmol), 1-isopropoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.512 g, 1.97 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **16c** was obtained as a colorless solid (0.216 g, 59%). M.p. 90–91°C; R_f=0.27 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=5.75 (br, 1H; =CH), 5.70 (br, 1H; =CH), 5.18 (sep, 1H, J=6.3 Hz; OCH), 2.74–2.30 (m, 7H; CH_2, OH), 1.94 (s, 3H; CH_3), 1.31 (d, 6H, J=6.3 Hz; CH_3), 1.24 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.72, 166.70, 165.98, 130.82 (C), 128.75 (2C, CH), 69.54 (C–OH), 68.91 (OCH), 54.51 (C), 48.81, 42.35, 38.18 (CH_2), 24.38, 21.58 (2C), 14.11 ppm (CH_3); IR (neat): $\tilde{\nu}$=3392 (br), 2982 (w), 1719 (s), 1664 (s), 1618 (m), 1379 (m), 1249 (s), 1105 cm^{-1} (m); MS (EI, 70 eV): m/z (%): 278.3 (3) [M^+], 260.3 (7), 218.2 (51), 200.2 (19), 186.2 (15), 160.1 (100), 132.2 (61), 91.1 (20), 43.1 (38); elemental analysis calcd (%) for $C_{16}H_{22}O_4$: C 69.04, H 7.97; found: C 69.09, H 8.70. The exact molecular mass for $C_{16}H_{22}O_4$: m/z= 278.1518±2 mD was confirmed by HRMS (EI, 70 eV).

Compound 18a: From 1-methyl-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1a**; 0.368 g, 1.51 mmol), 1-(2-acetylindan-2-yl)ethanone (**5f**; 0.202 g, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18a** was obtained as colorless crystals (0.230 g, 82%). M.p. 168–169°C; R_f=0.31 (hexane/ethyl acetate 3:2); ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.20 (s, 4H; ArH), 3.90–3.65 (br, 1H; CH_2), 3.39 (d, 1H, J=17.1 Hz; CH_2), 3.02 (d, 2H, J=17.1 Hz; CH_2), 2.32 (br, 2H; CH_2), 2.28 (s, 3H; CH_3), 2.21 (br, 1H; OH), 1.67 (s, 3H; CH_3), 1.22 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 204.96, 195.26, 163.60, 141.80, 141.14, 137.37 (C), 127.03, 126.94, 124.25, 123.98 (CH), 74.54 (C–OH), 56.39 (C), 49.88, 39.24 (2C, CH_2), 31.77, 25.02, 17.49 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3396 (s), 2970 (w), 1700 (s), 1662 (s), 1612 (m), 1485 (w), 1380 (m), 1336 (m), 1192 (m), 742 cm^{-1} (m); MS (EI; 70 eV): m/z (%)=284.2 (32) [M^+], 266.1 (71), 251.2 (33), 223.1 (60), 183.1 (64), 155.1 (46), 115.1 (90), 43.1 (100); elemental analysis calcd (%) for $C_{18}H_{20}O_3$: C 76.03, H 6.97; found: C 75.94, H 6.97.

Compound 18b: From 1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.390 g, 1.50 mmol), 1-(2-acetylindan-2-yl)ethanone (**5f**; 0.202 g, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18b** was obtained as a colorless solid (0.258 g, 86%). M.p. 164–165°C; R_f=0.24 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.19 (s, 4H; ArH), 3.81 (s, 3H; OCH_3), 3.90–3.65 (br, 1H; CH_2), 3.40 (d, 1H, J=16.8 Hz; CH_2), 3.05 (d, 2H, J=16.8 Hz; CH_2), 2.71 (br, 2H; CH_2), 2.20 (br, 1H; OH), 1.81 (s, 3H; CH_3), 1.28 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 193.55, 167.43, 164.00, 141.21, 141.09, 131.01 (C), 127.03, 126.92, 124.27, 123.98 (CH), 74.40 (C–OH), 56.52 (C), 52.29 (OCH_3), 49.56, 39.39 (2C, CH_2), 24.96, 18.31 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3398 (s), 2960 (w), 1732 (s), 1668 (s), 1629 (w), 1381 (m), 1241 (m), 1114 cm^{-1} (m); MS (EI, 70 eV): m/z (%)=300.2 (2) [M^+], 282.1 (61), 267.1 (21), 210.1 (27), 182.1 (100), 153.1 (47), 142.1 (40), 115.1 (26), 43.1 (58); elemental analysis calcd (%) for $C_{18}H_{20}O_4$: C 71.98, H 6.71; found: C 71.78, H 6.50.

Compound 18c: From 1-ethoxy-1,3-bis(trimethysilyloxy)buta-1,3-diene (**1c**; 0.415 g, 1.51 mmol), 1-(2-acetylindan-2-yl)ethanone (**5f**; 0.202 g, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18c** was obtained as colorless crystals (0.270 g, 86%). M.p. 132–133°C; R_f=0.31 (hexane/ethyl acetate 3:2); ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.19 (s, 4H; ArH), 4.28 (q, 2H, J=7.2 Hz; OCH_2), 3.90–3.65 (br, 1H; CH_2), 3.39 (d, 1H, J=17.1 Hz; CH_2), 3.04 (d, 2H, J=17.1 Hz; CH_2), 2.70 (br, 2H; CH_2), 2.45 (br, 1H; OH), 1.81 (s, 3H; CH_3), 1.30 (s, 3H; CH_3), 1.28 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=193.68, 167.07, 163.74, 141.81, 141.21, 131.14 (C), 126.95, 126.84, 124.24, 12.94 (CH), 74.44 (C–OH), 61.36 (OCH_2), 56.28 (C), 49.59, 39.33 (2C, CH_2), 24.87, 18.11, 14.10 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3421 (s), 2975 (w), 2947 (w), 2904 (w), 1727 (s), 1665 (s), 1619 (m), 1445 (w), 1381 (m), 1239 (m), 1129 (m), 1030 (m), 866 (w), 745 cm^{-1} (w); MS (EI; 70 eV): m/z (%)=314.2 (5) [M^+], 296.2 (88), 210.1 (37), 182.1 (100), 142.1 (38), 115.1 (23), 43.1 (20); elemental analysis calcd (%) for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found: C 72.75, H 6.94.

Compound 18d: From 1-isopropoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1d**; 0.430 g, 1.50 mmol), 1-(2-acetylindan-2-yl)ethanone (**5f**; 0.202 g, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18d** was obtained as a colorless solid (0.269 g, 82%). M.p. 185–186°C; R_f=0.33 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.20 (s, 4H; ArH), 5.18 (sep, 1H, J=6.3 Hz; OCH), 3.90–3.60 (br, 1H; CH_2), 3.38 (d, 1H, J= 17.1 Hz; CH_2), 3.02 (d, 2H, J=17.1 Hz; CH_2), 2.65 (br, 2H; CH_2), 2.38 (br, 1H; OH), 1.76 (s, 3H; CH_3), 1.31 (s, 3H; CH_3), 1.27 ppm (d, 6H, J= 6.3 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.58, 166.62, 163.70, 141.84, 141.24, 131.39 (C), 126.96, 126.86, 124.26, 123.96 (CH), 74.61 (C–OH), 69.04 (OCH), 56.25 (C), 49.52, 39.72 (2C, CH_2), 24.93, 21.71 (2C), 17.93 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3383 (s), 2978 (w), 1723 (s), 1655 (s), 1622 (w), 1381 (m), 1251 (m), 1104 cm^{-1} (m); MS (EI, 70 eV): m/z (%)= 328.8 (2) [M^+], 310.8 (64), 269.7 (32), 250.7 (36), 210.6 (66), 182.5 (96), 153.0 (65), 142.3 (53), 115.8 (38), 43.1 (100), 28.1 (38); elemental analysis calcd (%) for $C_{20}H_{24}O_4$: C 73.15, H 7.15; found: C 73.17, H 6.97.

Compound 18e: From 1-(2-methoxy)ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1e**; 0.455 g, 1.50 mmol), 1-(2-acetylindan-2-yl)ethanone (**5f**; 0.205 g, 1.01 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18e** was obtained as a colorless solid (0.213 g, 61%). M.p. 115–116°C; R_f=0.17 (hexane/ethyl acetate 3:2); ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.18 (s, 4H; ArH), 4.81 (t, 2H, J=4.5 Hz; OCH_2), 3.90–3.65 (br, 1H; CH_2), 3.62 (t, 2H, J=4.5 Hz; OCH_2), 3.46 (d, 1H, J=17.1 Hz; CH_2), 3.35 (s, 3H; OCH_3), 3.03 (d, 2H, J=17.1 Hz; CH_2), 2.68 (brs, 2H; CH_2), 2.26 (brs, 1H; OH), 1.82 (s, 3H; CH_3), 1.28 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=195.28, 166.90, 163.63, 141.76, 141.13, 137.36 (C), 127.02, 126.92, 124.28, 123.98 (CH), 74.51 (C–OH), 70.28, 64.04 (OCH_2), 58.82 (OCH_3), 56.35 (C), 49.85, 39.29 (2C, CH_2), 25.01, 18.19 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3421 (s), 2946 (w), 1727 (s), 1665 (s), 1619 (m), 1381 (m), 1239 (s), 1129 (s), 866 (w), 745 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=344.9 (4) [M^+], 326.9 (45), 268.7 (42), 250.7 (44), 210.5 (43), 182.5 (100), 153.0 (43), 114.6 (31), 59.6 (36), 43.1 (45); elemental analysis calcd (%) for $C_{20}H_{24}O_5$ (344.41): C 69.74, H 7.02; found: C 69.48, H 6.86.

Compound 18f: From 1-ethoxy-1,3-bis(trimethylsilyloxy)hexa-1,3-diene (**1g**; 0.453 g, 1.50 mmol), 1-(2-acetylindan-2-yl)ethanone (**5f**; 0.202 g, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18f** was obtained as a colorless solid (0.106 g, 31%). R_f=0.27 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.16 (br, 4H; ArH), 4.26 (q, 2H, J=7.2 Hz; OCH_2), 4.02 (d, 1H, J=16.8 Hz; CH_2), 3.47 (d, 1H, J=16.5 Hz; CH_2), 3.03 (d, 1H, J=16.8 Hz; CH_2), 2.92 (d, 1H, J=16.5 Hz; CH_2), 2.51 (br, 1H; CH), 1.95 (br, 1H; OH), 1.90–1.75 (m, 1H; CH_2), 1.69 (s, 3H; CH_3), 1.65–1.58 (m, 1H; CH_2), 1.29 (t, 3H, J=7.2 Hz; CH_3), 1.20 (s, 3H; CH_3), 1.11 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 196.16, 167.25, 162.43, 142.05, 141.23, 131.03 (C), 126.98, 126.79, 124.30, 123.72 (CH), 74.55 (C–OH), 61.24 (OCH_2), 57.69 (CH), 56.09 (C), 40.13, 37.47, 19.99 (CH_2), 17.54, 16.13, 14.52, 14.02 ppm (CH_3); IR (KBr): $\tilde{\nu}$= 3504 (s), 2983 (w), 1706 (s), 1676 (m), 1630 (w), 1380 (m), 1216 (m), 1129 (s), 760 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=342.3 (4) [M^+], 324.3 (53), 296.3 (42), 278.2 (24), 256.2 (30), 210.1 (57), 182.1 (100), 142.1 (70), 71.1

(38), 43.1 (54); elemental analysis calcd (%) for $C_{21}H_{26}O_4$: C 73.65, H 7.65; found: C 73.42, H 7.86.

Compound 18g: From 1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.390 g, 1.50 mmol), 1-(2-benzoylindan-2-yl)ethanone (**5f**; 0.264 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18g** was obtained as a colorless solid (0.084 g, 23%). R_f=0.36 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.54–6.97 (m, 9H; ArH), 3.87 (s, 3H; OCH_3), 3.81–3.63 (br, 1H; CH_2), 3.45 (d, 1H, J=19.2 Hz; CH_2), 3.40–3.25 (br, 1H; CH_2), 3.15 (d, 1H, J=17.1 Hz; CH_2), 3.06 (d, 1H, J=17.1 Hz; CH_2), 2.95–2.70 (br, 1H; CH_2), 2.46 (brs, 1H; OH), 1.85 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.33, 167.38, 164.24, 142.74, 141.86, 140.61, 132.63 (C), 131.36, 128.63, 128.03, 127.77, 127.10, 127.05, 126.75, 126.50, 123.79 (CH), 78.76, 56.74 (C), 52.25 (OCH_3), 49.11, 45.45, 40.74 (CH_2), 18.60 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3556 (s), 1739 (s), 1665 (s), 1656 (s), 1623 (m), 1349 (m), 1241 (m), 1072 (w), 768 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=362.4 (7) [M^+], 330.4 (49), 312.3 (32), 210.2 (62), 182.2 (95), 142.2 (100), 104.7 (99), 77.4 (70), 43.2 (17), 28.1 (13); elemental analysis calcd (%) for $C_{23}H_{22}O_4$: C 76.22, H 5.96; found: C 75.40, H 5.96.

Compound 18h: From 1-methoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1b**; 0.390 g, 1.50 mmol), 1-(2-benzoylindan-2-yl)ethanone (**5f**; 0.264 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18h** was obtained as a colorless solid (0.076 g, 21%). M.p. 139–140°C; R_f=0.28 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.16–6.80 (m, 9H; ArH), 3.38 (s, 3H; OCH_3), 3.90–3.65 (br, 1H; CH_2), 3.33 (br, 1H; CH_2), 3.17 (d, 2H, J=18.0 Hz; CH_2), 2.85 (br, 2H; CH_2), 2.45 (brs, 1H; OH), 1.85 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.01, 166.56 (2C), 141.91, 140.88, 136.24 (C), 132.87 (CH), 132.70 (C), 127.13, 128.70, 128.08, 127.39, 126.72 (2C), 126.57, 123.69 (CH), 75.20, 56.85 (C), 52.91 (OCH_3), 49.51, 40.22 (2C, CH_2), 25.10 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3537 (s), 1736 (s), 1661 (s), 1615 (w), 1344 (m), 1233 (m), 1074 (w), 734 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=362.0 (17) [M^+], 344.0 (89), 311.9 (39), 244.0 (86), 214.9 (71), 104.6 (100), 77.4 (52), 43.2 (77), 28.1 (34). The exact molecular mass for $C_{23}H_{22}O_4$: m/z=362.1518±2 mD was confirmed by HRMS (EI, 70 eV).

Compound 18i: From 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.410 g, 1.50 mmol), 1-(2-benzoylindan-2-yl)ethanone (**5f**; 0.263 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18i** was obtained as a colorless solid (0.083 g, 22%). M.p. 177–178°C; R_f=0.39 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.29–6.97 (m, 9H; ArH), 4.29 (q, 2H, J=7.2 Hz; OCH_2), 3.95–3.80 (br, 1H; CH_2), 3.48–3.25 (m, 2H; CH_2), 3.16 (d, 1H, J=17.1 Hz; CH_2), 3.06 (d, 1H, J=17.1 Hz; CH_2), 2.95–2.75 (m, 1H; CH_2), 2.56 (brs, 1H; OH), 1.85 (s, 3H; CH_3), 1.29 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.24, 166.95 (2C), 142.77, 141.91, 140.66, 131.66 (C), 128.66, 128.14, 127.83, 127.16 (2C), 126.79, 126.54, 123.89, 123.83 (CH), 78.86 (C), 61.36 (OCH_2), 56.76 (C), 49.21, 40.90, 39.50 (CH_2), 18.42, 14.15 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3400 (m), 1728 (s), 1656 (s), 1621 (m), 1447 (m), 1377 (m), 1240 (m), 1071 (w), 7660 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=376.0 (3) [M^+], 358.0 (3), 329.9 (12), 209.9 (23), 181.9 (66), 142.0 (68), 104.6 (58), 87.0 (100), 43.1 (63), 28.1 (77). The exact molecular mass for $C_{24}H_{24}O_4$: m/z=376.1675±2 mD was confirmed by HRMS (EI, 70 eV).

Compound 18j: From 1-ethoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.410 g, 1.50 mmol) and 1-(2-benzoylindan-2-yl)ethanone (**5f**; 0.263 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18j** was obtained as a colorless solid (0.064 g, 17%). M.p. 133–134°C; R_f=0.33 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.15–6.87 (m, 9H; ArH), 3.87 (q, 2H, J=7.2 Hz; OCH_2), 3.36 (d, 1H, J=16.8 Hz; CH_2), 3.18 (d, 1H, J=16.8 Hz; CH_2), 2.80 (br, 2H; CH_2), 2.43 (br, 1H; OH), 1.87 (br, 1H; CH_2), 1.37 (br, 3H; CH_3), 1.24 (br, 1H; CH_2), 0.80 ppm (t, 3H, J=7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.96, 166.95 (2C), 141.95, 141.91, 136.25, 133.00 (C), 128.71, 128.03, 127.34, 127.12, 126.94, 126.72, 126.57, 123.70 (2C, CH), 75.21 (C–OH), 61.04 (OCH_2), 56.92 (C), 49.56, 40.00 (2C, CH_2), 25.17, 13.61 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3447 (s), 1735 (s), 1664 (s), 1613 (w), 1373 (m), 1234 (s), 1026 (w), 763 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=376.9 (8) [M^+], 358.0 (6), 243.9 (42), 214.9 (28), 142.0 (43), 104.7 (100), 77.4 (41), 43.1 (89), 28.1 (63). The exact molecular mass for $C_{24}H_{24}O_4$: m/z=376.1675±2 mD was confirmed by HRMS (EI, 70 eV).

Compound 18k: From 1-isobutoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.455 g, 1.50 mmol), 1-(2-benzoylindan-2-yl)ethanone (**5f**; 0.264 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18k** was obtained as a colorless solid (0.085 g, 21%). M.p. 121–122°C; R_f=0.49 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.54–7.00 (m, 9H; ArH), 4.03 (d, 2H, J=6.7 Hz; OCH_2), 3.97–3.92 (br, 1H; CH_2), 3.49–3.42 (br, 1H; CH_2), 3.30–3.22 (br, 1H; CH_2), 3.16 (d, 1H, J=17.1 Hz; CH_2), 3.08 (d, 1H, J=17.1 Hz; CH_2), 2.92–2.86 (br, 1H; CH_2), 2.24 (brs, 1H; OH), 2.03 (sep, 1H, J=6.6 Hz; CH_2), 1.87 (s, 3H; CH_3), 0.94 ppm (d, 6H, J=6.6 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.23, 167.09, 163.61, 142.88, 141.90, 140.76, 131.82 (C), 128.69 (2C), 127.85, 127.16 (2C), 126.83, 126.59, 123.96, 123.85 (CH), 78.86 (C), 71.47 (CH_2), 56.80 (C), 52.25 (OCH_2), 49.32, 40.77, 39.36 (CH_2), 27.72 (CH), 19.11 (2C), 18.56 ppm (CH_3); IR (KBr): $\tilde{\nu}$=3368 (m), 2963 (w), 1719 (s), 1657 (s), 1616 (w), 1379 (m), 1240 (m), 1073 (w), 770 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 404.0 (9) [M^+], 386.1 (12), 330.0 (34), 311.9 (35), 210.1 (45), 182.0 (90), 142.1 (93), 104.7 (100), 77.4 (25), 41.2 (25); elemental analysis calcd (%) for $C_{26}H_{28}O_4$: C 77.20, H 6.98; found: C 77.58, H 7.49. The exact molecular mass for $C_{26}H_{28}O_4$: m/z=404.1988±2 mD was confirmed by HRMS (EI, 70 eV).

Compound 18l: From 1-isobutoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1c**; 0.455 g, 1.50 mmol), 1-(2-benzoylindan-2-yl)ethanone (**5f**; 0.264 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18l** was obtained as a colorless solid (0.060 g, 15%). M.p. 89–90°C; R_f=0.33 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.14–6.89 (m, 9H; ArH), 3.58 (d, 2H, J=6.7 Hz; OCH_2), 3.36 (d, 1H, J=17.1 Hz; CH_2), 3.17 (d, 1H, J=16.8 Hz; CH_2), 2.85 (brs, 2H; CH_2), 2.69 (brs, 1H; OH), 2.07–2.03 (m, 1H; CH_2), 1.57 (sep, 1H, J=6.9 Hz; CH_2), 1.36 (brs, 3H; CH_3), 0.95–0.85 (m, 1H; CH_2), 0.68 ppm (d, 6H, J=6.7 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.03, 166.24 (2C), 141.91, 140.92, 136.22, 133.01 (C), 128.63, 127.99, 127.35, 127.03, 126.80, 126.63, 126.47, 123.62 (2C, CH), 75.19, 71.30 (CH_2), 56.72 (C), 49.45, 40.70, 39.06 (CH_2), 27.27 (CH), 25.00, 18.88 ppm (2C, CH_3); IR (KBr): $\tilde{\nu}$=3472 (s), 1740 (s), 1656 (s), 1612 (w), 1351 (m), 1232 (m), 1068 (w), 773 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=403.9 (12) [M^+], 386.0 (75), 311.9 (53), 244.0 (100), 214.9 (77), 43.1 (25), 28.1 (54). The exact molecular mass for $C_{26}H_{28}O_4$: m/z=404.1988±2 mD was confirmed by HRMS (EI, 70 eV).

Compound 18m: From 1-isopropoxy-1,3-bis(trimethylsilyloxy)buta-1,3-diene (0.453 g, 2.11 mmol), 1-(2-propylindan-2-yl)propan-1-one (**5f**; 0.230 mg, 1.00 mmol), and $TiCl_4$ (0.22 mL, 2.00 mmol), **18m** was obtained as a colorless oil (0.160 g, 43%). R_f=0.50 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.18 (s, 4H; ArH), 4.00 (d, 2H, J=6.6 Hz; OCH_2), 3.37 (d, 1H, J=16.5 Hz; CH_2), 3.07 (d, 1H, J=16.8 Hz; CH_2), 2.69 (br, 2H; CH_2), 2.69 (br, 2H; CH_2), 2.17–2.03 (m, 2H; CH_2), 2.01–1.97 (m, 1H; CH), 1.95 (br, 1H; OH), 1.67–1.54 (m, 2H; CH_2), 0.99–0.81 ppm (m, 12H; CH_3); IR (KBr): $\tilde{\nu}$=3466 (br), 2970 (m), 1279 (s), 1670 (s), 1609 (m), 1465 (m), 1230 (m), 785 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=370.0 (4) [M^+], 352.1 (24), 322.9 (65), 297.0 (58), 223.9 (60), 196.0 (63), 181.9 (78), 101.9 (100), 57.4 (78), 28.4 (70). The exact molecular mass for $C_{23}H_{30}O_4$: m/z=370.2144±2 mD was confirmed by HRMS (EI, 70 eV).

Typical procedure for the preparation of bicyclo[4.4.0]deca-1,4-dien-3-ones 7, 14, 15, 17, and 19: TFA (0.4 mL, 5.2 mmol) was added dropwise to a stirred CH_2Cl_2 solution (0.4 mL) of **6a** (0.100 g, 0.42 mmol) at 20°C. The solution was stirred for 72 h until all starting material disappeared (TLC control). The solvent and TFA were removed in vacuo and the residue was purified by column chromatography (silica gel; hexane/ethyl acetate 7:3) to give **7a** as a colorless solid (0.088 g, 95%).

1-Acetyl-4,10-dimethyl-5,6,7,8-tetrahydro-10*H*-naphthalen-2-one (7a): From **6a** (0.100 g, 0.42 mmol), **7a** was obtained as a colorless solid (0.088 g, 95%). M.p. 56–57°C; R_f=0.16 (hexane/ethyl acetate 7:3); ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.10 (d, 1H, J=1.2 Hz; =CH), 2.45–2.30 (m, 2H; CH_2), 2.34 (s, 3H; CH_3), 2.10–1.95 (m, 2H; CH_2), 1.98 (d, 3H, J=1.2 Hz; CH_3), 1.75–1.62 (m, 2H; CH_2), 1.35–1.20 (m, 2H; CH_2), 1.32 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ=205.22, 183.45, 166.72, 163.20, 137.41 (C), 126.22 (CH), 43.32, 37.62 (CH_2), 32.14 (CH_3), 28.62, 28.31 (CH_2), 22.63 (CH_3) 21.03 (CH_2), 18.98 ppm (CH_3); IR (KBr): $\tilde{\nu}$=2944 (m), 1704 (s), 1654 (s), 1610 (s), 1446 (m), 1391 (m), 1142 (w), 958 (w), 880 cm^{-1} (w); MS (EI, 70 eV): m/z (%)=218.5 (65), 203.5 (68), 189.5 (100), 175.5 (33), 161.4 (36), 43.1 (85) [M^+]; elemental analysis calcd (%) for $C_{14}H_{18}O_2$: C 77.03, H 8.31; found: C 76.89, H 9.26. The exact molecular mass for $C_{14}H_{18}O_2$ m/z=218.1307±2 mD was confirmed by HRMS (EI, 70 eV).

4,10-Dimethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid methyl ester (7b): From **6b** (0.071 g, 0.28 mmol), **7b** was obtained as a colorless solid (0.064 g, 98%). M.p. 82–83 °C; R_f = 0.28 (hexane/ethyl acetate 3:2); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.15 (d, 1H, J = 1.2 Hz; =CH), 3.86 (s, 3H; OCH_3), 2.47–2.41 (m, 2H; CH_2), 2.14–2.04 (m, 2H; CH_2), 2.01 (d, 3H, J = 1.2 Hz; CH_3), 1.80–1.68 (m, 2H; CH_2), 1.46–1.28 (m, 2H; CH_2), 1.36 ppm (s, 3H; CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 181.91, 167.60, 166.06, 164.21, 130.79 (C), 126.04 (CH), 52.19 (OCH_3), 43.22, 37.49, 29.91, 28.10 (CH_2), 22.58 (CH_3), 21.09 (CH_2), 18.98 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 2951 (m), 1732 (s), 1660 (s), 1630 (m), 1608 (m), 1389 (m), 1268 (s), 1048 (m), 958 (w), 868 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 234.2 (31) [M^+], 203.1 (20), 187.1 (45), 175.1 (100), 147.1 (21), 91.1 (23); elemental analysis calcd (%) for $C_{14}H_{18}O_3$: C 71.77, H 7.14; found: C 71.90, H 7.12.

4,10-Dimethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid ethyl ester (7c): From **6c** (0.134 g, 0.5 mmol), **7c** was obtained as colorless crystals (0.120 g, 96%). M.p. 79–80 °C; R_f = 0.30 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.14 (q, 1H, J = 1.2 Hz; =CH), 4.33 (q, 2H, J = 7.2 Hz; OCH_2), 2.47–2.41 (m, 2H; CH_2), 2.12–1.98 (m, 2H; CH_2), 2.01 (d, 3H, J = 1.2 Hz; CH_3), 1.78–1.71 (m, 2H; CH_2), 1.44–1.37 (m, 2H; CH_2), 1.36 (s, 3H; CH_3), 1.34 ppm (t, 3H, J = 7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.02, 167.23, 165.95, 163.77, 131.08 (C), 126.26 (CH), 61.27 (OCH_2), 43.23 (C), 37.60, 29.83, 28.13 (CH_2), 22.60 (CH_3), 21.19 (CH_2), 19.00, 14.24 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 2941 (s), 1730 (s), 1658 (s), 1630 (m), 1447 (m), 1390 (m), 1324 (w), 1265 (s), 1245 (s), 1050 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 248.1 (71) [M^+], 233.1 (46), 203.1 (72), 178.1 (100); elemental analysis calcd (%) for $C_{15}H_{20}O_3$: C 72.55, H 8.11; found: C 72.59, H 8.39.

4,10-Dimethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid isopropyl ester (7d): From **6d** (0.054 g, 0.19 mmol), **7d** was obtained as colorless crystals (0.049 g, 97%). M.p. 62–63 °C; R_f = 0.34 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.19 (q, 1H, J = 1.2 Hz; = CH), 5.23 (sep, 1H, J = 6.3 Hz; OCH), 2.53–2.37 (m, 2H; CH_2), 2.14–2.04 (m, 2H; CH_2), 2.02 (d, 3H, J = 1.2 Hz; CH_3), 1.80–1.70 (m, 2H; CH_2), 1.54–1.38 (m, 2H; CH_2), 1.36 (s, 3H; CH_3), 1.32 ppm (dd, 6H, J = 1.2, 6.3 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.55, 167.13, 166.72, 164.49, 131.08 (C), 125.95 (CH), 69.06 (OCH), 43.44 (C), 37.68, 29.75, 28.14 (CH_2), 22.54, 21.83 (2C, CH_3), 21.15 (CH_2), 19.09 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 2939 (s), 1727 (s), 1660 (s), 1633 (m), 1450 (m), 1239 (m), 876 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 262.3 (51) [M^+], 203.2 (80), 187.2 (100), 175.2 (63), 161.2 (57), 91.1 (32), 43.1 (85); elemental analysis calcd (%) for $C_{16}H_{22}O_3$: C 73.25, H 8.45; found: C 73.38, H 8.71.

4,10-Dimethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid 2-methoxyethyl ester (7e): From **6e** (0.078 g, 0.26 mmol), **7e** was obtained as colorless crystals (0.071 g, 97%). M.p. 64–65 °C; R_f = 0.23 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.14 (q, 1H, J = 1.2 Hz; =CH), 4.50–4.36 (m, 2H; OCH_2), 3.66 (t, 2H, J = 4.8 Hz; OCH_2), 3.38 (s, 3H; OCH_3), 2.55–2.37 (m, 2H; CH_2), 2.13–1.98 (m, 2H; CH_2), 2.01 (d, 3H, J = 1.2 Hz; CH_3), 1.79–1.70 (m, 2H; CH_2), 1.52–1.38 (m, 2H; CH_2), 1.35 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.95, 167.13, 166.16, 164.37, 130.77 (C), 126.13 (CH), 70.39, 63.99 (OCH_2), 58.90 (OCH_3), 43.31 (C), 37.65, 29.87, 28.14 (CH_2), 22.55 (CH_3), 21.17 (CH_2), 19.04 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 2944 (s), 1733 (s), 1659 (s), 1630 (m), 1449 (m), 1268 (m), 1053 (m), 876 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 277.7 (54) [M^+], 220.9 (53), 203.2 (100), 187.9 (82), 175.7 (67), 161.0 (43), 90.9 (22); elemental analysis calcd (%) for $C_{16}H_{22}O_4$: C 69.04, H 7.97; found: C 68.83, H 7.95.

3,4,10-Trimethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid methyl ester (7f): From **6f** (0.135 g, 0.5 mmol), **7f** was obtained as colorless crystals (0.114 g, 92%). M.p. 110–111 °C; R_f = 0.28 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3H; OCH_3), 2.43–2.38 (m, 2H; CH_2), 2.18–2.11 (m, 1H; CH_2), 2.03–1.98 (m, 1H; CH_2), 1.96 (s, 3H; CH_3), 1.89 (s, 3H; CH_3), 1.77–1.67 (m, 2H; CH_2), 1.44–1.34 (m, 1H; CH_2), 1.31 (s, 3H; CH_3), 1.29–1.22 ppm (m, 1H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.82, 168.09, 163.05, 159.57, 130.45, 130.19 (C), 52.19 (OCH_3), 43.21 (C), 37.37, 29.90, 28.06 (CH_2), 22.13 (CH_3), 21.21 (CH_2), 15.78, 11.01 ppm (CH_3); IR (KBr): $\tilde{\nu}$ = 2951 (m), 1729 (s), 1656 (m), 1623 (s), 1438 (m), 1275 (m), 1219 (m), 1007 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 248.1 (45) [M^+], 201.0 (51), 189.1 (100), 173.0 (41), 144.8 (34), 91.0 (57), 41.2 (46); elemental analysis calcd (%) for $C_{15}H_{20}O_3$: C 72.55, H 8.11; found: C 72.59, H 8.39. The exact molecular mass for $C_{15}H_{20}O_3$ m/z = 248.1412 ± 2 mD was confirmed by HRMS (EI, 70 eV).

3-Ethyl-4,10-dimethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid ethyl ester (7g): From **6g** (0.060 g, 0.22 mmol), **7g** was obtained as a colorless oil (0.049 g, 88%). R_f = 0.31 (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35 (q, 2H, J = 7.2 Hz; OCH_2), 2.45–2.38 (m, 4H; CH_2), 2.16–2.11 (m, 1H; CH_2), 2.05–1.95 (m, 1H; CH_2), 1.98 (s, 3H; CH_3), 1.74–1.68 (m, 2H; CH_2), 1.45–1.22 (m, 2H; CH_2), 1.34 (t, 3H, J = 7.2 Hz; CH_3), 1.31 (s, 3H; CH_3), 0.98 ppm (t, 3H, J = 7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.42, 167.68, 162.67, 159.24, 136.23, 130.55 (C), 61.18 (OCH_2), 42.92 (C), 37.41, 29.73, 27.95 (CH_2), 22.17 (CH_3), 21.21, 18.63 (CH_2), 14.79, 14.19, 12.69 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 2936 (s), 2870 (w), 1733 (s), 1656 (m), 1629 (s), 1447 (m), 1393 (m), 1268 (m), 1149 (m), 1028 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 276.1 (63) [M^+], 230.1 (77), 215.0 (100), 203.1 (37), 28.0 (60). The exact molecular mass for $C_{17}H_{24}O_3$ m/z = 276.1725 ± 2 mD was confirmed by HRMS (EI, 70 eV).

4,10-Diethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalene-1-carboxylic acid methyl ester (7h): From 6,10-diethyl-10-hydroxy-8-oxo-spiro[4,5]dec-6-ene-7-carboxylic acid methyl ester (**6h**; 0.080 g, 0.28 mmol), **7h** was obtained as a colorless oil (0.062 g, 83%). R_f = 0.32 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.34 (s, 1H; =CH), 3.85 (s, 3H; OCH_3), 2.42–2.13 (m, 6H; CH_2), 2.04–1.98 (m, 1H; CH_2), 1.83–1.67 (m, 3H; CH_2), 1.48–1.35 (m, 2H; CH_2), 1.15 (t, 3H, J = 7.2 Hz; CH_3), 0.53 ppm (t, 3H, J = 7.1 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.76, 169.75, 167.62, 163.44, 132.86 (C), 125.85 (CH), 52.21 (OCH_3), 48.52 (C), 37.74, 29.92, 28.12, 27.50, 23.02, 20.95 (CH_2), 12.15, 7.96 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 2951 (m), 1729 (s), 1656 (m), 1623 (s), 1438 (m), 1275 (m), 1007 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 248.1 (45) [M^+], 201.1 (51), 189.1 (100), 173.0 (41), 144.8 (34), 91.0 (57), 77.4 (36), 41.2 (46); elemental analysis calcd (%) for $C_{16}H_{22}O_3$: C 73.25, H 8.45; found: C 73.20, H 8.68.

4,10-Diethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalen-1-carboxylic acid ethyl ester (7i): From **6i** (0.060 g, 0.22 mmol), **7i** was obtained as a colorless oil (0.048 g, 85%). R_f = 0.36 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.29 (s, 1H; =CH), 4.29 (q, 2H, J = 7.2 Hz; OCH_2), 2.41–2.09 (m, 6H; CH_2), 2.00–1.95 (m, 1H; CH_2), 1.79–1.60 (m, 3H; CH_2), 1.58–1.33 (m, 2H; CH_2), 1.30 (t, 3H, J = 7.1 Hz; CH_3), 1.12 (t, 3H, J = 7.5 Hz; CH_3), 0.50 ppm (t, 3H, J = 7.1 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.67, 169.31, 167.20, 162.26, 133.11 (C), 125.97 (CH), 61.17 (OCH_2), 48.38 (C), 37.72, 29.71, 28.06, 27.42, 22.96, 20.96 (CH_2), 14.25, 12.15, 7.99 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 1733 (s), 1658 (s), 1632 (m), 1448 (m), 1236 (m), 1044 (w), 887 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 276.1 (32) [M^+], 247.1 (55), 203.0 (100), 175.1 (46), 231.0 (30), 91.0 (24), 28.0 (35).

4,10-Diethyl-2-oxo-2,5,6,7,8,10-hexahydronaphthalen-1-carboxylic acid isopropyl ester (7j): From **6j** (0.066 g, 0.21 mmol), **7j** was obtained as a colorless oil (0.055 g, 89%). R_f = 0.44 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32 (d, 1H, J = 1.2 Hz; =CH), 5.22 (sep, 1H, J = 6.3 Hz; OCH), 2.45–2.13 (m, 7H; CH_2), 1.79–1.62 (m, 3H; CH_2), 1.46–1.35 (m, 2H; CH_2), 1.32 (d, 6H, J = 6.3 Hz; CH_3), 1.15 (t, 3H, J = 7.2 Hz; CH_3), 0.53 ppm (t, 3H, J = 7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.61, 169.40, 166.52, 162.30, 133.01 (C), 48.20 (C), 37.54, 29.38, 27.82, 27.22, 22.79 (CH_2), 21.66, 21.64 (CH_3), 20.77 (CH_2), 11.96, 7.81 ppm (CH_3); IR (neat): $\tilde{\nu}$ = 2933 (m), 1732 (s), 1659 (s), 1629 (m), 1439 (m), 1241 (m), 1044 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 290.0 (19) [M^+], 261.0 (19), 231.0 (46), 218.9 (85), 202.9 (96), 175.0 (62), 43.1 (78), 28.0 (100). The exact molecular mass for $C_{18}H_{26}O_3$: m/z = 290.1882 ± 2 mD was confirmed by HRMS (EI, 70 eV).

4-Methyl-2-oxo-10-phenyl-2,5,6,7,8,10-hexahydronaphthalen-1-carboxylic acid ethyl ester (7k): From **6k** (0.068 g, 0.22 mmol), **7k** was obtained as a colorless oil (0.088 g, 91%). R_f = 0.28 (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.16 (m, 5H; ArH), 6.09 (q, 1H, J = 1.2 Hz; =CH), 4.45–4.29 (m, 2H; OCH_2), 3.00–2.94 (m, 1H; CH_2), 2.44–2.39 (m, 1H; CH_2), 1.95–1.79 (m, 3H; CH_3), 1.71 (d, 3H, J = 1.5 Hz; CH_3), 1.54–1.54 (m, 2H; CH_2), 1.36 (t, 3H, J = 7.2 Hz; CH_3), 1.28–1.23 ppm (m, 1H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 182.65, 166.90, 165.25, 164.05, 138.08, 131.87 (C), 129.21 (2C), 127.59 (2C), 127.45, 124.80 (CH), 61.37 (OCH_2), 52.25 (C), 35.37, 31.22, 29.17, 21.61 (CH_2), 19.39, 14.27 ppm (CH_3); MS (EI, 70 eV): m/z (%) = 310.9 (36) [M^+],

282.8 (100), 265.8 (39), 237.7 (60), 209.6 (63), 165.1 (43), 91.2 (30), 29.1 (57).

Compound 14a: From **13a** (0.050 g, 0.2 mmol) and TFA (0.15 mL, 2.00 mmol), **14a** was obtained as a colorless oil (0.025 g, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.75$ (d, 1H, $J = 9.9$ Hz; CH), 6.24 (d, 1H, $J = 9.9$ Hz; CH), 4.33 (q, 2H, $J = 7.2$ Hz; OCH_2), 2.51–2.46 (m, 1H; CH_2), 2.37 (dd, 1H, $J = 13.5$, 5.1 Hz; CH_2), 2.08–1.98 (m, 1H; CH_2), 1.90–1.83 (m, 1H; CH_2), 1.75–1.69 (m, 2H; CH_2), 1.48–1.38 (m, 2H; CH_2), 1.34 (t, 3H, $J = 7.2$ Hz; CH_3), 1.31 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 182.77$, 167.01, 163.57 (C), 157.14 (CH), 131.02 (C), 126.25 (CH), 61.33 (CH_2), 40.62 (C), 38.46, 29.71, 27.65 (CH_2), 23.01 (CH_3), 20.68 (CH_2), 14.29 ppm (CH_3); IR (neat): $\tilde{\nu} = 2936$ (s); 1659 (s), 1233 (s), 1038 (s), 838 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 234.1 (21) [M^+], 188.1 (100), 162.4 (19), 116.0 (6), 30.1 (7), 28.0 (5); elemental analysis calcd (%) for $C_{14}H_{18}O_3$: C 71.79, H 7.63; found: C 71.20, H 7.40.

Compound 15a: From **13a** (0.050 g, 0.2 mmol) and TFA (0.15 mL, 2.00 mmol), **15a** was obtained as a colorless solid (0.012 g, 22%). M.p. 216–217 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.46$ (s, 1H; OH), 6.58 (s, 1H; ArH), 4.41 (q, 2H, $J = 6.9$ Hz; OCH_2), 2.73 (t, 4H, $J = 6.3$ Hz; CH_2), 2.58 (t, 4H, $J = 6.3$ Hz; CH_2), 2.39 (s, 3H; CH_3), 2.19–1.67 (m, 8H; CH_2), 1.43 ppm (t, 3H, $J = 7.2$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 171.78, 158.82, 144.73, 139.24, 128.01 (C), 115.21 (CH), 112.09 (C), 61.53, 30.99, 27.13, 23.80, 22.44 (CH_2), 18.07, 14.35 ppm (CH_3); IR (neat): $\tilde{\nu} =$ 3410 (br), 2932 (s), 1727 (m), 1658 (s), 1237 (s), 1155 (m), 1080 (m), 802 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 233.9 (17) [M^+], 187.9 (92), 160.9 (15), 86.9 (19), 43.0 (27), 28.0 (100); elemental analysis calcd (%) for $C_{14}H_{18}O_3$: C 71.79, H 7.63; found: C 71.38, H 7.23.

Compound 15b: From **13b** (0.047 g, 0.21 mmol) and TFA (0.16 mL, 2.11 mmol), **15b** was obtained as a colorless solid (0.022 g, 52%). M.p. 136–137 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 10.72$ (s, 1H; OH), 6.57 (s, 1H; ArH), 2.74 (t, 2H, $J = 6.3$ Hz; CH_2), 2.59 (s, 3H; CH_3), 2.56 (t, 2H, $J = 6.3$ Hz; CH_2), 2.35 (s, 3H; CH_3), 1.85–1.82 (m, 2H; CH_2), 1.76–1.71 ppm (m, 2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 206.40$, 157.19, 144.80, 136.97, 127.86, 122.50 (C), 115.29 (CH), 32.71 (CH_3), 30.79, 26.68, 23.50, 22.27 (CH_2), 19.03 ppm (CH_3); IR (neat): $\tilde{\nu} = 3306$ (br), 2933 (s), 1666 (s), 1599 (s), 1429 (s), 1302 (m), 1241 (m), 1149 (m), 855 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 204.2 (41) [M^+], 189.2 (100), 161.2 (9), 145.2 (5), 114.0 (7), 43.0 (8), 28.0 (12); elemental analysis calcd (%) for $C_{13}H_{16}O_2$: C 76.47, H 7.84; found: C 75.76, H 7.97.

Compound 14c: From **13c** (0.040 g, 0.152 mmol) and TFA (0.12 mL, 1.52 mmol), **14c** was obtained as a colorless oil (0.024 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.47$ (s, 1H; =CH), 4.33 (q, 2H, $J = 7.2$ Hz; OCH_2), 2.36 (q, 2H, $J = 7.1$ Hz; CH_2), 1.99 (t, 2H, $J = 3.0$ Hz; CH_2), 1.43–1.38 (m, 4H; CH_2), 1.34 (t, 3H, $J = 7.2$ Hz; CH_3), 1.32–1.28 (m, 2H; CH_2), 1.27 (s, 3H; CH_3), 1.07 ppm (t, 3H, $J = 7.5$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 183.03$, 167.40, 162.84 (C), 151.30 (CH), 137.71, 130.73 (C), 61.19, 38.76, 29.44, 27.63 (CH_2), 23.21 (CH_3), 21.79, 20.74 (CH_2), 14.23, 12.40 ppm (CH_3); IR (neat): $\tilde{\nu} = 2936$ (s), 1733 (s), 1663 (s), 1636 (s), 1440 (m), 1266 (s), 1184 (s), 1025 (m), 716 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 262.3 (22) [M^+], 247.3 (13), 217.2 (28), 189.2 (100), 161.2 (28), 91.0 (20), 28.0 (78); elemental analysis calcd (%) for $C_{16}H_{22}O_3$: C 73.00, H 8.36; found: C 72.32, H 8.34.

4,10-Dimethyl-2-oxo-2,5,6,10-tetrahydronaphthalene-1-carboxylic acid methyl ester (17a): From **16a** (0.118 g, 0.48 mmol), **17a** was obtained as a colorless oil (0.085 g, 76%). $R_f = 0.32$ (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.38$–6.33 (ddd, 1H, $J = 1.5$, 2.4, 9.9 Hz; =CH), 6.29–6.23 (m, 1H; =CH), 6.18 (q, 1H, $J = 1.2$ Hz; =CH), 3.88 (s, 3H; OCH_3), 2.47–2.39 (m, 2H; CH_2), 2.10–2.05 (m, 1H; CH_2), 2.04 (d, 3H, $J = 1.2$ Hz; CH_3), 1.71–1.61 (m, 1H; CH_2), 1.26 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 182.57$, 167.12, 164.83, 157.79 (C), 137.99 (CH), 128.96 (C), 126.84, 124.60 (CH), 52.52 (OCH_3), 40.56 (C), 30.32 (CH_2), 25.12 (CH_3), 23.38 (CH_2), 19.23 ppm (CH_3); IR (neat): $\tilde{\nu} = 3442$ (br), 2977 (m), 1784 (m), 1734 (s), 1653 (s), 1609 (m), 1435 (m), 1246 (s), 1159 (s), 875 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 232.1 (100) [M^+], 217.1 (36), 201.0 (46), 173.0 (74), 144.8 (99), 129.0 (63), 91.0 (18). The exact molecular mass for $C_{14}H_{16}O_3$: $m/z = 232.1099 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

4,10-Dimethyl-2-oxo-2,5,6,10-tetrahydronaphthalen-1-carboxylic acid ethyl ester (17b): From **16b** (0.118 g, 0.48 mmol), **17b** was obtained as a colorless oil (0.044 g, 76%). $R_f = 0.37$ (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.39$–6.34 (ddd, 1H, $J = 1.5$, 2.7, 9.9 Hz; =CH), 6.27–6.22 (m, 1H; =CH), 6.17 (q, 1H, $J = 1.2$ Hz; =CH), 4.35 (q, 2H, $J = 7.2$ Hz; OCH_2), 2.47–2.39 (m, 2H; CH_2), 2.10–2.05 (m, 1H; CH_2), 2.03 (d, 3H, $J = 1.2$ Hz; CH_3), 1.72–1.62 (m, 1H; CH_2), 1.36 (t, 3H, $J =$ 7.2 Hz; CH_3), 1.35 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 182.29, 166.54, 164.34, 156.89 (C), 137.47 (CH), 128.99 (C), 126.66, 124.27 (CH), 61.42 (OCH_2), 40.18 (C), 30.04 (CH_2), 24.85 (CH_3), 23.12 (CH_2), 19.01, 14.18 ppm (CH_3); IR (neat): $\tilde{\nu} = 3440$ (br), 2922 (m), 1784 (m), 1726 (s), 1657 (s), 1610 (m), 1449 (m), 1241 (s), 1160 (s), 732 cm^{-1} (m); MS (EI, 70 eV): m/z (%): 246.1 (70) [M^+], 231.0 (25), 201.0 (79), 187.0 (100), 173.0 (62), 144.8 (79), 129.0 (50), 91.0 (21). The exact molecular mass for $C_{15}H_{18}O_3$: $m/z = 246.1256 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

4,10-Dimethyl-2-oxo-2,5,6,10-tetrahydronaphthalen-1-carboxylic acid isopropyl ester (17c): From **16c** (0.058 g, 0.21 mmol), **17c** was obtained as a colorless oil (0.039 g, 73%). $R_f = 0.38$ (hexane/ethyl acetate 7:3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.38$ (ddd, 1H, $J = 1.5$, 2.7, 9.9 Hz; = CH), 6.26–6.21 (m, 1H; =CH), 6.15 (q, 1H, $J = 1.2$ Hz; =CH), 5.25 (sep, 1H, $J = 6.3$ Hz; OCH), 2.44–2.39 (m, 2H; CH_2), 2.08–2.03 (m, 1H; CH_2), 2.02 (d, 3H, $J = 1.2$ Hz; CH_3), 1.71–1.61 (m, 1H; CH_2), 1.36 (d, 6H, $J =$ 6.3 Hz; CH_3), 1.35 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 182.52, 166.34, 164.33, 156.52 (C), 137.33 (CH), 129.56 (C), 127.01, 124.51 (CH), 69.32 (OCH), 40.36 (C), 30.31 (CH_2), 25.05 (CH_3), 23.38 (CH_2), 22.07 (2C), 19.01 ppm (CH_3); IR (neat): $\tilde{\nu} = 3436$ (br), 2982 (m), 1784 (m), 1722 (s), 1656 (s), 1610 (m), 1372 (s), 1246 (s), 732 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 260.0 (26) [M^+], 217.9 (37), 200.9 (57), 173.9 (100), 144.7 (28), 114.3 (23), 43.1 (48). The exact molecular mass for $C_{16}H_{20}O_3$: $m/z = 260.1412 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19a: From **18a** (0.110 g, 0.39 mmol), **19a** was obtained as a yellow oil (0.084 g, 82%). $R_f = 0.45$ (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 16.55$ (s, 1H; OH), 7.19–7.03 (m, 4H; ArH), 6.12 (s, 1H; =CH), 5.93 (q, 1H, $J = 1.2$ Hz; =CH), 2.93 (d, 1H, $J = 15.0$ Hz; CH_2), 2.85 (d, 1H, $J = 15.0$ Hz; CH_2), 2.38 (s, 3H; CH_3), 2.04 (d, 3H, $J =$ 1.2 Hz; CH_3), 1.05 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 185.23, 182.27, 162.95, 138.40, 133.36, 131.57 (C), 128.17, 126.98, 126.65, 125.11 123.32, 122.53 (CH), 107.93, 43.53 (C), 38.19 (CH_2), 23.67, 20.50, 19.08 ppm (CH_3); IR (neat): $\tilde{\nu} = 2974$ (m), 1735 (m), 1657 (s), 1630 (m); 1601 (w), 1571 (m), 1441 (m), 1268 (m), 1235 (m), 1156 (w), 869 (m), 759 cm^{-1} (m); MS (EI, 70 eV): m/z (%) = 266.7 (96) [M^+], 251.6 (100), 209.5 (47), 178.3 (19), 43.1 (79), 28.0 (73). The exact molecular mass for $C_{18}H_{18}O_2$: $m/z = 266.1307 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19b: From **18b** (0.097 g, 0.32 mmol), **19b** was obtained as a yellow oil (0.072 g, 79%). $R_f = 0.48$ (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.28$ (s, 1H; OH), 7.17–6.96 (m, 5H; ArH, = CH), 5.86 (q, 1H, $J = 1.2$ Hz; =CH), 3.88 (s, 3H; CH_3), 3.01 (d, 1H, $J =$ 15.3 Hz; CH_2), 2.81 (d, 1H, $J = 15.3$ Hz; CH_2), 2.38 (s, 3H; CH_3), 2.00 (d, 3H, $J = 1.2$ Hz; CH_3), 1.25 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.80$, 168.60, 157.38, 136.69, 134.26, 130.60 (C), 127.89, 126.84, 126.24, 125.97, 121.39, 119.35 (CH), 96.05 (C), 51.82 (OCH_3), 41.27 (C), 37.97 (CH_2), 29.67, 21.88 (CH_3); IR (neat): $\tilde{\nu} = 3436$ (br), 1736 (m), 1658 (s), 1626 (m), 1567 (m), 1441 (m), 1269 (s), 751 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 281.9 (49) [M^+], 267.0 (34), 249.9 (35), 234.9 (100), 179.0 (41), 57.4 (18), 28.1 (22). The exact molecular mass for $C_{18}H_{18}O_3$: $m/z = 282.1256 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19c: From **18c** (0.115 g, 0.36 mmol), **19c** was obtained as orange crystals (0.093 g, 86%). M.p. 126–127 °C; $R_f = 0.45$ (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.37$ (s, 1H; OH), 7.10–7.03 (m, 5H; ArH, =CH), 5.86 (q, 1H, $J = 1.4$ Hz; =CH), 4.44–4.33 (m, 2H; OCH_2), 3.02 (d, 1H, $J = 15.2$ Hz; CH_2), 2.80 (d, 1H, $J = 15.2$ Hz; CH_2), 2.01 (d, 3H, $J = 1.4$ Hz; CH_3), 1.45 (t, 3H, $J = 7.2$ Hz; CH_3), 1.03 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.05$, 168.59, 157.18, 136.89, 134.43, 130.66 (C), 127.92, 126.86, 126.21, 125.94, 121.45, 119.45 (CH), 96.06 (C), 61.11 (CH_2), 41.31 (C), 38.04 (CH_2), 21.98, 19.14, 14.21 ppm (CH_3); IR (KBr): $\tilde{\nu} = 2960$ (m), 1725 (w), 1659 (s), 1613 (s), 1574 (s), 1408 (m), 1306 (s), 1272 (s), 1239 (s), 1073 (m), 1017 (w), 869 (m), 752 cm^{-1} (m); MS (EI, 70 eV) m/z (%) = 296.2 (43) [M^+], 281.4 (28), 250.2 (41), 235.2 (100), 179.2 (43); elemental analysis calcd (%) for $C_{19}H_{20}O_3$: C 77.00, H 6.80; found: C 77.33, H 6.95.

Compound 19d: From **18d** (0.113 g, 0.34 mmol), **19d** was obtained as a yellow oil (0.081 g, 76%). $R_f = 0.54$ (hexane/ethyl acetate 3:2); ^{1}H NMR

(300 MHz, $CDCl_3$): $\delta = 13.44$ (s, 1H; OH), 7.19–6.98 (m, 5H; ArH, =CH), 5.85 (q, 1H, $J = 1.5$ Hz; =CH), 5.25 (sep, 1H, $J = 6.0$ Hz; CH), 3.00 (d, 1H, $J = 15.0$ Hz; CH_2), 2.80 (d, 1H, $J = 15.0$ Hz; CH_2), 2.00 (d, 3H, $J = 1.5$ Hz; CH_3), 1.45 (d, 3H, $J = 6.0$ Hz; CH_3), 1.39 (d, 3H, $J = 6.0$ Hz; CH_3), 1.03 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 172.57$, 168.40, 156.96, 136.95, 134.37, 130.62 (C), 127.89, 126.80, 126.12, 125.86, 121.42, 119.44 (CH), 96.23 (C), 69.04 (OCH), 41.27 (C), 38.02 (CH_2), 22.05, 21.19 (2C), 19.07 ppm (CH_3); IR (neat): $\tilde{\nu} = 2979$ (w), 1733 (s), 1657 (s), 1630 (s), 1603 (w), 1569 (m), 1454 (w), 1269 (s), 1105 (s), 862 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 310.0 (36) [M^+], 250.0 (53), 234.9 (100), 209.4 (24), 179.0 (45), 43.2 (44), 28.0 (23). The exact molecular mass for $C_{20}H_{22}O_3$: $m/z = 310.1569 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19e: From **18e** (0.113 g, 0.34 mmol), **19e** was obtained as a yellow oil (0.089 g, 85%). $R_f = 0.50$ (hexane/ethyl acetate 3:2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.12$ (s, 1H; OH), 7.17–7.00 (m, 5H; ArH, =CH), 5.86 (q, 1H, $J = 1.2$ Hz; =CH), 4.57–4.51 (m, 1H; OCH_2), 4.39–4.32 (m, 1H; OCH_2), 3.77–3.73 (m, 2H; OCH_2), 3.48 (s, 3H; OCH_3), 3.00 (d, 1H, $J = 15.0$ Hz; CH_2), 2.80 (d, 1H, $J = 15.0$ Hz; CH_2), 2.00 (d, 3H, $J = 1.2$ Hz; CH_3), 1.03 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.05$, 168.59, 157.18, 136.89, 134.43, 130.66 (C), 127.92, 126.86, 126.21, 125.94, 121.45, 119.45 (CH), 96.06 (C), 61.11 (CH_2), 41.31 (C), 38.04 (CH_2), 21.98, 19.14, 14.21 ppm (CH_3); IR (neat): $\tilde{\nu} = 2969$ (w), 1714 (w), 1646 (s), 1621 (s), 1566 (s), 1454 (m), 1425 (s), 1283 (s), 962 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 326.0 (39) [M^+], 310.9 (20), 250.0 (51), 234.9 (100), 179.0 (32), 43.1 (55), 28.1 (48); elemental analysis calcd (%) for $C_{20}H_{22}O_4$: C 73.59, H 6.79; found: C 73.87, H 7.04. The exact molecular mass for $C_{20}H_{22}O_4$: $m/z = 326.1518 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19g: From **18g** (0.046 g, 0.13 mmol), **19g** was obtained as a yellow oil (0.032 g, 73%). $R_f = 0.82$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.21$ (s, 1H; OH), 7.30–6.92 (m, 10H; ArH, =CH), 5.99 (s, 1H; =CH), 3.96 (s, 3H; OCH_3), 2.97 (d, 1H, $J = 15.6$ Hz; CH_2), 2.48 (d, 1H, $J = 15.6$ Hz; CH_2), 1.26 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 173.47$, 167.80, 159.46, 139.55, 136.83, 134.10, 131.27 (C), 128.59 (2C), 128.25, 128.23 (2C), 127.93, 126.95, 126.61, 126.36, 122.16 (CH), 92.28 (C), 52.22 (CH_3), 41.62 (C), 39.31 (CH_2), 23.44 ppm (CH_3); IR (neat): $\tilde{\nu} = 3435$ (s), 2977 (w), 1739 (s), 1655 (s), 1601 (m), 1562 (m), 1441 (m), 1275 (m), 763 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 344.0 (47) [M^+], 329.0 (35), 311.9 (29), 297.0 (100), 241.0 (34), 70.0 (34), 28.1 (32). The exact molecular mass for $C_{23}H_{20}O_3$: $m/z = 344.1412 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19h: From **18h** (0.040 g, 0.11 mmol), **19h** was obtained as a yellow oil (0.032 g, 84%). $R_f = 0.39$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.29$–7.05 (m, 9H; ArH), 6.27 (d, 1H, $J = 1.2$ Hz; =CH), 3.90 (s, 3H; OCH_3), 3.88 (d, 1H, $J = 16.5$ Hz; CH_2), 3.63 (d, 1H, $J = 19.2$ Hz; CH_2), 3.33 (d, 1H, $J = 19.2$ Hz; CH_2), 3.08 (d, 1H, $J = 16.5$ Hz; CH_2), 1.79 ppm (d, 3H, $J = 1.1$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 182.18$, 166.85, 163.71, 159.88, 137.69, 132.22, 132.19, 131.37 (C), 129.00 (2C), 128.41, 128.00, 127.63, 127.11 (2C), 126.93, 126.86, 125.00 (CH), 52.41 (OCH_3), 50.47 (C), 38.36, 33.78 (CH_2), 19.50 ppm (CH_3); IR (neat): $\tilde{\nu} = 3435$ (s), 2977 (w), 1739 (s), 1655 (s), 1601 (m), 1562 (m), 1441 (m), 1275 (m), 763 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 344.4 (45) [M^+], 312.6 (100), 285.1 (8), 253.0 (19), 179.0 (12), 104.8 (12), 28.0 (9). The exact molecular mass for $C_{23}H_{20}O_3$: $m/z = 344.1412 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19i: From **18i** (0.050 g, 0.13 mmol), **19i** was obtained as a yellow oil (0.040 g, 84%). $R_f = 0.88$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.31$ (s, 1H; OH), 7.37–6.93 (m, 10H; ArH, =CH), 5.98 (s, 1H; =CH), 4.51–4.34 (m, 2H; OCH_2), 2.97 (d, 1H, $J = 15.6$ Hz; CH_2), 2.48 (d, 1H, $J = 15.6$ Hz; CH_2), 1.47 (t, 3H, $J = 7.2$ Hz; CH_3), 1.26 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 172.87$, 167.54, 159.10, 139.39, 136.77, 134.01, 131.08 (C), 128.40 (2C), 127.72 (3C), 126.72, 126.35, 126.09, 121.99 (2C, CH), 97.07 (C), 61.29 (CH_3), 41.42 (C), 39.13 (CH_2), 23.30, 14.18 ppm (CH_3); IR (neat): $\tilde{\nu} = 3435$ (s), 2977 (w), 1739 (s), 1655 (s), 1601 (m), 1562 (m), 1441 (m), 1275 (m), 763 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 358.4 (41) [M^+], 343.3 (28), 312.3 (33), 297.3 (100), 241.3 (39), 77.4 (3). The exact molecular mass for $C_{24}H_{22}O_3$: $m/z = 358.1569 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19j: From **18j** (0.043 g, 0.11 mmol), **19j** was obtained as a yellow oil (0.040 g, 83%). $R_f = 0.40$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.37$–7.27 (m, 9H; ArH), 6.27 (d, 1H, $J = 1.2$ Hz; =CH), 4.38 (d, 2H, $J = 7.2$ Hz; OCH_2), 3.88 (d, 1H, $J = 16.5$ Hz; CH_2), 3.64 (d, 1H, $J = 19.2$ Hz; CH_2), 3.32 (d, 1H, $J = 19.2$ Hz; CH_2), 3.08 (d, 1H, $J = 16.5$ Hz; CH_2), 1.78 (d, 3H, $J = 1.2$ Hz; CH_3), 1.35 ppm (t, 3H, $J = 7.2$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 182.26$, 164.40, 163.65, 159.40, 137.73, 133.29, 132.25 (C), 128.97 (2C), 128.37, 128.00, 127.58, 127.12 (2C), 126.91, 126.81, 125.93 (CH), 61.52 (OCH_2), 50.39 (C), 38.32, 33.61 (CH_2), 19.48, 14.19 ppm (CH_3); IR (neat): $\tilde{\nu} = 3435$ (s), 2977 (w), 1739 (s), 1655 (s), 1601 (m), 1562 (m), 1441 (m), 1275 (m), 763 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 358.3 (45) [M^+], 312.1 (100), 297.1 (19), 284.1 (18), 235.1 (47), 179.1 (20), 144.8 (9), 28.0 (8). The exact molecular mass for $C_{24}H_{24}O_3$: $m/z = 358.1569 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19k: From **18k** (0.052 g, 0.13 mmol), **19k** was obtained as a yellow oil (0.041 g, 83%); a small amount of impurity could not be separated. $R_f = 0.93$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 13.32$ (s, 1H; OH), 7.45–6.93 (m, 10H; ArH, =CH), 5.99 (s, 1H; =CH), 4.24–4.09 (m, 2H; OCH_2), 2.96 (d, 1H, $J = 15.6$ Hz; CH_2), 2.47 (d, 1H, $J = 15.6$ Hz; CH_2), 2.20–2.11 (m, 1H; CH), 1.27 (s, 3H; CH_3), 1.10 ppm (d, 6H, $J = 6.7$ Hz; CH_3); IR (KBr): $\tilde{\nu} = 2938$ (s), 1736 (s), 1602 (m), 1453 (m), 1276 (s), 1115 (s), 706 cm^{-1} (w); MS (EI, 70 eV): m/z (%) = 386.0 (51) [M^+], 311.0 (100), 284.9 (15), 234.9 (38), 179.0 (18), 144.8 (9), 43.1 (10), 28.1 (41). The exact molecular mass for $C_{26}H_{26}O_3$: $m/z = 386.1882 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

Compound 19l: From **18l** (0.050 g, 0.12 mmol), **19l** was obtained as a yellow oil (0.035 g, 73%); a small amount of impurity could not be separated. $R_f = 0.46$ (hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.30$–6.90 (m, 9H; ArH), 6.27 (d, 1H, $J = 1.2$ Hz; =CH), 4.16–4.05 (m, 2H; OCH_2), 3.95–3.80 (br, 1H; CH_2), 3.88 (d, 1H, $J = 16.7$ Hz; CH_2), 3.66 (d, 1H, $J = 19.1$ Hz; CH_2), 3.32 (d, 1H, $J = 17.2$ Hz; CH_2), 3.10 (d, 1H, $J = 16.7$ Hz; CH_2), 2.08–2.08 (m, 1H; CH), 1.78 (d, 3H, $J = 1.1$ Hz; CH_3), 0.98 ppm (dd, 6H, $J = 12.6$, 1.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 182.80$, 166.94, 164.31, 160.07, 138.18, 133.69 (C), 132.66, 132.00, 129.44, 129.20, 128.85, 128.80, 128.39, 120.36, 127.77, 127.60, 127.48, 126.34 (CH), 72.07 (CH_2), 50.90 (C–OH), 38.70, 34.18 (CH_2), 28.15 (CH), 20.00, 19.92, 19.57 ppm (CH_3); IR (KBr): $\tilde{\nu} = 2973$ (m), 1736 (s), 1677 (m), 1657 (s), 1600 (m), 1450 (m), 1257 (m), 1115 (m), 759 cm^{-1} (w); MS (EI, 70 eV): m/z (%): 386.0 (51) [M^+], 311.0 (100), 284.9 (15), 234.9 (38), 179.0 (18), 144.8 (9), 43.1 (10), 28.1 (41). The exact molecular mass for $C_{26}H_{26}O_3$: $m/z = 386.1882 \pm 2$ mD was confirmed by HRMS (EI, 70 eV).

6,10-Dimethyl-8-oxo-spiro[4,5]deca-6,9-dien-7-carboxylic acid ethyl ester (8): TFA (0.40 mL, 5.30 mmol) was added to a well-stirred CH_2Cl_2 solution (0.5 mL) of **7c** (0.130 g, 0.49 mmol) at 20 °C and the mixture was stirred for 1 h. The solvent and TFA were removed in vacuo and the residue was purified by column chromatography (silica gel, ethyl acetate/hexane 2:3) to give **8** as a colorless solid (0.068 g, 56%). M.p. 50–51 °C; $R_f = 0.30$ (ethyl acetate/hexane 2:3); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.06$ (s, 1H; =CH), 4.35 (q, 2H, $J = 7.2$ Hz; OCH_2), 2.02 (s, 3H; CH_3), 2.01 (s, 3H; CH_3), 1.93–1.85 (m, 8H; cyclopentane CH_2), 1.42 ppm (t, 3H, $J = 7.2$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 182.11$, 167.45, 164.76, 161.00, 132.09 (C), 125.08 (CH), 61.23 (CH_2), 53.40 (C), 37.33 (2C), 29.19 (2C, CH_2), 20.79, 17.46, 14.19 ppm (CH_3); IR (neat): $\tilde{\nu} = 2959$ (m), 1731 (s), 1657 (s), 1629 (m), 1607 (w), 1394 (m), 1243 (m), 1049 cm^{-1} (m); MS (EI, 70 eV): m/z (%): 248.3 (20) [M^+], 233.2 (6), 203.3 (37), 187.2 (20), 175.2 (100), 161.2 (30), 146.8 (30), 91.1 (11), 29.2 (17); elemental analysis calcd (%) for $C_{15}H_{20}O_3$: C 72.55, H 8.11; found: C 72.61, H 8.29.

Synthesis of ethyl 1-acetylcyclopropanecarboxylate (9): 1,4-Dibromobutane (46.6 mL, 395.3 mmol) was added dropwise through a dropping funnel to a stirred solution of ethyl acetoacetate (51.4 g, 395.3 mmol) and potassium carbonate (136.0 g, 987.5 mmol) in dimethyl sulfoxide (120 mL) at 20 °C. After three days of stirring, the reaction mixture was filtered and the residue was washed with Et_2O (2 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude reaction mixture was purified by column chromatography (hexane/ethyl acetate 9:1) to give **9** as a colorless oil (60.0 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.19$ (q, 2H, $J = 7.2$ Hz; OCH_2), 2.15 (s, 3H; CH_3), 2.13–2.08 (m, 2H; CH_2), 1.68–1.61 (m, 2H; CH_2),

1.26 ppm (t, 3H, $J=7.2$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 203.09, 172.87, 66.38 (C) 60.79, 32.50 (2C, CH_2), 25.82 (CH_3), 25.21 (2C, CH_2), 13.54 ppm (CH_3); IR (neat): $\tilde{\nu}=2960$ (s), 2874 (m), 1739 (s); 1710 (s), 1623 (m), 1448 (s), 1246 (s), 1171 (s), 858 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 184.0 (5) [M^+], 139.0 (2), 84.9 (4), 55.3 (5), 43.1 (10), 28.0 (100).

Synthesis of 10: 4-Methyl benzenesulfonic acid (PTSA; 0.028 g, 0.16 mmol) was added to a stirred benzene solution (200 mL) of **9** (30.4 g, 165.3 mmol) and ethane-1,2-diol (110.6 mL, 198.4 mmol) at 20 °C. The reaction mixture was heated to reflux by using a Dean–Stark apparatus until water was completely removed from the reaction mixture (8 h). The benzene was distilled off and the product was collected by fractional distillation to give **10** as a colorless oil (32.0 g, 85%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=4.15$ (q, 2H, $J=7.2$ Hz; OCH_2), 3.96 (s, 4H; $COCH_2$), 2.20–2.07 (m, 2H; CH_2), 1.83–1.62 (m, 6H; CH_2), 1.33 (s, 3H; CH_3), 1.26 ppm (t, 3H, $J=6.9$ Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 174.26, 110.44 (C), 64.41 (2C, CH_2), 62.91 (C), 59.91, 31.25 (2C), 24.48 (2C, CH_2), 21.24, 13.44 ppm (CH_3); IR (neat): $\tilde{\nu}=2982$ (m), 2877 (m), 1719 (s), 1248 (s), 1043 (s), 890 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 229.0 (5) [M^++1], 213.0 (46), 142.0 (24), 88.0 (22), 87.2 (100); elemental analysis calcd (%) for $C_{12}H_{20}O_4$: C 63.15, H 8.71; found: C 62.86, H 8.41.

Synthesis of 11: Lithium aluminium hydride (2.0 g, 52.6 mmol) was added to a three-necked round-bottom flask containing Et_2O (200 mL) under argon at 20 °C. The suspension was cooled to 0 °C and an Et_2O solution (100 mL) of **10** (10.0 g, 43.8 mmol) was added dropwise over 0.5 h by using a dropping funnel. After completion of addition, the reaction was warmed to 20 °C and was stirred for additional 3 h. The reaction was quenched by the slow addition of water (1.5 mL), followed by addition of an aqueous solution of NaOH (4.0 mL, 1.0 M) and water (4.0 mL). The reaction mixture was filtered and the residue was washed with Et_2O (2× 50 mL). The combined organic filtrates were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give **11** as a colorless oil (7.35 g, 90%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=4.01$–3.96 (br, 4H; CH_2), 3.49 (d, 2H, $J=5.4$ Hz; C*H*$_2$OH), 3.12 (t, 1H, $J=5.4$ Hz; CH_2O*H*), 1.68–1.52 (m, 6H; CH_2), 1.48–1.44 (m, 2H; CH_2), 1.36 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=114.66$ (C), 67.31, 64.46 (2C, CH_2), 54.29 (C), 30.65 (2C), 25.65 (2C, CH_2), 20.03 ppm (CH_3); IR (neat): $\tilde{\nu}=3453$ (s), 2954 (s), 2873 (s), 1376 (s), 1126 (m), 1038 (s), 881.27 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 187.4 (2) [M^++1], 171.4 (36), 87.2 (100), 82.2 (54), 68.1 (71), 43.1 (48), 31.1 (39); elemental analysis calcd (%) for $C_{10}H_{18}O_3$: C 64.48, H 9.74; found: C 63.95, H 9.45.

Synthesis of 12: An acetone solution (50 mL) of **11** (4.67 g, 25.10 mmol) and PTSA (2.15 g, 12.55 mmol) was stirred for 24 h at 20 °C. The acetone was removed in vacuo and the reaction mixture was extracted with Et_2O (50 mL). The organic layer was washed with water (50 mL), dried over anhydrous Na_2SO_4, filtered, and and concentrated in vacuo to give **12** as a colorless oil (3.09 g, 87%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=3.57$ (s, 2H; CH_2), 2.45 (s, 1H; OH), 2.18 (s, 3H; CH_3), 1.91–1.62 ppm (m, 8H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=214.14$ (C), 66.92 (CH_2), 60.89 (C), 32.08 (2C), 25.28 (2C, CH_2), 20.40 ppm (CH_3); IR (neat): $\tilde{\nu}=3431$ (br), 2953 (s), 1700 (s), 1357 (m), 1041 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)= 143.0 (12) [M^++1], 125.0 (17), 108.4 (88), 81.1 (39), 68.0 (68), 43.1 (100), 28.1 (40).

Synthesis of 5d: A CH_2Cl_2 solution (2 mL) of dimethyl sulfoxide (1.00 mL, 14.1 mmol) was added dropwise to a stirred CH_2Cl_2 solution (7 mL) of oxalyl chloride (0.88 mL, 7.04 mmol) at −78 °C under an argon atmosphere. After stirring for 10 min, a CH_2Cl_2 solution (3 mL) of **12** (1.00 g, 7.04 mmol) was added dropwise and the solution was stirred for 15 min. Triethylamine (3.9 mL, 28.2 mmol) was added slowly and the temperature of the mixture was allowed to rise to 20 °C over 30 min. Water (40 mL) was added to the reaction mixture and the latter was stirred for 10 min. The organic layer was separated and the aqueous layer was washed with CH_2Cl_2 (2×25 mL). The combined organic layers were washed with an aqueous solution of Na_2CO_3 (30 mL, 10%) and water (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give **5d** as a yellow oil (0.858 mg, 87%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=9.57$ (s, 1H; CHO), 2.20 (s, 3H; CH_3), 2.15–2.06 (m, 4H; CH_2), 1.71–1.61 ppm (m, 4H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 205.36 (C), 199.28 (CH), 72.23 (C), 30.05 (2C, CH_2), 27.10 (CH_3), 25.51 ppm (2C, CH_2); IR (neat): $\tilde{\nu}=2952$ (s), 2870 (m), 1702 (s), 1357 (m), 1158 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%)=141 (3) [M^++1], 125.0 (11), 111.1 (44), 98 (18), 81 (33), 67.9 (57), 43.1 (100), 28.1 (42).

1-(1-Propionylcyclopentyl)propan-1-one (5b): The reaction was carried out by following the procedure as given for the synthesis of **9**. From heptane-3,5-dione (3.20 g, 25.0 mmol), 1,4-dibromobutane (5.40 g, 25.0 mmol), and potassium carbonate (7.60 g, 55.0 mmol), **5b** was obtained as a colorless oil (3.00 g, 66%). $R_f=0.66$ (hexane/ethyl acetate 9:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=2.37$ (q, 4H, $J=7.2$ Hz; CH_2), 2.12–2.18 (m, 4H; CH_2), 1.60–1.56 (m, 4H; CH_2), 1.04 ppm (t, 6H, $J=$ 7.2 Hz; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=208.26$ (2C), 74.52 (C), 32.00 (2C), 31.26 (2C), 25.29 (2C, CH_2), 8.11 ppm (2C, CH_3); IR (neat): $\tilde{\nu}=2973$ (s), 1697 (s), 1456 (m), 1346 (m), 1139 (m), 1024 cm^{-1} (w).

1-(2-Benzoylcyclopentyl)ethanone (5c): The reaction was carried out by following the procedure as given for the synthesis of **9**. From benzoylacetone (4.05 g, 25.0 mmol), 1,4-dibromobutane (5.40 g, 25.0 mmol), and potassium carbonate (7.60 g, 55.0 mmol), **5c** was obtained as a colorless oil (3.95 g, 75%). $R_f=0.68$ (hexane/ethyl acetate 9:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.86$–7.82 (m, 2H; ArH), 7.53–7.50 (m, 1H; ArH), 7.44–7.38 (m, 2H; ArH), 3.43 (m, 1H; CH_2), 2.32–2.20 (m, 4H; CH_2), 2.01 (s, 3H; CH_3), 1.66–1.61 ppm (m, 3H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 205.75, 197.41, 135.21 (C), 132.95, 129.02 (2C), 128.50 (2C, CH), 72.32 (C), 33.09 (2C, CH_2), 27.05 (CH_3), 26.07 ppm (2C, CH_2); IR (neat): $\tilde{\nu}=$ 2957 (m), 1713 (m), 1674 (s), 1598 (w), 1447 (m), 1243 (s), 710 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 215.8 (1) [M^+], 173.9 (5), 144.6 (2), 104.5 (100), 77.3 (36), 43.0 (7).

Preparation of 1-(1-acetylcyclopent-3-enyl)ethanone (5e): $Ti(OiPr)_4$ (0.3 mL, 1.01 mmol) was added to a CH_2Cl_2 solution (degassed, 70 mL) of 3,3-diallylpentane-2,4-dione (1.30 g, 7.22 mmol). After stirring for 1 h at 35 °C, Grubbs catalyst (0.594 g, 0.7 mmol in 5 mL of CH_2Cl_2) was added. The solution was stirred for 48 h at the same temperature. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, ethyl acetate/hexane 1:9) to give **5e** as an oil (0.626 g, 57%). $R_f=0.66$ (ethyl acetate/hexane 1:9); ^1H NMR (300 MHz, $CDCl_3$): $\delta=5.59$ (s, 2H; =CH), 2.90 (s, 4H; CH_2), 2.15 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=204.99$ (2C, C), 127.89 (2C, CH), 73.16 (C), 37.66 (2C, CH_2), 26.37 ppm (2C, CH_3); IR (neat): $\tilde{\nu}=1700$ (s), 1433 (m), 1358 (m), 1216 (m), 1151 (m), 633 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 151.3 (1) [M^+], 138.1 (2), 124.1 (5), 108.4 (15), 97.0 (5), 81.0 (4), 43.1 (100), 28.0 (7).

1-(2-Acetylindan-2-yl)ethanone (5f): The reaction was carried out by following the procedure as given for the synthesis of **9**. From acetylacetone (2.10 g, 25.0 mmol), 1,2-bis(bromomethyl)benzene (6.60 g, 25.0 mmol), and potassium carbonate (7.60 g, 55.0 mmol), **5f** was obtained as a colorless oil (4.10 g, 81%). $R_f=0.66$ (hexane/ethyl acetate 9:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.17$–7.11 (m, 4H; ArH), 3.47 (s, 4H; CH_2), 2.14 ppm (s, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=214.56$ (2C), 139.53 (2C, C), 126.84 (2C), 124.22 (2C, CH), 74.39 (C), 37.38 (2C, CH_2), 26.29 ppm (2C, CH_3); IR (neat): $\tilde{\nu}=1695$ (s), 1585 (s), 1430 (s), 1357 (s), 1032 (m), 771 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 201.9 (1) [M^+], 186.8 (1), 158.8 (80), 144.6 (6), 114.3 (21), 88.9 (4), 43.0 (100), 28.0 (16).

1-(2-Propionylindan-2-yl)propan-1-one (5g): The reaction was carried out by following the procedure as given for the synthesis of **9**. From heptane-3,5-dione (3.20 g, 25.0 mmol), 1,2-bis(bromomethyl)benzene (6.60 g, 25.0 mmol), and potassium carbonate (7.60 g, 55.0 mmol), **5g** was obtained as a colorless oil (3.91 g, 68%). ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 7.20–7.13 (m, 4H; ArH), 3.51 (s, 4H; CH_2), 2.44 (q, 4H, $J=7.2$ Hz; CH_2), 1.04 ppm (t, 6H, $J=7.2$ Hz; CH_3); IR (neat): $\tilde{\nu}=2980$ (m), 1697 (s), 1456 (m), 1348 (m), 1163 (m), 995 (w), 745 cm^{-1} (m).

1-(2-Benzoylindan-2-yl)ethanone (5h): The reaction was carried out by following the procedure as given for the synthesis of **9**. From benzoylacetone (4.05 g, 25.0 mmol), 1,2-bis(bromomethyl)benzene (6.60 g, 25.0 mmol), and potassium carbonate (7.60 g, 55 mmol), **1** was obtained as a colorless oil (4.50 g, 68%). $R_f=0.59$ (hexane/ethyl acetate 9:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.89$–7.84 (m, 2H; ArH), 7.56–7.51 (m, 1H; ArH), 7.45–7.39 (m, 2H; ArH), 7.18–7.11 (m, 4H; ArH), 3.78 (d, 2H, $J=16.5$ Hz; CH_2), 3.68 (d, 2H, $J=16.5$ Hz; CH_2), 2.11 ppm (s, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=204.51$, 196.41, 139.43 (2C), 134.86 (C), 133.29, 129.14 (2C), 128.72 (2C), 126.84 (2C), 124.18 (2C, CH), 72.02 (C), 39.05 (2C, CH_2), 26.75 ppm (CH_3); IR (neat): $\tilde{\nu}=2944$ (m),

1715 (m), 1679 (s), 1601 (m), 1589 (m), 1447 (m), 1355 (m), 1243 (s), 721 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 263.9 (1) [M^+], 248.8 (1), 220.7 (80), 158.9 (53), 104.5 (100), 77.3 (44), 43.0 (16).

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