Synthesis of 2,4-Furanophanes by Palladium-Catalyzed Macrocyclization Reactions of 1,*n*-Diallenyl Diketones

A. Stephen K. Hashmi,*[a] Lothar Schwarz,[b] and Michael Bolte[b][‡]

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The 1,*n*-diallenyl diketones **8a–j** were prepared and subjected to reactions with the [$PdCl_2(MeCN)_2$] catalyst. Upon decreasing the length of the bridge between the allenyl ketone units, first we obtained the (*E*) isomer **10** as the macrocyclic product and then the (*Z*) isomer **11** accompanied by the exocyclic double bond isomer **12**. In all cases, the open-chained 1,*n*-difuryl alkanes were isolated as side-products. The analogous preparation and conversion of the diallenyl diketones **19** and **24**, which have even longer bridges and ether-functionalities, delivered the 20- to 52-membered macrocycles **21a**, **21b**, **26a**, and **26b** with only the expected (*E*) configuration of the double bond. The ring closure of a furan derivative, having vinyl groups in its substituents at the 2- and 4-positions, to a related product by Ru-catalyzed olefin metathesis delivered yields similar to the Pd-catalyzed macrocyclization, but provided a mixture of both double bond isomers.

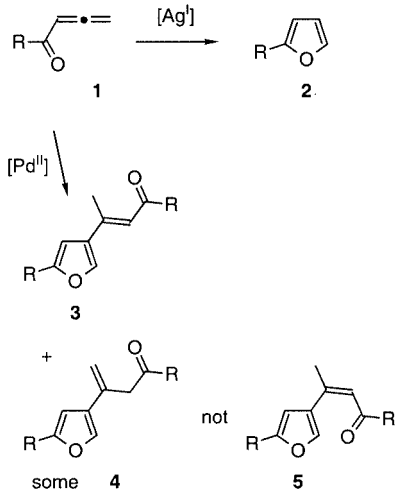
Introduction

The field of furanophanes is dominated by macrocycles that contain several heterocyclic units;[1–7] in most cases, several furans are present in a macrocycle obtained from the condensation of furans with aldehydes or ketones.[8]

Because of the difficulties encountered in their synthesis, single furan moieties in furanophanes are quite rare. Recent examples of such systems having 2,5-bridging are found in model studies toward the total syntheses of chatancin[9–11] and eleutherobin.[12] There are other synthetic targets featuring 2,4-bridging that have aroused interest in furanophanes having only one furan unit; for example, a class of furanocembrenoids found in ant venoms is of biological importance.[13] The silver-catalyzed isomerization of allenyl ketones **1** to furans **2**[14–20] has been utilized successfully by Marshall et al. for the synthesis of macrocyclic furans.[21] In these reactions, the allenyl ketone was already part of a macrocycle; the isomerization had the character of a ring-contraction reaction, adding strain to the macrocycle through the 2,5-bridging of the furan system. Similar structural motifs can be found in natural products, such as lophotoxin,[22] or have been prepared by other methods.[23–27]

We have described the palladium-catalyzed cycloisomerization/dimerization of allenyl ketones **1**, which, apart from C–O bond formation, also involves C–C bond formation.[28–32] Under optimized conditions, **3** was the major product, accompanied by small amounts of **2**. It was only during early experiments under non-optimized conditions that we observed some **4** as a side-product; we never observed compound **5**, the (*Z*) isomer of **3**.

We were interested in investigating whether this C–C bond formation can, in principle, be used for the synthesis of macrocyclic furanophanes from open-chained diallenyl diketones as precursors.



Scheme 1. Different furans obtained from allenyl ketones

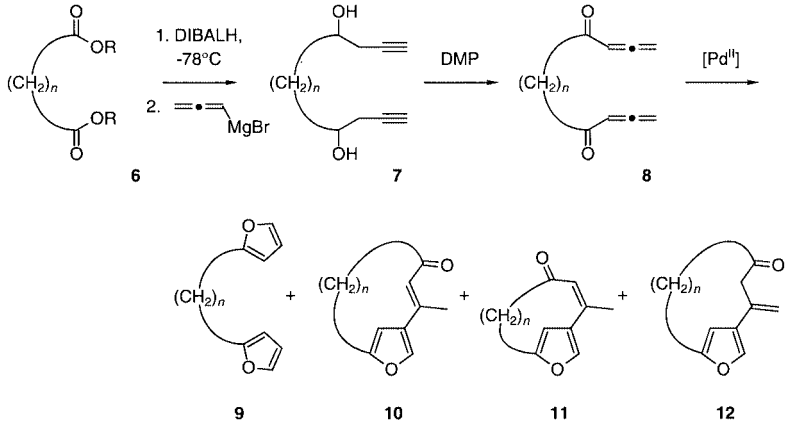
[a] Institut für Organische Chemie, Universität Stuttgart
Pfaffenwaldring 55, 70569 Stuttgart, Germany
Fax:(internat.) +49-(0)711-685-4321
E-mail: hashmi@hashmi.de
[b] Institut für Organische Chemie und Chemische Biologie, Johann Wolfgang Goethe-Universität Frankfurt am Main
Marie-Curie-Straße 11, 60439 Frankfurt, Germany
[‡] Crystallographic investigation.

Results and Discussion

Bidirectional synthesis delivered the 1,*n*-diallenyl diketones **8**. Starting from dialkyl 1,*n*-alkanedicarboxylates **6**, a DIBALH reduction at −78 °C and a subsequent reaction of the 1,*n*-alkanedialdehydes with allenylmagnesium bromide delivered the bis(homopropargylic alcohol)s **7** as mixtures of diastereoisomers, which, because of the 4−14 atoms between the stereogenic centers, do not exhibit significantly different spectroscopic data. The latter compounds were oxidized to **8** using the Dess−Martin periodinane[33−37] reagent (this step includes a subsequent isomerization of the propargyl to the allenyl ketone during the workup[38]).

Then solutions of **8** (0.125 M) in acetonitrile were slowly added to a solution of the $[PdCl_2(MeCN)_2]$ catalyst in about the same volume of acetonitrile. The results are listed in Scheme 1. Four different non-oligomeric/ non-polymeric products were isolated: (a) The 1,*n*-difurylalkanes **9** formed by Marshall reactions[21−27] at both ends of the chain. (b) The furanophanes **10**, each having an (*E*) configuration of the olefin in the bridge. These compounds correspond to the known products from Pd-catalyzed intermolecular coupling of allenyl ketones.[28−32] (c) The furanophanes **11**, each possessing a (*Z*) configuration of the olefin in the bridge; such (*Z*) olefins have never been observed previously in such intermolecular couplings. (d) The furanophanes **12**, each having an exocyclic double bond; this type of product has been observed only in early investigations of the intermolecular coupling of allenyl ketones,[28] but had never formed when the $[PdCl_2(MeCN)_2]$ catalyst was applied.[30]

The results depend strongly on the length of the tether between the carbonyl groups. With a short bridge of only four or five CH_2 units, no macrocycles were formed (Scheme 2, Entries 1 and 2). The yield of **9** corresponds to the yield of the analogous monosubstituted furans obtained in the intermolecular reactions of simple allenyl ketones with the $[PdCl_2(MeCN)_2]$ catalyst.[30] A bridge of six−eight methylene units (Entries 3−5) lead to only a very small amount of **10**; **11** was the major product and the proportion of **12** increased sequentially over these three Entries. The different products could be differentiated conveniently by their ^1H NMR spectra. The allylic methyl group of **10** appears at δ = 2.3−2.4 ppm while the same signal for **11** is found at δ = 2.0−2.1 ppm; **12** is characterized by a singlet at δ = 3.3−3.4 ppm. When *n* = 9 (Entry 6), we obtained more of **10** and less of **11**, while the amount of **12** still increased. With ten and eleven CH_2 units (Entries 7 and 8), this trend remained for **9**: together with **10**, it was the major product, while the amounts of **11** and **12** decreased sharply. When *n* = 12 and 14 (Entries 9 and 10), **10** was the only macrocycle observed. In Entries 3−10, the amount of **9** was



6-12	*n*	Σ macrocycles	9	10	11	12
a	4	-	2%	-	-	-
b	5	-	3%	-	-	-
c	6	23%	14%	1% [a]	18%	4%
d	7	17%	9%	1% [a]	10%	6%
e	8	31%	7%	1% [a]	19%	11%
f	9	33%	11%	5% [a]	15%	13%
g	10	29%	10%	24%	3% [a]	2% [a]
h	11	38%	16%	35%	1%	2% [a]
i	12	28%	6%	28%	-	-
j	14	27%	7%	27%	-	-

a) identified by ^1H NMR only

Scheme 2. Synthesis and palladium-catalyzed cyclization of 1,*n*-diallenyl diketones **8a−j**

higher than it was in the first Entries (7−16%). Apart from the first four Entries, the sum of the yields of macrocycles was between 27 and 38%.

How can these results be explained? For long bridges, the *meta* bridging of the furan ring and the (*E*) configuration of the double bond in this bridges are tolerated without serious difficulties being encountered. Fortunately, we were able to obtain crystals from the 16-membered ring of **10g** ($n = 10$) that were suitable for X-ray crystallographic investigation (Figure 1).[39] The furan ring and the neighboring carbon atoms are coplanar; no unusual bond lengths or angles are observed.

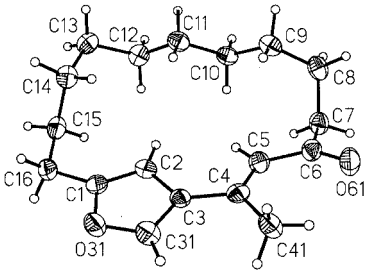


Figure 1. X-ray crystal structure of the furanophane **10g** (ORTEP plot)

With $n = 9$, the strain seemed to increase: the double bond geometry in the bridge switches to the (*Z*) configuration and some of the exocyclic olefin is formed. We obtained an X-ray crystal structure of the twelve-membered macrocycle **12c** ($n = 6$, Figure 2).[39] Here, we see that C12 and C4 are bent out of the plane of the furan ring (the ring itself is planar; the rmsd of the five atoms from the ring plane is 0.0045 Å) by 0.195(4) Å (C4) and 0.234 Å (C12) in the direction of the bridge, which reflects the strain originating from the 2,4-bridging of the furan ring.

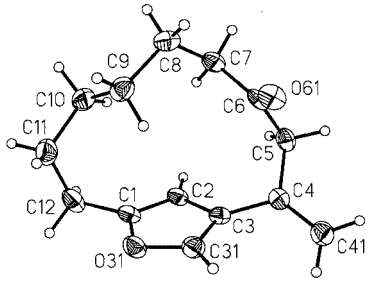
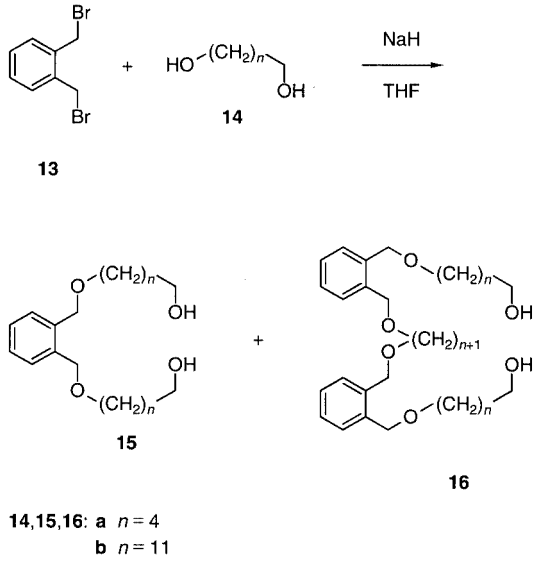


Figure 2. X-ray crystal structure of the furanophane **12c** (ORTEP plot)

Finally, with $n \leq 5$, the macrocyclization was no longer possible.

Compounds **10**, **11** and **12** do not interconvert under the reaction conditions[30] and, thus, the different double bond geometries are the result of kinetic control — for example, different regio- and facial selectivities of the ring closing step — rather than thermodynamic control.

Next, we explored even larger rings. Again, we used a bidirectional synthesis. The precursors **15** and **16** were synthesized from the benzyl bromide **13** and the diols **14** (Scheme 3).



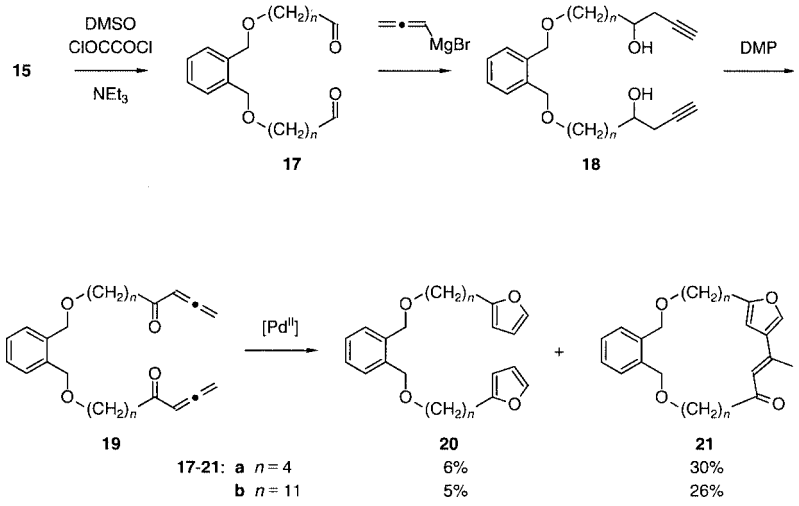
Scheme 3. Synthesis of the 1,*n*-diols **15** and **16**

Swern oxidation of **15** delivered **17** (Scheme 4), and the dialdehydes **22** were obtained from **16** (Scheme 5). Addition of allenylmagnesium bromide provided **18** or **23**, each as a mixture of diastereoisomers that, like **7**, show practically identical spectroscopic data because of the 14−48 spacer atoms between the stereogenic centers. Finally, Dess−Martin oxidation led to the diallenyl diketones **19** and **24**.

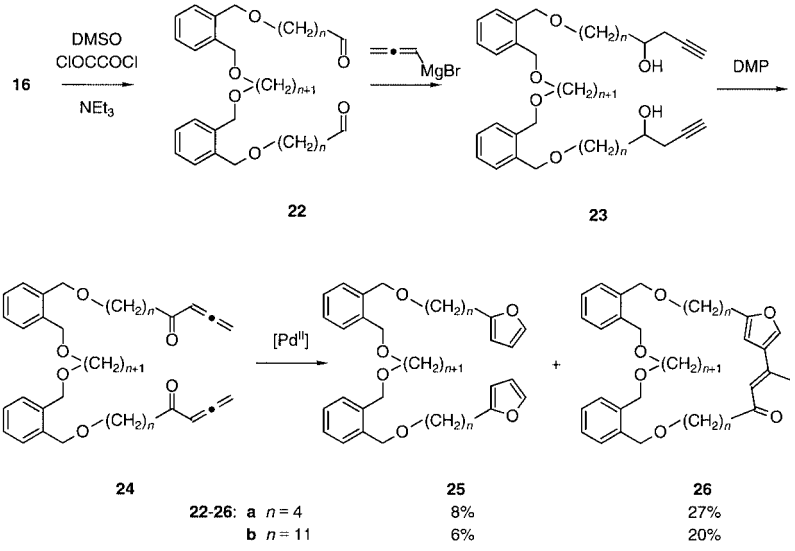
From **19** we obtained the twenty- and thirty-four-membered **21a** and **21b**, respectively, and from **24** we obtained the thirty-one- and fifty-two-membered **26a** and **26b**, respectively. Again the Marshall-type products **20** or **25** were isolated in low yields.

How do these yields compare to those obtained from other macrocyclization methods? One of today's most popular methods for macrocyclization is olefin-metathesis.[40] Thus, we prepared the divinyl compounds **27** and subjected it to Grubbs' $[Cl_2(PCy_3)_2Ru{=}CH{-}C{=}CPh_2]$ catalyst. While the reaction with **27a** delivered only polymeric material, from **27b** we obtained only 31% of **28b** (the length of the bridge corresponded to a bridge of 16 methylene groups) as an (*E*)/(*Z*) mixture. This reaction is not an ideal model for a comparison because of the additional double bond in **28**, but a better one was not readily available (Scheme 6). Still, the reaction proved the difficulties encountered in bridging the furan in the 2,4-position and having an (*E*) double bond in that bridge.

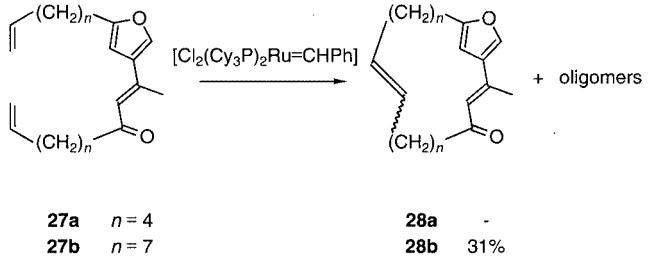
We obtained no evidence of any dynamic behavior from the NMR spectra of any of the macrocycles reported herein.[41,42]



Scheme 4. Synthesis and palladium-catalyzed cyclization of the 1,*n*-diallenyl diketones **19a**,**b**



Scheme 5. Synthesis and palladium-catalyzed cyclization of the 1,*n*-diallenyl diketones **24a**,**b**



Scheme 6. Ru-catalyzed macrocyclization of the furans **27a**,**b**.

Conclusion

The results of the palladium-catalyzed reaction of the diallenyl diketones depend strongly on the length of the bridge. Besides the products of types **10** and **12**, of which both, in principle, are known from intermolecular versions of this reaction, we observed a new type of product in the intramolecular case: the (*Z*) olefin **11**. In the range from sixteen- to fifty-two-membered macrocycles, the (*E*) olefins were the major products.

Experimental Section

1. General Procedure for the Preparation of Homopropargylic Alcohols 7: DIBAH solution (1.2 equiv.) was added with stirring to the ester (1 equiv.) in absolute diethyl ether at −78 °C over 30 min. Stirring at −78 °C was continued for 5 h before a solution of propargylmagnesium bromide (1.1 equiv.) in diethyl ether was added at −78 °C over 15 min; after another 5 min, the solution was warmed to room temperature. A suspension of NaF (7−8 equiv.) in a saturated NH_4Cl solution was then added slowly at −20 °C. Extraction of the aqueous phase three times with diethyl ether, dry-

ing of the combined organic phases over $MgSO_4$, filtration and evaporation of the solvent in vacuo, and purification of the residue by column chromatography on silica gel delivered the homopropargylic alcohols **7**.

7a: Diethyl adipate (2.02 g, 10.0 mmol), DIBAH (1.5 M, 17.3 mL, 26.0 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 13.1 mL, 21.0 mmol), diethyl ether (25 mL). Yield: 558 mg (29%). R_f (H/EA, 1:2) = 0.4. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.31−1.61 (br. s, 8 H), 2.08 (t, J = 2.7 Hz, 2 H), 2.32 (ddd, J = 2.7, 6.5, 16.7 Hz, 2 H), 2.43 (ddd, J = 2.6, 5.1, 16.7 Hz, 2 H), 2.51 (br. s, 2 H), 2.72−3.81 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.32 (t, 2 C), 27.22 (t, 2 C), 35.83 (t, 2 C), 69.58 (d, 2 C), 70.70 (d, 2 C), 80.92 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3401 (−OH), 3280 (≡C−H), 2938, 2910, 2879, 2855, 2115 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 195 (0.3) [MH^+], 155 (52), 137 (86), 119 (48), 93 (100), 79 (59), 67 (72), 55 (51). $C_{12}H_{18}O_2$ (194.27): calcd. C 74.19, H 9.34; found C 73.98, H 9.17.

7b: Diethyl pimelate (2.16 g, 10.0 mmol), DIBAH (1.2 M, 18.3 mL, 22.0 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 13.1 mL, 21.0 mmol), diethyl ether (25 mL). Yield: 1.37 g (66%). R_f (H/EA, 1:2) = 0.4. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.37−1.56 (br., 10 H), 2.07 (t, J = 2.6 Hz, 2 H), 2.09 (br. s, 2 H), 2.32 (ddd, J = 2.7, 6.6, 16.7 Hz, 2 H), 2.44 (ddd, J = 2.6, 4.9, 16.7 Hz, 2 H), 3.71−3.80 (br., 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.31 (t, 2 C), 27.18 (t, 2 C), 29.19 (t), 35.87 (t, 2 C), 69.62 (d, 2 C), 70.65 (d, 2 C), 80.87 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3374 (−OH), 3296 (≡C−H), 2934, 2858, 2118 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 209 (0.5) [MH^+], 169 (0.5) [$M - C_3H_3]^+$, 133 (36), 109 (21), 107 (97), 91 (95), 79 (84), 67 (88), 55 (100). $C_{13}H_{20}O_2$ (208.30): calcd. C 74.96, H 9.68; found C 75.10, H 9.84.

7c: Dimethyl suberate (2.02 g, 10.0 mmol), DIBAH (1.5 M, 14.7 mL, 22.0 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 13.1 mL, 21.0 mmol), diethyl ether (25 mL). Yield: 715 mg (32%). M.p. 67 °C. R_f (H/EA, 1:2) = 0.5. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.29−1.53 (m, 12 H), 2.05−2.08 (m, 2 H), 2.33 (br. s, 2 H), 2.33−2.37 (m, 2 H), 2.43 (ddd, J = 2.7, 4.9, 16.7 Hz, 2 H), 3.70−3.82 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.31 (t, 2 C), 27.17 (t, 2 C), 29.22 (t, 2 C), 35.95 (t, 2 C), 69.65 (d, 2 C), 70.62 (d, 2 C), 80.87 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3404 (−OH), 3282 (≡C−H), 2928, 2854, 2114 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 223 (0.5) [MH^+], 183 (0.5), 119 (25), 105 (60), 91 (45), 81 (100), 67 (63), 55 (82). $C_{14}H_{22}O_2$ (222.33): calcd. C 75.63, H 9.97; found C 75.49, H 9.95.

7d: Dimethyl azelate (2.16 g, 10.0 mmol), DIBAH (1.5 M, 14.7 mL, 22.0 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 13.1 mL, 21.0 mmol), diethyl ether (25 mL). Yield: 1.32 g (56%). M.p. 32−38 °C. R_f (H/EA, 1:2) = 0.5. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26−1.55 (m, 14 H), 2.07 (t, J = 2.6 Hz, 2 H), 2.21 (br. s, 2 H), 2.31 (ddd, J = 2.7, 6.5, 16.5 Hz, 2 H), 2.43 (ddd, J = 2.7, 4.8, 16.7 Hz, 2 H), 3.70−3.80 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.37 (t, 2 C), 27.18 (t, 2 C), 29.24 (t, 3 C), 36.00 (t, 2 C), 69.68 (d, 2 C), 70.71 (d, 2 C), 80.86 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3378 (−OH), 3300 (≡C−H), 2931, 2855, 2118 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 237 (0.2) [MH^+], 197 (0.6) [$M - C_3H_3]^+$, 119 (2), 105 (23), 95 (74), 81 (100), 67 (57), 55 (53). $C_{15}H_{24}O_2$ (236.35): calcd. C 76.23, H 10.24; found C 75.97, H 10.15.

7e: Diethyl sebacate (2.30 g, 10.0 mmol), DIBAH (1.5 M, 17.3 mL, 26.0 mmol), propargylmagnesium bromide solution (1.6 M, 13.1 mL, 21.0 mmol), diethyl ether (25 mL). Yield: 2.07 g (83%). M.p. 64−65 °C. R_f (H/EA, 2.5:1) = 0.2. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.20−1.59 (m, 16 H), 2.06 (t, J = 2.7 Hz, 2 H), 2.13 (br. s, 2 H), 2.31 (ddd, J = 2.7, 6.6, 16.7 Hz, 2 H), 2.44 (ddd, J = 2.6, 4.8, 16.7 Hz, 2 H), 3.70−3.80 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.38 (t, 2 C), 27.18 (t, 2 C), 29.27 (t, 2 C), 29.30 (t, 2 C), 36.03 (t, 2 C), 69.70 (d, 2 C), 70.59 (d, 2 C), 80.84 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3404 (−OH), 3283 (≡C−H), 2913, 2848, 2114 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 211 (16) [$M - C_3H_3]^+$, 171 (37), 133 (18), 119 (17), 109 (39), 95 (100), 81 (94), 67 (66), 55 (60). $C_{16}H_{26}O_2$ (250.38): calcd. C 76.75, H 10.47; found C 76.88, H 10.52.

7f: Dimethyl 1,9-nonanedicarboxylate (4.64 g, 19.0 mmol), DIBAH (1 M, 41.9 mL, 41.9 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 26.1 mL, 41.8 mmol), diethyl ether (200 mL). Yield: 2.31 g (46%). M.p. 55 °C. R_f (H/EA, 1:2) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.25−1.52 (m, 18 H), 1.95 (s, 2 H), 2.02 (t, J = 2.6 Hz, 2 H), 2.28 (ddd, J = 2.7, 6.6, 16.7 Hz, 2 H), 2.40 (ddd, J = 2.6, 4.8, 16.7 Hz, 2 H), 3.67−3.77 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.12 (t, 2 C), 22.88 (t, 2 C), 25.06 (t, 5 C), 31.73 (t, 2 C), 65.41 (d, 2 C), 66.28 (d, 2 C), 76.69 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3406 (−OH), 3281 (≡C−H), 2916, 2850, 2114 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 265 (0.5) [MH^+], 225 (1), 121 (19), 109 (25), 107 (29), 95 (81), 81 (100), 67 (67), 55 (65). $C_{17}H_{28}O_2$ (264.41): calcd. C 77.22, H 10.67; found C 77.24, H 10.62.

7g: Diethyl 1,10-decanedicarboxylate (5.73 g, 20.0 mmol), DIBAH (1.5 M, 30.0 mL, 45.0 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 26.3 mL, 42.0 mmol), diethyl ether (40 mL). Yield: 1.89 g (34%). M.p. 76−77 °C. R_f (H/EA, 1:1) = 0.5. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (br. s, 16 H), 1.34−1.53 (m, 4 H), 2.04 (t, J = 2.6 Hz, 2 H), 2.09 (d, J = 4.7 Hz, 2 H), 2.30 (ddd, J = 2.7, 6.6, 16.7 Hz, 2 H), 2.41 (ddd, J = 2.6, 4.8, 16.7 Hz, 2 H), 3.68−3.79 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.42 (t, 2 C), 27.19 (t, 2 C), 29.35 (t, 6C), 36.05 (t, 2 C), 69.72 (d, 2 C), 70.61 (d, 2 C), 80.86 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3395 (−OH), 3282 (≡C−H), 2915, 2848, 2115 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 279 (0.3) [MH^+], 243 (3), 239 (1), 121 (38), 109 (35), 95 (100), 81 (98), 67 (52), 55 (63). $C_{18}H_{30}O_2$ (278.44): calcd. C 77.65, H 10.86; found C 77.38, H 10.84.

7h: Dimethyl 1,11-undecanedicarboxylate (4.90 g, 18.0 mmol), DIBAH (1 M, 39.6 mL, 39.6 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 24.8 mL, 39.6 mmol), diethyl ether (200 mL). Yield: 2.26 g (43%). R_f (H/EA, 1:2) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26−1.65 (br. s, 22 H), 1.94 (m, 2 H), 2.05 (t, J = 2.6 Hz, 2 H), 2.30 (ddd, J = 2.6, 6.7, 16.6 Hz, 2 H), 2.43 (ddd, J = 2.6, 4.7, 16.6 Hz, 2 H), 3.66−3.75 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.40 (t, 2 C), 27.14 (t, 2 C), 29.35 (t, 7 C), 36.02 (t, 2 C), 69.68 (d, 2 C), 70.54 (d, 2 C), 80.92 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3396 (−OH), 3284 (≡C−H), 2916, 2850, 2114 (C≡C) cm^{-1}. MS (70 eV): *m*/*z* (%) = 293 (0.2) [MH^+], 253 (1), 135 (16), 121 (16), 109 (29), 95 (88), 81 (100), 67 (64), 55 (61). $C_{19}H_{32}O_2$ (292.46): calcd. C 78.03, H 11.03; found C 77.72, H 10.73.

7i: Diethyl 1,12-dodecanedicarboxylate (5.66 g, 18.0 mmol), DIBAH (1.5 M, 27.0 mL, 40.5 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 26.8 mL, 43.0 mmol), diethyl ether (120 mL). Yield: 506 mg (9%). M.p. 99−101 °C. R_f (H/EA, 1:1) = 0.5. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (br. s, 20 H), 1.36−1.55 (br. m, 4 H), 1.93 (d, J = 5.1 Hz, 2 H), 2.05 (t, J = 2.7 Hz, 2 H), 2.30 (ddd, J = 2.6, 6.7, 16.7 Hz, 2 H), 2.43 (ddd, J = 2.7, 4.7, 16.7 Hz, 2 H), 3.69−3.81 (br. m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.44 (t, 2 C), 27.20 (t, 2 C), 29.39 (t, 6 C), 29.44 (t, 2 C), 36.09 (t, 2 C), 69.75 (d, 2 C), 70.61 (d, 2 C), 80.81 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3396 (−OH), 3284 (≡C−H), 2916, 2849, 2114

(C≡C) cm^{-1}. MS (70 eV): *m/z* (%) = 307 (0.8) [MH^+], 267 (1), 249 (10), 135 (17), 121 (17), 109 (41), 95 (91), 81 (100), 67 (69), 55 (64). $C_{20}H_{34}O_2$ (306.49): calcd. C 78.38, H 11.18; found C 78.34, H 11.38.

7j: Diethyl 1,14-tetradecanedicarboxylate (3.43 g, 10.0 mmol), DIBAH (1.5 M, 14.7 mL, 22.0 mmol), propargylmagnesium bromide in diethyl ether (1.6 M, 13.1 mL, 21.0 mmol), diethyl ether (140 mL). Yield: 2.59 g (77%). M.p. 95−96 °C. R_f (H/EA, 1:1) = 0.5. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.26−1.59 (m, 28 H), 1.90 (d, *J* = 5.0 Hz, 2 H), 2.06 (t, *J* = 2.6 Hz, 2 H), 2.31 (ddd, *J* = 2.6, 6.7, 16.7 Hz, 2 H), 2.44 (ddd, *J* = 2.6, 4.7, 16.7 Hz, 2 H), 3.76 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.57 (t, 2 C), 27.35 (t, 2 C), 29.51 (t, 2 C), 29.53 (t, 4 C), 29.60 (t, 4 C), 36.24 (t, 2 C), 69.89 (d, 2 C), 70.73 (d, 2 C), 80.94 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3396 (−OH), 3285 (≡C−H), 2916, 2848, 2114 (C≡C) cm^{-1}. MS (70 eV): *m/z* (%) = 333 (1) [M − H]$^+$, 295 (34), 277 (58), 121 (15) 109 (49), 95 (98), 81 (100), 69 (36), 67 (32) 55 (30). $C_{22}H_{38}O_2$ (334.54): calcd. C 78.99, H 11.45; found C 78.98, H 11.45.

2. General Procedure for the Dess−Martin Oxidation of 7 to 8: The oxidation[33−37] itself oxidizes the homopropargylic alcohols to propargyl ketones; the latter compounds then isomerize spontaneously to the allenyl ketones during the chromatographic workup.[38]

Dess−Martin periodinane (DMP; 1.2 equiv.) was added in small portions to a stirred solution of **7** (1 equiv.) in DCM (ca. 1−3 mL) at room temperature. A water bath was used for thermoregulation. Stirring was continued until the reaction was complete, as monitored by TLC (in most cases, about 20 min). The resulting mixture was placed directly on a silica gel column for workup. After the DCM phase entered the column, some hexane was placed on the column; when the hexane had entered the column, the requisite solvent mixture for separation was then applied.

8a: 7a (412 mg, 2.12 mmol), DMP (1.70 g, 4.00 mmol), DCM (4 mL). Yield: 327 mg (81%). R_f (H/EA, 1:1) = 0.7. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.53−1.68 (m, 4 H), 2.57−2.69 (m, 4 H), 5.24 (d, *J* = 6.5 Hz, 4 H), 5.77 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 23.82 (t, 2 C), 38.76 (t, 2 C), 79.41 (t, 2 C), 96.56 (d, 2 C), 200.32 (s, 2 C), 216.55 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2987, 2939, 2868, 1958, 1933 (C=C=C), 1681 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 190 (2) [M^+], 151 (54) [M − C_3H_3]$^+$, 133 (27), 123 (64), 105 (81), 67 (100). $C_{12}H_{14}O_2$ (190.24): calcd. 190.09938, found 190.09945 (MS).

8b: 7b (400 mg, 1.92 mmol), DMP (2.08 g, 4.96 mmol), DCM (6 mL). Yield: 372 mg (95%). R_f (H/EA, 1:1) = 0.6. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.26−1.38 (br., 2 H), 1.55−1.67 (br., 4 H), 2.61 (t, *J* = 7.4 Hz, 4 H), 5.25 (d, *J* = 6.5 Hz, 4 H), 5.76 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 23.95 (t, 2 C), 28.42 (t), 38.66 (t, 2 C), 79.26 (t, 2 C), 96.46 (d, 2 C), 200.47 (s, 2 C), 216.42 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2987, 2936, 2862, 1958 (C=C=C), 1934 (C=C=C), 1681 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 205 (1) [MH^+], 165 (18), 137 (9), 119 (37), 95 (14), 91 (21), 81 (10), 67 (100), 55 (44). $C_{13}H_{16}O_2$ (204.26): calcd. C 76.44, H 7.90; found C 76.15, H 8.09.

8c: 7c (300 mg, 1.35 mmol), DMP (1.38 g, 3.25 mmol), DCM (4 mL). Yield: 148 mg (50%). M.p. 39−40 °C. R_f (H/EA, 1:1) = 0.6. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28−1.34 (m, 4 H), 1.54−1.62 (m, 4 H), 2.60 (t, *J* = 7.4 Hz, 4 H), 5.25 (d, *J* = 6.5 Hz, 4 H), 5.76 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.09 (t, 2 C), 28.66 (t, 2 C), 38.80 (t, 2 C), 79.20 (t, 2 C), 96.40 (d, 2 C), 200.52 (s, 2 C), 216.37 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2988, 2933, 2858, 1958 (C=C=C), 1934 (C=C=C), 1680 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 218 (3) [M^+], 179 (94), 151 (13), 133 (34), 109 (25), 95 (29), 81 (25), 67 (100), 55 (44). $C_{14}H_{18}O_2$ (218.30): calcd. C 77.03, H 8.31; found C 76.98, H 8.29.

8d: 7d (380 mg, 1.61 mmol), DMP (1.65 g, 3.89 mmol), DCM (6 mL). Yield: 308 mg (82%). R_f (H/EA, 1:1) = 0.6. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.30 (br. s, 6 H), 1.58 (m, 4 H), 2.59 (t, *J* = 7.4 Hz, 4 H), 5.24 (d, *J* = 6.5 Hz, 4 H), 5.76 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.25 (t, 2 C), 28.76 (t, 2 C), 28.91 (t), 38.93 (t, 2 C), 79.15 (t, 2 C), 96.46 (d, 2 C), 200.64 (s, 2 C), 216.40 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2987, 2930, 2856, 1958 (C=C=C), 1934 (C=C=C), 1681 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 233 (8) [MH^+], 193 (29), 165 (3), 147 (8), 109 (5), 95 (23), 81 (28), 67 (100), 55 (88). $C_{15}H_{20}O_2$ (232.32): calcd. C 77.55, H 8.68; found C 77.72, H 8.42.

8e: 7e (500 mg, 2.00 mmol), DMP (1.49 g, 3.51 mmol), DCM (6 mL). Yield: 407 mg (83%). R_f (H/EA, 1:1) = 0.6. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (br. s, 8 H), 1.55−1.61 (br. m, 4 H), 2.59 (t, *J* = 7.4 Hz, 4 H), 5.24 (d, *J* = 6.5 Hz, 4 H), 5.76 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.38 (t, 2 C), 28.97 (t, 2 C), 29.05 (t, 2 C), 39.04 (t, 2 C), 79.24 (t, 2 C), 96.55 (d, 2 C), 200.86 (s, 2 C), 216.49 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2988, 2936, 2851, 1961m (C=C=C), 1934 (C=C=C), 1678 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 247 (8) [MH^+], 207 (88), 179 (1), 161 (5), 147 (4), 135 (6), 109 (26), 95 (38), 81 (29), 67 (100), 55 (86). $C_{16}H_{22}O_2$ (246.35): calcd. C 78.01, H 9.00; found C 77.76, H 9.05.

8f: 7f (500 mg, 1.89 mmol), DMP (2.00 g, 4.72 mmol), DCM (8 mL). Yield: 404 mg (82%). R_f (H/EA, 1:1) = 0.6. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.25 (br. s, 10 H), 1.53−1.59 (m, 4 H), 2.57 (t, *J* = 7.4 Hz, 4 H), 5.21 (d, *J* = 6.5 Hz, 4 H), 5.74 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.28 (t, 2 C), 28.89 (t, 2 C), 29.00 (t), 29.05 (t, 2 C), 38.93 (t, 2 C), 79.10 (t, 2 C), 96.39 (d, 2 C), 200.55 (s, 2 C), 216.34 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2988, 2928, 2854, 1959 (C=C=C), 1934 (C=C=C), 1682 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 261 (6) [MH^+], 221 (27), 109 (11), 95 (15), 81 (13), 67 (100), 55 (61). $C_{17}H_{24}O_2$ (260.38): calcd. C 78.42, H 9.29; found C 78.31, H 9.32.

8g: 7g (400 mg, 1.44 mmol), DMP (453 mg, 3.61 mmol), DCM (4 mL). Yield: 244 mg (62%). M.p. 25−36 °C. R_f (H/EA, 2:1) = 0.5. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.25 (br. s, 12 H), 1.54−1.59 (br. m, 4 H), 2.57 (t, *J* = 7.4 Hz, 4 H), 5.21 (d, *J* = 6.5 Hz, 4 H), 5.75 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.34 (t, 2 C), 28.96 (t, 2 C), 29.17 (t, 4 C), 39.00 (t, 2 C), 79.14 (t, 2 C), 96.47 (d, 2 C), 200.74 (s, 2 C), 216.41 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2988, 2927, 2854, 1959 (C=C=C), 1934 (C=C=C), 1682 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 274 (3) [M^+], 235 (100), 207 (3), 110 (59), 95 (30), 81 (27), 67 (50), 55 (32). $C_{18}H_{26}O_2$ (274.40): calcd. C 78.79, H 9.55; found C 78.64, H 9.51.

8h: 7h (500 mg, 1.71 mmol), DMP (1.82 g, 4.29 mmol), DCM (6 mL). Yield: 400 mg (81%). M.p. 66 °C. R_f (H/EA, 1:1) = 0.6. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (s, 14 H), 1.54−1.59 (br. m, 4 H), 2.57 (t, *J* = 7.4 Hz, 4 H), 5.21 (d, *J* = 6.5 Hz, 4 H), 5.74 (t, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.31 (t, 2 C), 28.93 (t, 2 C), 29.13 (t, 2 C), 29.18 (t, 2 C), 29.27 (t), 38.94 (t, 2 C), 79.08 (t, 2 C), 96.39 (d, 2 C), 200.54 (s, 2 C), 216.33 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065, 2988, 2926, 2853, 1959 (C=C=C), 1934 (C=C=C), 1682 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 289 (1) [M^+], 249 (3), 221 (10), 139 (9), 121 (10), 95 (5), 67 (100), 55 (41). $C_{19}H_{28}O_2$ (288.43): calcd. C 79.12, H 9.79; found C 78.90, H 9.77.

8i: 7i (260 mg, 848 μmol), DMP (891 mg, 2.10 mmol), DCM (15 mL). Yield: 162 mg (63%). M.p. 42−43 °C. R_f (H/EA, 1:1) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.23 (br. s, 16 H), 1.53 −1.58 (m, 4 H), 2.56 (t, J = 7.5 Hz, 4 H), 5.20 (d, J = 6.5 Hz, 4 H), 5.73 (t, J = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.41 (t, 2 C), 29.02 (t, 2 C), 29.21 (t, 2 C), 29.27 (t, 2 C), 29.39 (t, 2 C), 39.07 (t, 2 C), 79.12 (t, 2 C), 96.51 (d, 2 C), 200.83 (s, 2 C), 216.45 (s, 2 C) ppm. IR (neat): ṽ = 3064, 2985, 2932, 2850, 1960 (C=C=C), 1926 (C=C=C), 1672 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 303 (13) [MH^+], 263 (47), 235 (4), 123 (28), 121 (28), 110 (76), 95 (75), 81 (74), 67 (94), 55 (100). $C_{20}H_{30}O_2$ (302.46): calcd. C 79.42, H 10.00; found C 79.36, H 9.99.

8j: 7j (1.37 g, 4.10 mmol), DMP (4.16 mg, 9.81 mmol), DCM (40 mL). Yield: 543 mg (40%). M.p. 46−48 °C. R_f (H/EA, 1:1) = 0.7. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.25 (br. s, 20 H), 1.52−1.65 (br. m, 4 H), 2.59 (t, J = 7.5 Hz, 4 H), 5.23 (d, J = 6.5 Hz, 4 H), 5.77 (t, J = 6.5 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.44 (t, 2 C), 29.05 (t, 2 C), 29.24 (t, 2 C), 29.32 (t, 2 C), 29.44 (t, 2 C), 29.47 (t, 2 C), 39.11 (t, 2 C), 79.12 (t, 2 C), 96.54 (d, 2 C), 200.89 (s, 2 C), 216.48 (s, 2 C) ppm. IR (neat): ṽ = 3063, 2986, 2918, 2850, 1959 (C=C=C), 1928 (C=C=C), 1673 (C=O) cm^{-1}. MS (70 eV): *m/z* (%) = 330 (6) [M^+], 291 (100), 263 (10), 121 (19), 110 (51), 95 (28), 81 (26), 67 (28), 55 (27). $C_{22}H_{34}O_2$ (330.51): calcd. C 79.95, H 10.37; found C 79.69, H 10.08.

3. General Procedure for the Formation of the Bisfurans 9

The starting material (ca. 50 mg) in dry acetone (ca. 3 mL) was subjected to $AgNO_3$ (10−30 mol %).[14,19] The reaction mixture was then either stirred at room temperature overnight or heated under reflux for 1 h. The solvent was evaporated in vacuo and the crude product purified by column chromatography on silica gel.

9a: This compound is known; it was identified by its NMR spectra.[43,44]

9b: 8b (40.0 mg, 196 μmol), $AgNO_3$ (10.0 mg, 58.8 μmol), acetone (3 mL). Yield: 23.6 mg (59%). R_f (H/EA, 5:1) = 0.60. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.36−1.45 (br., 2 H), 1.61−1.72 (m, 4 H), 2.62 (t, J = 7.5 Hz, 4 H), 5.96 (dd, J = 0.8, 3.1 Hz, 2 H), 6.26 (dd, J = 1.9, 3.1 Hz, 2 H), 7.28 (dd, J = 0.8, 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.63 (t, 2 C), 27.72 (t, 2 C), 28.52 (t), 104.49 (d, 2 C), 109.90 (d, 2 C), 140.55 (d, 2 C), 156.21 (s, 2 C) ppm. IR (neat): ṽ = 3114, 2926, 2854, 1597, 1507, 1459, 1147, 1007, 794, 726 cm^{-1}. MS (70 eV): *m/z* (%) = 203 (4) [$M - H]^+$, 151 (11), 137 (7), 123 (12), 95 (74), 81 (100). $C_{13}H_{16}O_2$ (204.26).

9c: 8c (60.0 mg, 275 μmol), $AgNO_3$ (11.0 mg, 64.7 μmol), acetone (3 mL). Yield: 35.0 mg (58%). R_f (H/EA, 5:1) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.37−1.45 (m, 4 H), 1.61−1.70 (m, 4 H), 2.64 (t, J = 7.5 Hz, 4 H), 5.99 (dd, J = 0.8, 3.2 Hz, 2 H), 6.30 (dd, J = 1.9, 3.1 Hz, 2 H), 7.32 (dd, J = 0.8, 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.79 (t, 4 C), 28.74 (t, 2 C), 104.46 (d, 2 C), 109.89 (d, 2 C), 140.52 (d, 2 C), 156.32 (s, 2 C) ppm. IR (neat): ṽ = 3115, 2933, 2859, 1598, 1507, 1463, 1147, 1008, 796, 727 cm^{-1}. MS (70 eV): *m/z* (%) = 218 (14) [M^+], 95 (57), 81 (100), 53 (26). $C_{14}H_{18}O_2$ (218.30): calcd. C 77.03, H 8.31; found C 77.19, H 8.46.

9d: 8d (50.0 mg, 215 μmol), $AgNO_3$ (11.0 mg, 64.7 μmol), acetone (3 mL). Yield: 42.6 mg (85%). R_f (H/EA, 5:1) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.33 (br. s, 6 H), 1.57−1.68 (br. m, 4 H), 2.60 (t, J = 7.5 Hz, 4 H), 5.96 (dd, J = 0.8, 3.1 Hz, 2 H), 6.26 (dd, J = 1.9, 3.1 Hz, 2 H), 7.28 (dd, J = 0.8, 1.9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.82 (t, 2 C), 27.88 (t, 2 C), 28.90 (t), 28.94 (t, 2 C), 104.42 (d, 2 C), 109.89 (d, 2 C), 140.49 (d, 2 C), 156.39 (s, 2 C) ppm. IR (neat): ṽ = 3115, 2930, 2856, 1597, 1508, 1464, 1147, 1008, 796, 726 cm^{-1}. MS (70 eV): *m/z* (%) = 232 (10) [M^+], 95 (68), 81 (100), 53 (25). $C_{15}H_{20}O_2$ (232.32): calcd. 232.14633, found 232.14639 (MS).

9e: 8e (50.0 mg, 203 μmol), $AgNO_3$ (15.0 mg, 88.3 μmol), acetone (3 mL). Yield: 39.8 mg (80%). R_f (H/EA, 5:1) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.32 (br. s, 8 H), 1.61 (br. m, 4 H), 2.60 (t, J = 7.5 Hz, 4 H), 5.96 (dd, J = 0.8, 3.1 Hz, 2 H), 6.27 (dd, J = 1.9, 3.1 Hz, 2 H), 7.28 (dd, J = 0.8, 1.9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.84 (t, 2 C), 27.89 (t, 2 C), 29.01 (t, 2 C), 29.12 (t, 2 C), 104.40 (d, 2 C), 109.89 (d, 2 C), 140.49 (d, 2 C), 156.44 (s, 2 C) ppm. IR (neat): ṽ = 3115, 2929, 2856, 1597, 1507, 1465, 1147, 1006, 796, 727 cm^{-1}. MS (70 eV): *m/z* (%) = 246 (23) [M^+], 95 (42), 81 (100), 53 (12). $C_{16}H_{22}O_2$ (246.35): calcd. C 78.01, H 9.00; found C 78.15, H 8.98. calcd. 246.16198, found 246.16171 (MS).

9f: 8f (53.0 mg, 204 μmol), $AgNO_3$ (10.0 mg, 58.8 μmol), acetone (1 mL). Yield: 34.6 mg (65%). R_f (H/EA, 5:1) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): d = 1.30 (br. s, 10 H), 1.57−1.66 (m, 4 H), 2.61 (t, J = 7.6 Hz, 4 H), 5.96−5.97 (m, 2 H), 6.26−6.28 (m, 2 H), 7.29−7.30 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.85 (t, 2 C), 27.91 (t, 2 C), 29.03 (t, 2 C), 29.19 (t), 29.29 (t, 2 C), 104.38 (d, 2 C), 109.88 (d, 2 C), 140.48 (d, 2 C), 156.47 (s, 2 C) ppm. IR (neat): ṽ = 3115, 2928, 2855, 1596, 1508, 1464, 1147, 1007, 795, 725 cm^{-1}. MS (70 eV): *m/z* (%) = 260 (49) [M^+], 151 (6), 123 (19), 95 (80), 81 (100). $C_{17}H_{24}O_2$ (260.38): calcd. 260.17763, found 260.17715 (MS).

9g: 8g (104 mg, 379 μmol), $AgNO_3$ (20.0 mg, 118 μmol), acetone (5 mL). Yield: 53.0 mg (51%). M.p. 37−38 °C. R_f (H/EA, 5:1) = 0.6. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.30 (br. s, 12 H), 1.58−1.67 (br. m, 4 H), 2.62 (t, J = 7.5 Hz, 4 H), 5.98 (dd, J = 0.9, 3.1 Hz, 2 H), 6.28 (dd, J = 1.9, 3.1 Hz, 2 H), 7.30 (dd, J = 0.8, 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.86 (t, 2 C), 27.91 (t, 2 C), 29.05 (t, 2 C), 29.22 (t, 2 C), 29.38 (t, 2 C), 104.38 (d, 2 C), 109.89 (d, 2 C), 140.48 (d, 2 C), 156.49 (s, 2 C) ppm. IR (neat): ṽ = 3114, 2927, 2854, 1596, 1508, 1465, 1146, 1006, 795, 726 cm^{-1}. MS (70 eV): *m/z* (%) = 274 (14) [M^+], 95 (59), 81 (100), 53 (16). $C_{18}H_{26}O_2$ (274.40): calcd. C 78.79, H 9.55; found C 78.59, H 9.63.

9h: 8h (100 mg, 347 mmol), $AgNO_3$ (20.0 mg, 118 μmol), acetone (3 mL). Yield: 21.0 mg (21%). M.p. 37−38 °C. R_f (H/EA, 5:1) = 0.7. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.28−1.31 (m, 14 H), 1.61−1.67 (m, 4 H), 2.62 (t, J = 7.5 Hz, 4 H), 5.98 (dd, J = 0.8, 3.1 Hz, 2 H), 6.28 (dd, J = 1.9, 3.1 Hz, 2 H), 7.30 (dd, J = 0.8, 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.84 (t, 2 C), 27.90 (t, 2 C), 29.05 (t, 2 C), 29.21 (t, 2 C), 29.38 (t, 2 C), 29.44 (t), 104.35 (d, 2 C), 109.87 (d, 2 C), 140.46 (d, 2 C), 156.49 (s, 2 C) ppm. IR (neat): ṽ = 3114, 2926, 2854, 1596, 1507, 1464, 1146, 1007, 794, 725 cm^{-1}. MS (70 eV): *m/z* (%) = 288 (57) [M^+], 151 (5), 123 (13), 95 (62), 81 (100). $C_{19}H_{28}O_2$ (288.43): calcd. 288.20893, found 288.20848 (MS).

9i: 8i (34 mg, 112 μmol), $AgNO_3$ (12.0 mg, 70.6 μmol), acetone (3 mL). Yield: 25.0 mg (74%). M.p. 37−38 °C. R_f (H/EA, 5:1) = 0.7. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26−1.29 (br., 16 H), 1.57−1.68 (br., 4 H), 2.61 (t, J = 7.5 Hz, 4 H), 5.96 (dd, J = 0.8, 3.1 Hz, 2 H), 6.27 (dd, J = 1.9, 3.1 Hz, 2 H), 7.29 (dd, J = 0.8, 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.85 (t, 2 C), 27.91 (t, 2 C), 29.06 (t, 2 C), 29.24 (t, 2 C), 29.41 (t, 2 C), 29.47 (t, 2 C), 104.36 (d, 2 C), 109.87 (d, 2 C), 140.46 (d, 2 C), 156.49 (s, 2 C) ppm. IR (neat): ṽ = 3129, 2916, 2847, 1599, 1507, 1468, 1135, 1004, 808, 724 cm^{-1}. MS (70 eV): *m/z* (%) = 303 (0.3) [M^+], 81

(100), 53 (20). $C_{20}H_{30}O_2$ (302.46): calcd. C 79.42, H 10.00; found C 79.22, H 9.86.

9j: 8j (40.0 mg, 121 μmol), $AgNO_3$ (11.0 mg, 64.7 μmol), acetone (3 mL). Yield: 29.0 mg (73%). M.p. 45−46 °C. R_f (H/EA, 5:1) = 0.7. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (m, 20 H), 1.54−1.65 (m, 4 H), 2.61 (t, *J* = 7.5 Hz, 4 H), 5.96 (dd, *J* = 0.8, 3.1 Hz, 2 H), 6.27 (dd, *J* = 1.9, 3.1 Hz, 2 H), 7.29 (dd, *J* = 0.8, 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 27.84 (t, 2 C), 27.90 (t, 2 C), 29.05 (t, 2 C), 29.23 (t, 2 C), 29.41 (t, 2 C), 29.50 (t, 4 C), 104.35 (d, 2 C), 109.86 (d, 2 C), 140.46 (d, 2 C), 156.50 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3129, 2917, 2848, 1599, 1505, 1470, 1139, 1010, 813, 723 cm^{-1}. MS (70 eV): *m/z* (%) = 330 (2) [M^+], 95 (19), 81 (100), 53 (11). $C_{22}H_{34}O_2$ (330.51): calcd. C 79.95, H 10.37; found C 79.68, H 10.37.

4. General Procedure for the Palladium-Catalyzed Reactions

A solution of **8** in acetonitrile (2 mL) was added by syringe pump to a stirred solution of $[Pd(MeCN)_2Cl_2]$[45] in acetonitrile (3 mL) at 40 °C over 60−62 h, and then stirring was continued for another 8−10 h at 40 °C. The quantities of the reactants are listed in Table 1.

Table 1. Amount of substrate **8** and catalyst

n	Starting material	Quantity	Quantity of catalyst
4	**8a**	60 mg (315 μmol)	3.5 mg (13 μmol, 4 mol%)
5	**8b**	68 mg (333 μmol)	4.4 mg (17 μmol, 5 mol%)
6	**8c**	65 mg (298 μmol)	4.0 mg (15 μmol, 5 mol%)
7	**8d**	60 mg (258 μmol)	3.6 mg (14 μmol, 5 mol%)
8	**8e**	60 mg (244 μmol)	3.6 mg (14 μmol, 6 mol%)
9	**8f**	63 mg (242 μmol)	3.4 mg (13 μmol, 5 mol%)
10	**8g**	55 mg (200 μmol)	2.8 mg (11 μmol, 6 mol%)
11	**8h**	73 mg (253 μmol)	3.4 mg (13 μmol, 5 mol%)
12	**8i**	74 mg (245 μmol)	2.4 mg (9.0 μmol, 4 mol%)
13	**8j**	60 mg (182 μmol)	2.7 mg (10 μmol, 5 mol%)

The solvent was then removed in vacuo and the crude product was purified by direct column chromatography on silica gel.

10g: R_f (H/EA, 5:1) = 0.38. M.p. 77−78 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.20−1.42 (m, 12 H), 1.62−1.76 (m, 4 H), 2.41 (d, *J* = 1.1 Hz, 3 H), 2.43−2.48 (m, 2 H), 2.65 (t, *J* = 5.8 Hz, 2 H), 6.26 (d, *J* = 1.0 Hz, 1 H), 6.55 (s, 1 H), 7.55 (s, 1 H) ppm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.26−1.43 (m, 12 H), 1.65−1.75 (m, 4 H), 2.41 (d, *J* = 1.1 Hz, 3 H), 2.44−2.47 (m, 2 H), 2.64−2.67 (m, 2 H), 6.26 (d, *J* = 0.9 Hz, 1 H), 6.55 (s, 1 H), 7.55 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 15.96 (q), 24.22 (t), 24.59 (t), 25.42 (t), 26.22 (t), 27.14 (t), 27.55 (t), 28.11 (t), 28.46 (t), 28.94 (t), 42.87 (t), 103.01 (d), 120.79 (d), 129.17 (s), 141.51 (d), 144.32 (s), 157.82 (s), 202.47 (s) ppm. IR (neat): $\tilde{\nu}$ = 3124, 2927, 2852, 1665, 1584, 1438, 1367, 1333, 1305, 1204, 1072, 1036 cm^{-1}. MS (70 eV): *m/z* (%) = 274 (100) [M^+], 122 (61), 91 (30). $C_{18}H_{26}O_2$ (274.40): calcd. C 78.79, H 9.55; found C 78.87, H 9.50. HRMS calcd. 274.19328, found 274.19318 (MS).

10h: R_f (H/EA, 5:1) = 0.40. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.14−1.41 (m, 14 H), 1.51−1.67 (m, 4 H), 2.01 (d, *J* = 1.3 Hz, 3 H), 2.34−2.39 (m, 2 H), 2.56−2.61 (m, 2 H), 5.91 (d, *J* = 1.3 Hz, 1 H), 6.01 (d, *J* = 0.9 Hz, 1 H), 7.04 (d, *J* = 0.9 Hz, 1 H) ppm. IR (neat): $\tilde{\nu}$ = 3144, 2927, 2855, 1765, 1718, 1678, 1589, 1453, 1404, 1368, 1338, 1208, 1137, 1080, 996, 938 cm^{-1}. MS (70 eV): *m/z* (%) = 288 (100) [M^+], 276 (20), 135 (39), 84 (60). $C_{19}H_{28}O_2$ (288.43): calcd. C 79.12, H 9.79; found C 79.30, H 9.71. HRMS calcd. 288.20893, found 288.20791 (MS).

10i: R_f (H/EA, 5:1) = 0.44. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.25−1.39 (m, 16 H), 1.65−1.73 (m, 4 H), 2.42 (t, *J* = 7.1 Hz, 2 H), 2.42 (d, *J* = 1.1 Hz, 3 H), 2.64−2.69 (m, 2 H), 6.24 (d, *J* = 1.0 Hz, 1 H), 6.48 (d, *J* = 0.9 Hz, 1 H), 7.56 (d, *J* = 0.7 Hz, 1 H) ppm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.23−1.29 (m, 12 H), 1.36−1.39 (m, 4 H), 1.66−1.73 (m, 4 H), 2.41 (d, *J* = 1.0 Hz, 3 H), 2.39−2.43 (m, 2 H), 2.64−2.67 (m, 2 H), 6.24 (d, *J* = 0.8 Hz, 1 H), 6.47 (d, *J* = 0.4 Hz, 1 H), 7.55 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.23 (q), 25.32 (t), 25.51 (t), 26.40 (t), 26.45 (t), 27.07 (t), 27.59 (t), 27.78 (t), 28.08 (t), 28.25 (t), 28.39 (t), 28.68 (t), 43.61 (t), 102.54 (d), 120.71 (d), 128.99 (s), 141.71 (d), 144.94 (s), 157.71 (s), 202.79 (s) ppm. IR (neat): $\tilde{\nu}$ = 3134, 2927, 2855, 1765, 1676, 1589, 1443, 1367, 1331, 1201, 1134, 1077, 1038, 934 cm^{-1}. MS (70 eV): *m/z* (%) = 302 (100) [M^+], 290 (32), 121 (68). $C_{20}H_{30}O_2$ (302.46): calcd. C 79.42, H 10.00; found C 79.53, H 10.15. calcd. 302.22458, found 302.22487 (MS).

10j: R_f (H/EA, 5:1) = 0.50. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.26−1.40 (br., 20 H), 1.63−1.74 (br., 4 H), 2.40−2.45 (m, 2 H), 2.42 (d, *J* = 1.0 Hz, 3 H), 2.63−2.68 (m, 2 H), 6.22 (s, 1 H), 6.45 (d, *J* = 0.7 Hz, 1 H), 7.57 (s, 1 H) ppm. ^1H NMR (C_6D_6, 250 MHz): δ = 1.21−1.30 (m, 20 H), 1.41−1.55 (m, 2 H), 1.58−1.63 (m, 2 H), 2.33 (t, *J* = 7.1 Hz, 2 H), 2.40 (s, 3 H), 2.44−2.49 (m, 2 H), 6.06 (s, 1 H), 6.42 (s, 1 H), 6.13 (s, 1 H) ppm. ^1H NMR (C_6D_6, 400 MHz): δ = 1.18−1.30 (m, 20 H), 1.50−1.53 (m, 2 H), 1.57−1.66 (m, 2 H), 2.34 (t, *J* = 7.1 Hz, 2 H), 2.42 (d, *J* = 1.2 Hz, 3 H), 2.46−2.49 (m, 2 H), 6.07 (d, *J* = 0.9 Hz, 1 H), 6.43 (d, *J* = 1.1 Hz, 1 H), 7.15 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.34 (q), 25.37 (t), 25.95 (t), 26.61 (t), 26.90 (t), 27.48 (t, 2 C), 27.80 (t), 27.83 (t), 27.98 (t), 28.08 (t, 2 C), 28.12 (t), 28.72 (t), 44.41 (t), 102.46 (d), 120.24 (d), 128.86 (s), 141.54 (d), 145.09 (s), 157.60 (s), 202.53 (s) ppm. IR (neat): $\tilde{\nu}$ = 3141, 2926, 2855, 1676, 1589, 1456, 1367, 1331, 1200, 1137, 1049, 929 cm^{-1}. MS (70 eV): *m/z* (%) = 330 (100) [M^+], 287 (24), 135 (23). $C_{22}H_{34}O_2$ (330.51): calcd. 330.25588, found 330.25518 (MS).

11c: R_f (H/EA, 5:1) = 0.34. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.80−0.89 (m, 2 H), 1.13−1.25 (m, 2 H), 1.51 −1.70 (m, 4 H), 2.11 (d, *J* = 1.4 Hz, 3 H), 2.15 (t, *J* = 6.5 Hz, 2 H), 2.66 (t, *J* = 6.7 Hz, 2 H), 5.84 (d, *J* = 1.2 Hz, 1 H), 5.95 (s, 1 H), 7.36 (s, 1 H) ppm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.81−0.87 (m, 2 H), 1.15−1.22 (m, 2 H), 1.53−1.59 (m, 2 H), 1.62−1.68 (m, 2 H), 2.12 (d, *J* = 1.4 Hz, 3 H), 2.15 (t, *J* = 6.5 Hz, 2 H), 2.66 (t, *J* = 6.7 Hz, 2 H), 5.85 (d, *J* = 1.4 Hz, 1 H), 5.96 (s, 1 H), 7.37 (d, *J* = 0.9 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.35 (t), 23.15 (t), 23.46 (q), 23.88 (t), 24.53 (t), 25.49 (t), 38.54 (t), 111.06 (d), 125.62 (s), 129.05 (d), 137.11 (d), 138.45 (s), 156.02 (s), 207.07 (s) ppm. IR (neat): $\tilde{\nu}$ = 3127, 2934, 2862, 1683, 1598, 1536, 1440, 1408, 1361, 1325, 1286, 1248, 1180, 1121, 1081, 1008, 951, 911 cm^{-1}. MS (70 eV): *m/z* (%) = 218 (13) [M^+], 206 (27), 149 (100). $C_{14}H_{18}O_2$ (218.30): calcd. C 77.03, H 8.31; found C 76.80, H 8.27. HRMS calcd. 218.13068, found 218.12861 (MS).

11d: R_f (H/EA, 5:1) = 0.40. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.74−0.83 (m, 2 H), 1.14−1.24 (m, 2 H), 1.30−1.40 (m, 2 H), 1.49−1.64 (m, 4 H), 2.05 (d, *J* = 1.3 Hz, 3 H), 2.29 (t, *J* = 7.0 Hz, 2 H), 2.59 (t, *J* = 6.0 Hz, 2 H), 5.82 (d, *J* = 1.2 Hz, 1 H), 5.88 (s, 1 H), 7.34 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.46 (t), 24.04 (q), 24.88 (t), 25.39 (t), 25.57 (t), 28.00 (t), 28.51 (t), 39.53 (t), 108.03 (d), 126.07 (s), 128.53 (d), 137.61 (d), 138.87 (s), 156.46 (s), 207.02 (s) ppm. $C_{15}H_{20}O_2$ (232.32).

11e: R_f (H/EA, 5:1) = 0.40. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.90−0.99 (m, 2 H), 1.06−1.20 (m, 2 H), 1.21−1.32 (m, 4 H), 1.46−1.59 (m, 2 H), 1.65−1.75 (m, 2 H), 2.07 (d, *J* = 1.4 Hz, 3 H), 2.27 (t, *J* = 8.2 Hz, 2 H), 2.66 (t, *J* = 1.4 Hz, 2 H), 5.90 (d, *J* = 1.4 Hz, 1 H), 6.00 (d, *J* = 0.8 Hz, 1 H), 7.26 (d, *J* = 0.8 Hz, 1 H) ppm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86−0.97 (m, 2 H), 1.08−1.14 (m, 2 H), 1.19−1.32 (m, 4 H), 1.49−1.58 (m, 2 H), 1.67−1.73 (m, 2 H), 2.07 (d, *J* = 2.2 Hz, 3 H), 2.25−2.29 (m, 2 H), 2.64−2.67 (m, 2 H), 5.91 (d, *J* = 1.1 Hz, 1 H), 6.01 (s, 1 H), 7.27 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.18 (t), 24.79 (q), 25.23 (t), 25.40 (t), 25.82 (t), 25.98 (t), 27.15 (t), 27.25 (t), 40.86 (t), 107.07 (d), 126.01 (s), 129.15 (d), 138.49 (d), 139.23 (s), 156.88 (s), 206.56 (s) ppm. IR (neat): ṽ = 3135, 2928, 2857, 1674 (C=O), 1598, 1538, 1442, 1371, 1335, 1271, 1129, 1075, 1030, 927 cm^{-1}. MS (70 eV): *m*/*z* (%) = 246 (21) [M$^+$], 234 (42), 149 (100). $C_{16}H_{22}O_2$ (246.35): calcd. C 78.01, H 9.00; found C 78.26, H 8.96. HRMS calcd. 246.16198, found 246.16122 (MS).

11f: R_f (H/EA, 5:1) = 0.46. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.98−1.17 (m, 10 H), 1.42−1.57 (m, 4 H), 2.00 (d, *J* = 1.0 Hz, 3 H), 2.32 (t, *J* = 7.1 Hz, 2 H), 2.55 (t, *J* = 6.0 Hz, 2 H), 5.85 (d, *J* = 1.2 Hz, 1 H), 6.00 (s, 1 H), 7.24 (s, 1 H) ppm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.99−1.04 (m, 2 H), 1.11−1.17 (m, 8 H), 1.44−1.51 (m, 2 H), 1.54−1.58 (m, 2 H), 2.00 (d, *J* = 1.4 Hz, 3 H), 2.31 (t, *J* = 7.1 Hz, 2 H), 2.54−2.57 (m, 2 H), 5.85 (d, *J* = 1.4 Hz, 1 H), 6.00 (d, *J* = 0.9 Hz, 1 H), 7.24 (d, *J* = 1.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.24 (t), 24.50 (q), 25.00 (t), 25.47 (t), 25.87 (t), 25.90 (t), 26.11 (t), 26.72 (t), 26.91 (t), 41.55 (t), 106.23 (d), 125.28 (s), 128.36 (d), 137.39 (s), 139.08 (d), 156.61 (s), 205.90 (s) ppm. IR (neat): ṽ = 3140, 2930, 2857, 1767, 1686, 1598, 1539, 1443, 1405, 1369, 1260, 1136, 1083, 930 cm^{-1}. MS (70 eV): *m*/*z* (%) = 260 (100) [M$^+$], 248 (60), 121 (99), 109 (70). $C_{17}H_{24}O_2$ (260.38). HRMS calcd. 260.177038, found 260.17715 (MS).

11h: R_f (H/EA, 5:1) = 0.40. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.14−1.41 (m, 14 H), 1.51−1.67 (m, 4 H), 2.32 (d, *J* = 1.2 Hz, 3 H), 2.34−2.39 (m, 2 H), 2.56−2.61 (m, 2 H), 6.19 (d, *J* = 0.9 Hz, 1 H), 6.42 (d, *J* = 0.7 Hz, 1 H), 7.47 (d, *J* = 0.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.36 (q), 25.28 (t), 25.70 (t), 26.04 (t), 26.62 (t), 27.39 (t), 27.75 (t), 28.25 (t), 28.36 (t), 28.64 (t), 28.80 (t), 43.95 (t), 103.05 (d), 120.68 (d), 129.18 (s), 141.31 (d), 144.48 (s), 157.60 (s), 202.49 (s) ppm. IR: ṽ = 3127, 2927, 2856, 1765, 1674, 1588, 1443, 1367, 1204, 1136, 1076, 1036, 920 cm^{-1}. $C_{19}H_{28}O_2$ (288.43): calcd. C 79.12, H 9.79; found C 79.02, H 9.66.

12c: R_f (H/EA, 5:1) = 0.26. M.p. 122−124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.29−0.36 (m, 2 H), 1.11−1.18 (m, 2 H), 1.42−1.58 (m, 4 H), 2.41−2.44 (m, 2 H), 2.58 (t, *J* = 6.3 Hz, 2 H), 3.37 (s, 2 H), 5.03 (d, *J* = 1.5 Hz, 1 H), 5.20 (m, 1 H), 6.10 (s, 1 H), 7.25 (d, *J* = 0.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.39 (t), 25.25 (t), 26.33 (t), 26.49 (t), 28.14 (t), 42.54 (t), 50.15 (t), 108.06 (d), 114.05 (t), 126.34 (s), 135.09 (s), 138.44 (d), 155.66 (s), 210.93 (s) ppm. IR (neat): ṽ = 3102, 2927, 2856, 1700 (C=O), 1545, 1456, 1434, 1412, 1362, 1211, 1158, 1111, 1048, 934, 910 cm^{-1}. $C_{14}H_{18}O_2$ (218.30): calcd. C 77.03, H 8.31; found C 77.03, H 8.39.

12d: R_f (H/EA, 5:1) = 0.48. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.47−0.56 (m, 2 H), 0.97−1.08 (m, 2 H), 1.15−1.25 (m, 2 H), 1.38−1.48 (m, 2 H), 1.52−1.61 (m, 2 H), 2.27−2.32 (m, 2 H), 2.55−2.60 (m, 2 H), 3.34 (s, 2 H), 5.03 (d, *J* = 1.1 Hz, 1 H), 5.28 (s, 1 H), 5.97 (s, 1 H), 7.38 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.57 (t), 25.46 (t), 25.64 (t), 26.56 (t), 27.95 (t), 28.25 (t), 39.25 (t), 51.51 (t), 106.54 (d), 114.16 (t), 127.80 (s), 134.67 (s), 137.90 (d), 157.21 (s), 210.31 (s) ppm. $C_{15}H_{20}O_2$ (232.32).

12e: R_f (H/EA, 5:1) = 0.48. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.80−0.91 (m, 2 H), 1.00−1.15 (m, 4 H), 1.17−1.26 (m, 2 H), 1.40−1.51 (m, 2 H), 1.57−1.67 (m, 2 H), 2.33 (t, *J* = 7.1 Hz, 2 H), 2.61 (t, *J* = 6.1 Hz, 2 H), 3.38 (s, 2 H), 5.05 (d, *J* = 1.1 Hz, 1 H), 5.36 (d, *J* = 1.2 Hz, 1 H), 6.08 (s, 1 H), 7.33 (s, 1 H) ppm. ^{1}H NMR (C_6D_6, 250 MHz): δ = 0.27−0.80 (m, 2 H), 0.84−0.95 (m, 2 H), 0.99−1.20 (m, 4 H), 1.34−1.54 (m, 4 H), 2.02 (t, *J* = 7.0 Hz, 2 H), 2.34 (t, *J* = 6.1 Hz, 2 H), 3.05 (s, 2 H), 4.80 (s, 1 H), 5.17 (d, *J* = 1.3 Hz, 1 H), 5.76 (s, 1 H), 7.11 (s, 1 H) ppm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.82−0.92 (m, 2 H), 1.01−1.14 (m, 4 H), 1.17−1.28 (m, 2 H), 1.42−1.49 (m, 2 H), 1.59−1.65 (m, 2 H), 2.39−2.43 (m, 2 H), 2.59−2.62 (m, 2 H), 3.38 (s, 2 H), 5.05 (d, *J* = 1.2 Hz, 1 H), 5.36 (d, *J* = 1.2 Hz, 1 H), 6.07 (s, 1 H), 7.32 (d, *J* = 0.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.70 (t), 25.70 (t), 26.16 (t), 26.23 (t), 26.40 (t), 26.72 (t), 27.45 (t), 39.16 (t), 50.81 (t), 105.69 (d), 114.49 (t), 126.83 (s), 134.36 (s), 137.83 (d), 157.05 (s), 206.84 (s) ppm. IR (neat): ṽ = 3088, 2929, 2857, 1710 (C=O), 1637, 1598, 1540, 1457, 1364, 1287, 1214, 1129, 1068, 927 cm^{-1}. MS (70 eV): *m*/*z* (%) = 246 (47) [M$^+$], 234 (37), 205 (18), 163 (17), 161 (20), 149 (100), 136 (38), 121 (44), 108 (28), 91 (26). $C_{16}H_{22}O_2$ (246.35): calcd. C 78.01, H 9.00; found C 77.79, H 8.87. HRMS calcd. 246.16198, found 246.16146 (MS).

12f: R_f (H/EA, 5:1) = 0.50. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.85−1.05 (m, 8 H), 1.17−1.28 (m, 2 H), 1.42−1.52 (m, 2 H), 1.56−1.66 (m, 2 H), 2.39−2.44 (m, 2 H), 2.56−2.61 (m, 2 H), 3.35 (s, 2 H), 5.08 (s, 1 H), 5.39 (s, 1 H), 6.12 (s, 1 H), 7.30 (s, 1 H) ppm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.79−0.86 (m, 2 H), 0.87−0.94 (m, 2 H), 0.95−1.00 (m, 4 H), 1.10−1.22 (m, 2 H), 1.33−1.44 (m, 2 H), 1.51−1.57 (m, 2 H), 2.35 (t, *J* = 6.2 Hz, 2 H), 2.50−2.53 (m, 2 H), 3.28 (d, *J* = 1.0 Hz, 2 H), 5.02 (d, *J* = 1.2 Hz, 1 H), 5.33 (d, *J* = 1.1 Hz, 1 H), 6.05 (d, *J* = 0.8 Hz, 1 H), 7.24 (d, *J* = 0.8 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.81 (t), 25.05 (t), 25.95 (t), 26.66 (t), 26.94 (t), 26.98 (t), 27.41 (t), 27.64 (t), 37.55 (t), 51.92 (t), 104.84 (d), 114.32 (t), 126.19 (s), 134.15 (s), 138.61 (d), 157.08 (s), 210.00 (s) ppm. IR (neat): ṽ = 2930, 2857, 1767, 1710, 1636, 1599, 1540, 1440, 1363, 1226, 1134, 928 cm^{-1}.

5. Preparation of the Diols 15a and 16a

1,5-Pentanediol (26.0 g, 250 mmol), 60% NaH-suspension (4.00 g, 100 mmol), 1,2-bis(bromomethyl)benzene (10.6 mg, 40.2 mmol), THF_{abs} (300+50 mL). Purification by column chromatography on silica gel (H/EE/methanol, 12:12:1). Yield: **16a** (1.06 g, 5%) and **15a** (6.85 g, 55%).

15a: Yield: 55%. R_f (H/EA/MeOH, 6:6:0.75) = 0.16. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.39−1.69 (m, 12 H), 1.22 (d, *J* = 5.4 Hz, 2 H), 3.48 (t, *J* = 6.4 Hz, 4 H), 3.60 (t, *J* = 6 Hz, 4 H), 4.56 (s, 4 H), 7.25−7.30 (m, 2 H), 7.34−7.39 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.11 (t, 2 C), 29.09 (t, 2 C), 32.02 (t, 2 C), 61.93 (t, 2 C), 70.14 (t, 2 C), 70.16 (t, 2 C), 127.36 (d, 2 C), 128.34 (d, 2 C), 136.22 (s, 2 C) ppm. IR (neat): ṽ = 3384 (OH), 3069 (Ar−H), 3030 (Ar−H), 2935, 2863, 1455, 1362, 1217, 1186, 1091, 914, 752 cm^{-1}. MS (70 eV): *m*/*z* (%) = 206 (32) [M − HO(CH$_2$)$_5$OH]$^+$, 120 (100), 104 (18), 87 (14). $C_{18}H_{30}O_4$ (310.43): calcd. C 69.64, H 9.74; found C 69.47, H 9.65. **16a:** Yield: 5%. R_f (H/EA/MeOH, 6:6:0.75) = 0.20. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.39−1.69 (m, 18 H), 1.88 (s, 2 H), 3.48 (t, *J* = 6 Hz, 8 H), 3.60 (t, *J* = 6 Hz, 4 H), 4.56 (s, 8 H), 7.25−7.30 (m, 4 H), 7.35−7.40 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.25 (t, 2 C), 22.73 (t), 29.25 (t, 2 C), 29.36 (t, 2 C), 32.22 (t, 2 C), 62.32 (t, 2 C), 70.24 (t, 8 C), 127.42 (d, 2 C), 127.45 (d, 2 C), 128.36 (d, 2 C), 128.40 (d, 2 C), 136.33 (s, 2 C), 136.43 (s, 2 C) ppm. IR (neat): ṽ = 3410 (OH), 3067 (Ar−H), 3028 (Ar−H), 2935, 2862, 1455, 1362, 1218, 1187, 1092, 915, 754 cm^{-1}. MS (70 eV): *m*/*z* (%) = 412 (1.7) [M −

$HO(CH_2)_5OH]^+$, 206 (87), 120 (100), 105 (75), 87 (69). $C_{31}H_{48}O_4$ (516.72): calcd. C 72.06, H 9.36; found C 71.89, H 9.38.

6. Preparation of the Diols 15b and 16b

1,12-Dodecandiol (58.4 g, 289 mmol), 60% NaH-suspension (4.62 g, 116 mmol), 1,2-bis(bromomethyl)benzene (12.2 g, 46.2 mmol), THF_{abs} (350 + 50 mL). Purification by several recrystallizations: the products stay in solution and the dodecandiol precipitates. Subsequently, column chromatography on silica gel (H/EE, 2:1). Yield: **16b** (2.25 g, 6%) and **15b** (8.72 g, 37%).

15b: Yield: 37%. M.p. 51 °C. R_f (H/EA, 1:1) = 0.30. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27−1.30 (m, 32 H), 1.49 (br. s, 2 H), 1.50−1.64 (m, 8 H), 3.47 (t, *J* = 6.6 Hz, 4 H), 3.63 (t, *J* = 6.5 Hz, 4 H), 4.56 (s, 4 H), 7.25−7.30 (m, 2 H), 7.35−7.42 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.58 (t, 2 C), 26.08 (t, 2 C), 29.26 (t, 2 C), 29.31 (t, 2 C), 29.42 (t, 8 C), 29.62 (t, 2 C), 32.60 (t, 2 C), 62.78 (t, 2 C), 70.28 (t, 2 C), 70.50 (t, 2 C), 127.41 (d, 2 C), 128.37 (d, 2 C), 136.53 (s, 2 C) ppm. IR (neat): ṽ = 3301 (OH), 3066 (Ar−H), 3028 (Ar−H), 2921, 2853, 1465, 1360, 1217, 1188, 1103, 1061, 746 cm^{-1}. MS (70 eV): *m*/*z* (%) = 504 (0.2), 304 (82), 120 (100), 105 (44). MS [FAB(+), Xenon]: *m*/*z* (%) = 507 (3) $[MH^+]$, 305 (12), 121 (36), 105 (100), 92 (4). $C_{32}H_{58}O_4$ (506.81): calcd. C 75.84, H 11.54; found C 75.53, H 11.22. **16b:** Yield: 6%. M.p. 47 °C. R_f (H/EA, 1:1) = 0.38. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (br., 48 H), 1.44 (s, 2 H), 1.51−1.64 (m, 12 H), 3.47 (t, *J* = 6.6 Hz, 8 H), 3.63 (t, *J* = 6.6 Hz, 4 H), 4.56 (s, 8 H), 7.25−7.30 (m, 4 H), 7.35−7.41 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.58 (t, 2 C), 26.09 (t, 4 C), 29.26 (t, 2 C), 29.31 (t, 2 C), 29.34 (t, 2 C), 29.42 (t, 8 C), 29.45 (t, 4 C), 29.63 (t, 4 C), 32.63 (t, 2 C), 62.81 (t, 2 C), 70.27 (t, 4 C), 70.51 (t, 4 C), 127.40 (d, 4 C), 128.36 (d, 4 C), 136.54 (s, 4 C) ppm. IR (neat): ṽ = 3410 (OH), 3066 (Ar−H), 3028 (Ar−H), 2926, 2854, 1459, 1361, 1216, 1186, 1095, 752 cm^{-1}. MS (70 eV): *m*/*z* (%) = 808 (0.1), 608 (16), 406 (23), 304 (100), 120 (36), 105 (15). MS [FAB(−), Xenon]: *m*/*z* (%) = 810 (0.7) $[M - H]^+$, 153 (100). $C_{52}H_{90}O_6$ (811.29): calcd. C 76.99, H 11.18; found C 76.91, H 11.11.

7. Sequence 15a to 19a

17a: 15a (5.00 g, 16.1 mmol), oxalyl chloride (9.81 g, 77.3 mmol), DMSO (10.1 g, 129 mmol), Et_3N (19.6 g, 194 mmol), purification by column chromatography (H/EE, 2:1). Yield: 4.42 mg (90%). R_f (H/EA, 1:1) = 0.36. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.58−1.80 (m, 8 H), 2.46 (dt, *J* = 1.6, 7.1 Hz, 4 H), 3.49 (t, *J* = 6.0 Hz, 4 H), 4.55 (s, 4 H), 7.26−7.31 (m, 2 H), 7.34−7.39 (m, 2 H), 9.76 (t, *J* = 1.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 18.73 (t, 2 C), 28.92 (t, 2 C), 43.31 (t, 2 C), 69.69 (t, 2 C), 70.24 (t, 2 C), 127.46 (d, 2 C), 128.35 (d, 2 C), 136.24 (s, 2 C), 202.20 (d, 2 C) ppm. IR (neat): ṽ = 3066 (Ar−H), 3029 (Ar−H), 2937, 2863, 2723 (H-CO), 1723 (C=O), 1454, 1362, 1218, 1188, 1095, 756 cm^{-1}. MS (70 eV): *m*/*z* (%) = 306 (0.7) $[M^+]$, 204 (31), 120 (27), 105 (25), 85 (100). $C_{18}H_{26}O_4$ (306.40): calcd. C 70.56, H 8.55; found C 70.39, H 8.56.

18a: 17a (4.20 mg, 13.7 mmol), propargylmagnesium bromide (1.6 M, 24.0 mL, 38.4 mmol), purification by column chromatography (H/EE, 2:1). Yield: 1.99 mg (38%). R_f (H/EA, 1:1) = 0.18. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.38−1.67 (m, 12 H), 2.04−2.06 (m, 2 H), 2.14 (s, 2 H), 2.30 (ddd, *J* = 2.7, 6.6, 16.7 Hz, 2 H), 2.41 (ddd, *J* = 2.6, 5.0, 16.7 Hz, 2 H), 3.49 (t, *J* = 6.2 Hz, 4 H), 3.70−3.79 (m, 2 H), 4.56 (s, 4 H), 7.25−7.31 (m, 2 H), 7.34−7.39 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.03 (t, 2 C), 27.04 (t, 2 C), 29.26 (t, 2 C), 35.58 (t, 2 C), 69.37 (d, 2 C), 70.04 (d, 2 C), 70.17 (t, 2 C), 70.43 (t, 2 C), 80.78 (s, 2 C), 127.38 (d, 2 C), 128.36 (d, 2 C), 136.27 (s, 2 C) ppm. IR (neat): ṽ = 3410 (OH), 3295 (≡C−H), 3069 (Ar−H), 3029 (Ar−H), 2935, 2863, 2117 (C≡C), 1454, 1360, 1218, 1188, 1092, 756 cm^{-1}. MS (70 eV): *m*/*z* (%) = 386 (0.05) $[M^+]$, 244 (21), 142 (48), 120 (100), 105 (61), 91 (26), 85 (89). $C_{24}H_{34}O_4$ (386.53): calcd. C 74.58, H 8.87; found C 74.36, H 8.95.

19a: 18a (1.00 g, 2.61 mmol), DMP (2.63 g, 6.20 mmol), DCM (3 mL), purification by column chromatography (H/EE, 2.5:1). Yield: 729 mg (73%). R_f (H/EA, 1:1) = 0.50. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.58−1.73 (m, 8 H), 2.60−2.65 (m, 4 H), 3.45−3.50 (m, 4 H), 4.54 (s, 4 H), 5.20 (d, *J* = 6.5 Hz, 4 H), 5.76 (t, *J* = 6.5 Hz, 2 H), 7.25−7.30 (m, 2 H), 7.34−7.39 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.11 (t, 2 C), 29.03 (t, 2 C), 38.63 (t, 2 C), 69.99 (t, 2 C), 70.27 (t, 2 C), 79.24 (t, 2 C), 96.47 (d, 2 C), 127.44 (d, 2 C), 128.34 (d, 2 C), 136.38 (s, 2 C), 200.33 (s, 2 C), 216.41 (s, 2 C) ppm. IR (neat): ṽ = 3064 (Ar−H), 2937, 2863, 1934 (C=C=C), 1679 (C=O), 1453, 1410, 1361, 1161, 1095, 857, 756 cm^{-1}. MS (70 eV): *m*/*z* (%) = 382 (1.6) $[M^+]$, 242 (20), 123 (100), 104 (43), 81 (16). $C_{24}H_{30}O_4$ (382.50): calcd. C 75.36, H 7.91; found C 75.15, H 7.98.

8. Sequence 15b to 19b

17b: 15b (5.00 g, 9.87 mmol), oxayl chloride (7.80 g, 61.5 mmol), DMSO (8.05 g, 103 mmol), Et_3N (15.6 g, 154 mmol), purification by column chromatography (H/EE, 7:1). Yield: 3.97 g (80%). R_f (H/EA, 5:1) = 0.30. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (br. s, 28 H), 1.55−1.68 (m, 8 H), 2.42 (dt, *J* = 1.9, 7.3 Hz, 4 H), 3.47 (t, *J* = 6.6 Hz, 4 H), 4.56 (s, 4 H), 7.25−7.30 (m, 2 H), 7.35−7.40 (m, 2 H), 9.76 (t, *J* = 1.9 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.90 (t, 2 C), 26.08 (t, 2 C), 28.97 (t, 2 C), 29.16 (t, 2 C), 29.22 (t, 2 C), 29.29 (t, 2 C), 29.33 (t, 2 C), 29.38 (t, 2 C), 29.63 (t, 2 C), 43.71 (t, 2 C), 70.26 (t, 2 C), 70.47 (t, 2 C), 127.37 (d, 2 C), 128.31 (d, 2 C), 136.55 (s, 2 C), 202.61 (d, 2 C) ppm. IR (neat): ṽ = 3066 (Ar−H), 3027 (Ar−H), 2927, 2854, 2716 (H-CO), 1725 (C=O), 1459, 1361, 1216, 1187, 1096, 754 cm^{-1}. MS (70 eV): *m*/*z* (%) = 502 (0.7) $[M^+]$, 484 (0.7) $[M - H_2O]^+$, 459 (3) $[M - CH_2CHO]^+$, 274 (46), 120 (100), 105 (23). $C_{32}H_{54}O_4$ (502.78): calcd. C 76.45, H 10.83; found C 76.21, H 10.59.

18b: 17b (2.60 g, 5.17 mmol), propargylmagnesium bromide (1.6 M, 11.3 mL, 18.1 mmol), purification by HPLC (H/dioxane, 10:2). Yield: 2.51 mg (83%). R_f (H/EA, 2:1) = 0.24. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (br. s, 32 H), 1.50−1.64 (m, 8 H), 1.87 (br. s, 2 H), 2.05 (t, *J* = 2.6 Hz, 2 H), 2.31 (ddd, *J* = 2.7, 6.7, 16.7 Hz, 2 H), 2.43 (ddd, *J* = 2.6, 4.8, 16.7 Hz, 2 H), 3.47 (t, *J* = 6.6 Hz, 4 H), 3.71−3.80 (m, 2 H), 4.56 (s, 4 H), 7.25−7.30 (m, 2 H), 7.35−7.40 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.41 (t, 2 C), 26.08 (t, 2 C), 27.17 (t, 2 C), 29.30 (t, 2 C), 29.38 (t, 10 C), 29.61 (t, 2 C), 36.04 (t, 2 C), 69.67 (d, 2 C), 70.25 (t, 2 C), 70.47 (t, 2 C), 70.52 (d, 2 C), 80.89 (s, 2 C), 127.39 (d, 2 C), 128.36 (d, 2 C), 136.52 (s, 2 C) ppm. IR (neat): ṽ = 3422 (OH), 3307 (≡C−H), 3067 (Ar−H), 3028 (Ar−H), 2926, 2854, 2118 (C≡C), 1459, 1361, 1219, 1188, 1091, 753 cm^{-1}. MS (70 eV): *m*/*z* (%) = 582 (0.2) $[M^+]$, 543 (8), $[M - C_3H_3]^+$, 342 (9), 324 (5), 303 (8), 171 (4), 142 (100), 120 (57), 105 (61). $C_{38}H_{62}O_4$ (582.91): calcd. C 78.30 H, 10.72; found C 78.05, H 10.48. M.p. 44−45 °C.

19b: 18b (1.21 g, 2.08 mmol), DMP (2.21 g, 5.21 mmol), DCM (3 mL), purification by column chromatography (H/EE, 7:1). Yield: 1.00 g (83%). R_f (H/EA, 5:1) = 0.28. M.p. 37−38 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (br. s, 28 H), 1.58−2.02 (m, 8 H), 2.59 (t, *J* = 7 Hz, 4 H), 3.47 (t, *J* = 6.6 Hz, 4 H), 4.56 (s, 4 H), 5.22 (d, *J* = 6.5 Hz, 4 H), 5.77 (t, *J* = 6.5 Hz, 2 H), 7.25−7.29 (m, 2 H), 7.30−7.41 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.40 (t, 2 C), 26.08 (t, 2 C), 29.02 (t, 2 C), 29.20 (t, 2 C), 29.27 (t,

2 C), 29.30 (t, 2 C), 29.36 (t, 2 C), 29.40 (t, 2 C), 29.63 (t, 2 C), 39.63 (t, 2 C), 70.26 (t, 2 C), 70.48 (t, 2 C), 79.09 (t, 2 C), 96.50 (d, 2 C), 127.38 (d, 2 C), 128.32 (d, 2 C), 136.54 (s, 2 C), 200.76 (s, 2 C), 216.42 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065 (Ar−H), 2926, 2854, 1934 (C=C=C), 1682 (C=O), 1459, 1411, 1361, 1161, 1096, 851, 752 cm^{-1}. MS (70 eV): *m/z* (%) = 578 (3) [M^+], 379 (2), 340 (100), 237 (12), 197 (7), 183 (11), 120 (10), 105 (8). $C_{38}H_{58}O_4$ (578.88): calcd. C 78.85, H 10.10; found C 78.53, H 10.13.

9. Sequence 16a to 24a

22a: 16a (1.03 g, 1.99 mmol), oxalyl chloride (1.50 g, 11.8 mmol), DMSO (1.54 g, 19.7 mmol), Et_3N (2.99 g, 29.5 mmol), purification by column chromatography (H/EE, 2:1). Yield: 943 mg (92%). R_f (H/EA, 1:1) = 0.40. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.42−1.51 (m, 2 H), 1.57−1.76 (m, 12 H), 2.44 (dt, *J* = 1.6, 7.1 Hz, 4 H), 3.45−3.50 (m, 8 H), 4.55 (s, 8 H), 7.23−7.30 (m, 4 H), 7.34−7.39 (m, 4 H), 9.74 (d, *J* = 1.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 18.82 (t, 2 C), 22.81 (t), 29.01 (t, 2 C), 29.46 (t, 2 C), 43.40 (t, 2 C), 69.75 (t, 2 C), 70.31 (t, 6 C), 127.48 (d, 2 C), 127.51 (d, 2 C), 128.35 (d, 2 C), 128.42 (d, 2 C), 136.33 (s, 2 C), 136.46 (s, 2 C), 202.27 (d, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3066 (Ar−H), 3029 (Ar−H), 2936, 2861, 2722 (H−CO), 1723 (C=O), 1454, 1361, 1218, 1188, 1095, 755 cm^{-1}. MS (70 eV): *m/z* (%) = 410 (0.8), 204 (20), 119 (20), 105 (47), 85 (100). MS [FAB(+), Xenon]: *m/z* (%) = 513 (1.2) [MH^+], 327 (1.2), 205 (10), 119 (20), 105 (84), 85 (100). $C_{31}H_{44}O_6$ (512.69), ($C_{26}H_{34}O_4$): calcd. 410.24571, found 410.24562 (MS).

23a: 22 (918 mg, 1.79 mmol), (1.6 M, 4.5 mL, 7.2 mmol) propargylmagnesium bromide, purification by column chromatography (H/EE, 2:1). Yield: 649 mg (61%). R_f (H/EA, 1:1) = 0.26. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.40−1.69 (m, 18 H), 1.99 (br. s, 2 H), 2.05 (t, *J* = 2.6 Hz, 2 H), 2.30 (ddd, *J* = 2.7, 6.6, 16.7 Hz, 2 H), 2.41 (ddd, *J* = 2.6, 4.9, 16.7 Hz, 2 H), 3.45−3.51 (m, 8 H), 3.70−7.79 (m, 2 H), 4.56 (s, 8 H), 7.25−7.31 (m, 4 H), 7.35−7.40 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.20 (t, 2 C), 22.79 (t), 27.20 (t, 2 C), 29.43 (t, 4 C), 35.75 (t, 2 C), 69.52 (d, 2 C), 70.18 (t, 2 C), 70.30 (t, 6 C), 70.61 (t, 2 C), 80.85 (s, 2 C), 127.49 (d, 2 C), 127.52 (d, 2 C), 128.43 (d, 2 C), 128.46 (d, 2 C), 136.38 (s, 2 C), 136.48 (s, 2 C) ppm; 1 ≡CH hidden/overlapping, 1 CH_2 hidden/overlapping. IR (neat): $\tilde{\nu}$ = 3426 (OH), 3297 (≡C−H), 3066 (Ar−H), 3029 (Ar−H), 2935, 2862, 2117 (C≡C), 1454, 1360, 1218, 1187, 1093, 755 cm^{-1}. MS (70 eV): *m/z* (%) = 450 (0.2), 410 (0.3), 327 (1), 245 (2), 205 (17), 142 (19), 120 (68), 105 (86), 85 (100). MS [FAB(+), Xenon]: *m/z* (%) = 615 (0.6) [M + Na]$^+$, 593 (4) [MH^+], 472 (3), 245 (12), 207 (9), 120 (27), 105 (100), 91 (47). $C_{37}H_{52}O_6$ (592.82).

24a: 23a (641 mg, 1.08 mmol), DMP (1.38 mg, 3.25 mmol), DCM (3 mL), purification by HPLC (H/EE, 10:4.33 + 30% DMC). Yield: 244 mg (38%). R_f (H/EA, 1:1) = 0.42. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.41−1.51 (m, 2 H), 1.54−1.76 (m, 12 H), 2.59−2.64 (m, 4 H), 3.47 (t, *J* = 6.2 Hz, 8 H), 4.54 (s, 8 H), 5.19 (d, *J* = 6.6 Hz, 4 H), 5.75 (t, *J* = 6.5 Hz, 2 H), 7.24−7.29 (m, 4 H), 7.34−7.39 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.23 (t, 2 C), 22.80 (t), 29.04 (t, 2 C), 29.46 (t, 2 C), 38.65 (t, 2 C), 69.99 (t, 2 C), 70.28 (t, 6 C), 79.21 (t, 2 C), 96.48 (d, 2 C), 127.41 (d, 2 C), 127.43 (d, 2 C), 128.33 (d, 4 C), 136.41 (s, 2 C), 136.47 (s, 2 C), 200.27 (s, 2 C), 261.41 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3064 (Ar−H), 3028 (Ar−H), 2936, 2861, 1934 (C=C=C), 1680 (C=O), 1453, 1412, 1361, 1160, 1094, 857, 754 cm^{-1}. MS (70 eV): *m/z* (%) = 588 (0.3) [M^+], 488 (0.5), 324 (2), 242 (13), 206 (13), 183 (13), 135 (43), 119 (81), 104 (100), 91 (53), 81 (5). $C_{37}H_{48}O_6$ (588.72): calcd. C 75.48, H 8.22; found C 75.27, H 8.19.

10. Sequence 16b to 24b

22b: 16b (1.97 g, 2.43 mmol), oxalyl chloride (1.90 g, 15.0 mmol), DMSO (1.99 g, 25.5 mmol), Et_3N (3.90 g, 38.5 mmol), purification by column chromatography (H/EE, 7:1). Yield: 1.83 mg (93%). M.p. 36 °C. R_f (H/EA, 5:1) = 0.36. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.17−1.28 (m, 44 H), 1.45−1.56 (m, 12 H), 2.28 (dt, *J* = 1.8, 7.3 Hz, 4 H), 3.36 (t, *J* = 6.5 Hz, 8 H), 4.45 (s, 8 H), 7.12−7.18 (m, 4 H), 7.24−7.31 (m, 4 H), 9.62 (t, *J* = 1.8 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.90 (t, 2 C), 26.10 (t, 4 C), 28.98 (t, 2 C), 29.18 (t, 2 C), 29.23 (t, 2 C), 29.30 (t, 2 C), 29.34 (t, 4 C), 29.39 (t, 4 C), 29.45 (t, 4 C), 29.66 (t, 2 C), 43.70 (t, 2 C), 70.28 (t, 4 C), 70.46 (t, 4 C), 127.35 (d, 4 C), 128.30 (d, 4 C), 136.57 (s, 4 C), 202.43 (d, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3066 (Ar−H), 3028 (Ar−H), 2926, 2854, 2715 (H−CO), 1726 (C=O), 1459, 1361, 1216, 1187, 1096, 753 cm^{-1}. MS (70 eV): *m/z* (%) = 806 (0.1) [M − H]$^+$, 788 (1), 606 (33), 406 (42), 302 (78), 274 (44), 206 (20), 120 (100), 105 (86). MS [FAB(+), Xenon]: *m/z* (%) = 807 (0.7) [M^+], 607 (0.5), 406 (1), 303 (8), 207 (8), 105 (100), 91 (22). $C_{52}H_{86}O_6$ (807.25): calcd. C 77.37, H 10.74; found C 77.35 H, 10.55.

23b: 22b (1.81 g, 2.24 mmol), propargylmagnesium bromide (1.6 M, 4.88 mL, 7.80 mmol), purification by HPLC (H/E/EE, 10:10:1). Yield: 1.45 g (73%). R_f (H/EA, 2:1) = 0.36. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (br. s, 44 H), 1.50−1.64 (m, 16 H), 1.89 (br. s, 2 H), 2.05 (t, *J* = 2.6 Hz, 2 H), 2.30 (ddd, *J* = 2.7, 6.7, 16.7 Hz, 2 H), 2.43 (ddd, *J* = 2.6, 4.7, 16.7 Hz, 2 H), 3.47 (t, *J* = 6.6 Hz, 8 H), 3.70−3.79 (m, 2 H), 4.56 (s, 8 H), 7.25−7.30 (m, 4 H), 7.35−7.41 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 25.43 (t, 2 C), 26.10 (t, 4 C), 27.18 (t, 2 C), 29.40 (t, 10 C), 29.46 (t, 8 C), 29.64 (t, 4 C), 36.06 (t, 2 C), 69.68 (d, 2 C), 70.27 (t, 4 C), 70.50 (t, 4 C), 70.54 (t, 2 C), 80.85 (s, 2 C), 127.41 (d, 4 C), 128.36 (d, 4 C), 136.53 (s, 4 C) ppm. IR (neat): $\tilde{\nu}$ = 3442 (OH), 3308 (≡C−H), 3066 (Ar−H), 3028 (Ar−H), 2926, 2854, 2118 (C≡C), 1495, 1361, 1317, 1187, 1093, 752 cm^{-1}. MS (70 eV): *m/z* (%) = 887 (0.7) [M^+], 606 (23), 442 (17), 340 (100), 302 (69), 274 (43), 206 (29), 135 (38), 120 (69), 105 (97); [FAB^+]: *m/z* (%) = 888 (0.1) [MH^+], 646 (0.2), 406 (0.3), 343 (2), 305 (2), 254 (15), 119 (50), 105 (100). $C_{58}H_{94}O_6$ (887.38): calcd. C 78.50, H 10.68; found C 78.24, H 10.71.

24b: 23b (712 mg, 802 μmol), DMP (852 mg, 2.01 mmol), DCM (3 mL), purification by column chromatography (H/EE, 6:1). Yield: 639 mg (90%). M.p. 47 °C. R_f (H/EA, 5:1) = 0.32. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (br. s, 44 H), 1.55−1.63 (m, 12 H), 2.58 (t, *J* = 7 Hz, 4 H), 3.46 (t, *J* = 6.6 Hz, 8 H), 4.56 (s, 8 H), 5.21 (d, *J* = 6.5 Hz, 4 H), 5.76 (t, *J* = 6.5 Hz, 2 H), 7.24−7.29 (m, 4 H), 7.35−7.40 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.41 (t, 2 C), 26.11 (t, 4 C), 29.03 (t, 2 C), 29.22 (t, 2 C), 29.29 (t, 2 C), 29.32 (t, 2 C), 29.35 (t, 2 C), 29.38 (t, 2 C), 29.42 (t, 2 C), 29.46 (t, 4 C), 29.65 (t, 4 C), 39.70 (t, 2 C), 70.28 (t, 4 C), 70.49 (t, 4 C), 79.11 (t, 2 C), 96.51 (d, 2 C), 127.39 (d, 4 C), 128.33 (d, 4 C), 136.55 (s, 4 C), 200.77 (s, 2 C), 216.43 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3065 (Ar−H), 3025 (Ar−H), 2926, 2854, 1934 (C=C=C), 1683 (C=O), 1459, 1411, 1361, 1158, 1096, 850, 753 cm^{-1}. MS (70 eV): *m/z* (%) = 883 (0.8) [M^+], 644 (3), 578 (6), 442 (14), 406 (11), 341 (33), 340 (100), 274 (49), 197 (12), 183 (17), 135 (49), 120 (74), 105 (90); [FAB^+] *m/z* (%) = 884 (0.2) [MH^+], 645 (0.2), 406 (0.4), 341 (5), 207 (6), 154 (14), 136 (14), 119 (44), 105 (100). $C_{58}H_{90}O_6$ (883.35): calcd. C 78.86, H 10.27; found C 78.99, H 10.19.

11. Cyclization/Macrocyclization of 15a,b and 16a,b to 20a,b/21a,b and 25a,b/26a,b

The conditions for the cyclizations are similar to the conditions described for the cyclization of the diallenyl diketones **8** (details listed in Table 2).

Table 2. Amount of substrates **19**, **24** and catalyst

Starting material	Quantity	Quantity of catalyst
19a	95.6 mg (250 μmol)	3.1 mg (11.9 μmol, 5 mol%)
19b	147 mg (250 μmol)	3.2 mg (12.3 μmol, 5 mol%)
24a	145 mg (247 μmol)	3.3 mg (12.7 μmol, 5 mol%)
24b	220 mg (249 μmol)	3.3 mg (12.7 μmol, 5 mol%)

20a: 19a (90.0 mg, 235 μmol), $AgNO_3$ (2.7 mg, 15.9 μmol), acetone (1 mL), column chromatography (H/EE, 5:1). Yield: 17.7 mg (20%). R_f (H/EA, 5:1) = 0.46. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.61−1.78 (m, 8 H), 2.62−2.68 (m, 4 H), 3.48−3.52 (m, 4 H), 4.57 (s, 4 H), 5.98−5.99 (m, 2 H), 6.27−6.29 (m, 2 H), 7.29−7.30 (m, 2 H), 7.26−7.32 (m, 2 H), 7.36−7.41 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 24.65 (t, 2 C), 27.58 (t, 2 C), 29.10 (t, 2 C), 70.01 (t, 2 C), 70.34 (t, 2 C), 104.63 (d, 2 C), 109.89 (d, 2 C), 127.49 (d, 2 C), 128.40 (d, 2 C), 136.45 (s, 2 C), 140.57 (d, 2 C), 155.95 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3115 (Ar−H), 3067 (Ar−H), 3029 (Ar−H), 2938, 2861, 1596, 1506, 1454, 1362, 1095, 1008, 921, 797 cm^{-1}. MS (70 eV): *m/z* (%) = 382 (0.5) [M^+], 242 (15), 183 (45), 139 (46), 121 (57), 104 (100), 81 (64). $C_{24}H_{30}O_4$: calcd. 382.21441, found 382.21425 (MS). $C_{24}H_{30}O_4$ (382.50): calcd. C 75.36, H 7.91; found C 75.35, H 8.12.

21a: Yield: 30.1 mg (31%). R_f (H/EA, 5:1) = 0.24. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.54−1.78 (m, 8 H), 2.32 (s, 3 H), 2.32 (t, *J* = 7.2 Hz, 2 H), 2.58 (m, 2 H), 3.39−3.48 (m, 4 H), 4.52 (s, 2 H), 4.56 (s, 2 H), 6.28 (s, 1 H), 6.47 (s, 1 H), 7.18−7.23 (m, 2 H), 7.26−7.37 (m, 2 H), 7.46 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.36 (q), 22.74 (t), 22.85 (t), 26.85 (t), 28.01 (t), 28.83 (t), 44.34 (t), 69.61 (t), 69.63 (t), 69.94 (t), 70.64 (t), 102.72 (d), 119.93 (d), 127.48 (d), 127.50 (d), 128.43 (d), 128.51 (d), 129.20 (s), 136.33 (s), 136.43 (s), 141.44 (d), 145.09 (s), 157.68 (s), 202.06 (s) ppm. IR (neat): $\tilde{\nu}$ = 3125 (Ar−H), 3065 (Ar−H), 3029 (Ar−H), 2936, 2862, 1764, 1674 (C=O), 1589, 1447, 1365, 1130, 1095, 945, 804, 752 cm^{-1}. MS (70 eV): *m/z* (%) = 382 (100) [M^+], 281 (49), 277 (77), 233 (53), 104 (83). $C_{24}H_{30}O_4$ (382.50). HRMS calcd. 382.214410, found 382.214240 (MS).

20b: 19b (90.0 mg, 155 μmol), $AgNO_3$ (2.8 mg, 16.5 μmol), acetone (1 mL), column chromatography (H/EE, 20:1). Yield: 71.0 mg (79%). M.p. 30−35 °C. R_f (H/EA, 10:1) = 0.50. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (br. s, 28 H), 1.58−1.66 (m, 8 H), 2.62 (t, *J* = 7.5 Hz, 4 H), 3.48 (t, *J* = 6.6 Hz, 4 H), 4.57 (s, 4 H), 5.97 (dd, *J* = 0.7, 3.1 Hz, 2 H), 6.28 (dd, *J* = 2.0, 3.0 Hz, 2 H), 7.26−7.31 (m, 4 H), 7.36−7.41 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 26.14 (t, 2 C), 27.84 (t, 2 C), 27.91 (t, 2 C), 29.05 (t, 2 C), 29.23 (t, 2 C), 29.35 (t, 2 C), 29.40 (t, 2 C), 29.44 (t, 4 C), 29.68 (t, 2 C), 70.32 (t, 2 C), 70.52 (t, 2 C), 104.36 (d, 2 C), 109.86 (d, 2 C), 127.42 (d, 2 C), 128.38 (d, 2 C), 136.59 (s, 2 C), 140.45 (d, 2 C), 156.44 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3114 (Ar−H), 3066 (Ar−H), 3028 (Ar−H), 2926, 2854, 1596, 1507, 1460, 1360, 1096, 1008, 928, 794 cm^{-1}. MS (70 eV): *m/z* (%) = 578 (0.8) [M^+], 340 (100), 237 (12), 197 (6), 183 (11), 169 (10), 120 (8), 105 (6). $C_{38}H_{58}O_4$ (578.88): calcd. C 78.85, H 10.10; found C 78.54, H 10.06.

21b: Yield: 34.2 mg (26%). R_f (H/EA, 5:1) = 0.42. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (br. s, 28 H), 1.55−1.68 (m, 8 H), 2.41 (d, *J* = 1.1 Hz, 3 H), 2.44−2.50 (m, 2 H), 2.58−2.64 (m, 2 H), 3.46 (t, *J* = 6.4 Hz, 2 H), 3.48 (t, *J* = 6.5 Hz, 2 H), 4.57 (s, 2 H), 4.58 (s, 2 H), 6.21 (d, *J* = 0.8 Hz, 1 H), 6.43 (d, *J* = 1.1 Hz, 1 H), 7.23−7.30 (m, 2 H), 7.31−7.41 (m, 2 H), 7.55 (d, *J* = 0.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.53 (q), 24.72 (t), 25.92 (t), 26.13 (t), 27.03 (t), 27.54 (t), 28.42 (t), 28.77 (t), 28.86 (t), 28.92 (t), 29.01 (t), 29.06 (t, 2 C), 29.16 (t, 3 C), 29.19 (t), 29.25 (t), 29.59 (t, 2 C), 44.76 (t), 70.35 (t), 70.43 (t), 70.48 (t), 70.57 (t), 102.25 (d), 120.43 (d), 127.38 (d), 127.52 (d), 128.39 (d), 128.58 (d), 128.97 (s), 136.45 (s), 136.77 (s), 141.41 (d), 144.84 (s), 158.05 (s), 201.76 (s) ppm. IR (neat): $\tilde{\nu}$ = 3124, 3029, 2926, 2854, 1765, 1678 (C=O), 1591, 1459, 1364, 1186, 1128, 1096, 942, 801, 752 cm^{-1}. MS (70 eV): *m/z* (%) = 578 (16) [M^+], 459 (14), 379 (100), 135 (50). $C_{38}H_{58}O_4$ (578.88). HRMS calcd. 578.433510, found 578.433140 (MS).

25a: 24a (25.1 mg, 42.5 μmol), $AgNO_3$ (5.0 mg, 29 μmol), acetone (2 mL), column chromatography (H/EE, 6:1). Yield: 19.0 mg (76%). R_f (H/EA, 2:1) = 0.48. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.45−1.51 (m, 2 H), 1.58−1.76 (m, 12 H), 2.61−2.67 (m, 4 H), 3.44−3.50 (m, 8 H), 4.56 (s, 8 H), 5.97 (dd, *J* = 0.8, 3.1 Hz, 2 H), 6.27 (d, *J* = 1.9 Hz, 3.1 Hz, 2 H), 7.25−7.30 (m, 6 H), 7.35−7.40 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.81 (t), 24.65 (t, 2 C), 27.57 (t, 2 C), 29.10 (t, 2 C), 29.47 (t, 2 C), 70.00 (t, 2 C), 70.32 (t, 6 C), 104.62 (d, 2 C), 109.88 (d, 2 C), 127.44 (d, 2 C), 127.47 (d, 2 C), 128.38 (d, 4 C), 136.42 (s, 2 C), 136.52 (s, 2 C), 140.56 (d, 2 C), 155.95 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3114 (Ar−H), 3067 (Ar−H), 3029 (Ar−H), 2937, 2860, 1596, 1505, 1453, 1360, 1094, 1010, 920, 794, 751 cm^{-1}. MS (70 eV): *m/z* (%) = 588 (0.3) [M^+], 448 (2), 344 (5), 242 (27), 206 (17), 183 (32), 123 (45), 104 (100), 81 (56). $C_{37}H_{48}O_6$ (588.79): calcd. 588.34509, found 588.34561 (MS).

26a: Yield: 40.0 mg (27%). R_f (H/EA, 2:1) = 0.34. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.44−1.80 (m, 14 H), 2.41 (d, *J* = 1.0 Hz, 3 H), 2.48−2.54 (m, 2 H), 2.61−2.66 (m, 2 H), 3.44−3.53 (m, 8 H), 4.57 (s, 4 H), 4.58 (s, 4 H), 6.21 (s, 1 H), 6.40 (s, 1 H), 7.25−7.32 (m, 4 H), 7.33−7.41 (m, 4 H), 7.54 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.61 (q), 21.55 (t), 22.83 (t), 24.23 (t), 27.40 (t), 28.87 (t, 2 C), 29.47 (t, 2 C), 44.35 (t), 69.76 (t, 2 C), 70.35 (t, 4 C), 70.54 (t), 70.70 (t), 102.46 (d), 120.38 (d), 127.43 (d), 127.49 (d), 127.60 (d), 127.66 (d), 128.40 (d), 128.51 (d), 128.69 (d, 2 C), 128.98 (s), 136.21 (s), 136.32 (s), 136.65 (s), 136.77 (s), 141.42 (d), 144.99 (s), 157.73 (s), 201.24 (s) ppm. IR (neat): $\tilde{\nu}$ = 3066 (Ar−H), 3029 (Ar−H), 2936, 2861, 1763, 1678 (C=O), 1590, 1452, 1363, 1187, 1096, 914, 801, 752 cm^{-1}. MS (70 eV): *m/z* (%) = 588 (16) [M^+], 487 (10), 469 (12), 397 (14), 381 (10), 119 (63), 105 (100). $C_{37}H_{48}O_6$ (588.79). calcd. 588.34509, found 588.345610 (MS).

25b: 24b (93.0 mg, 105 μmol), $AgNO_3$ (2.5 mg, 15 μmol), acetone (2 mL), column chromatography (H/EE, 20:1). Yield: 57.8 mg (62%). R_f (H/EA, 5:1) = 0.64. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.27 (br. s, 44 H), 1.56−1.63 (m, 12 H), 2.61 (t, *J* = 7.6 Hz, 4 H), 3.47 (t, *J* = 6 Hz, 8 H), 4.57 (s, 8 H), 5.96−5.97 (m, 2 H), 6.26−6.28 (m, 2 H), 7.24−7.31 (m, 6 H), 7.36−7.41 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 26.14 (t, 4 C), 27.84 (t, 2 C), 27.90 (t, 2 C), 29.05 (t, 2 C), 29.23 (t, 2 C), 29.35 (t, 2 C), 29.39 (t, 4 C), 29.44 (t, 4 C), 29.49 (t, 4 C), 29.68 (t, 4 C), 70.31 (t, 4 C), 70.52 (t, 4 C), 104.36 (d, 2 C), 109.86 (d, 2 C), 127.42 (d, 4 C), 128.37 (d, 4 C), 136.58 (s, 4 C), 140.44 (d, 2 C), 156.44 (s, 2 C) ppm. IR (neat): $\tilde{\nu}$ = 3113 (Ar−H), 3066 (Ar−H), 3028 (Ar−H), 2926, 2854, 1596, 1506, 1459, 1361, 1096, 1008, 917, 794, 749 cm^{-1}. MS (70 eV): *m/z* (%) = 883 (0.4) [M^+], 644 (6), 442 (14), 340 (100), 304 (12), 237 (13), 120 (33), 105 (25). $C_{58}H_{90}O_6$ (883.35): calcd. C 78.86, H 10.27; found C 78.69, H 10.23.

26b: Yield: 44.2 mg (20%). R_f (H/EA, 5:1) = 0.30. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.28 (br. s, 44 H), 1.57−1.65 (m, 12 H), 2.41 (d, *J* = 1.0 Hz, 3 H), 2.49 (t, *J* = 7 Hz, 2 H), 2.61 (t, *J* =

7.4 Hz, 2 H), 3.48 (t, J = 6.5 Hz, 8 H), 4.57 (s, 4 H), 4.58 (s, 4 H), 6.21 (s, 1 H), 6.41 (d, J = 1.0 Hz, 1 H), 7.25−7.30 (m, 4 H), 7.35−7.41 (m, 4 H), 7.55 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.16 (q), 24.98 (t), 26.59 (t, 1 C), 26.65 (t, 2 C), 27.94 (t), 28.26 (t), 29.29 (t), 29.60 (t, 2 C), 29.64 (t), 29.72 (t, 3 C), 29.75 (t, 3 C), 29.79 (t, 2 C), 29.85 (t, 4 C), 29.97 (t, 3 C), 30.11 (t, 2 C), 30.17 (t, 2 C), 45.30 (t), 70.91 (t, 2 C), 70.98 (t, 4 C), 71.04 (t, 2 C), 102.82 (d), 121.11 (d), 127.95 (d, 2 C), 128.00 (d, 2 C), 128.96 (d, 2 C), 129.04 (d, 2 C), 129.51 (s), 137.09 (s, 2 C), 137.22 (s, 2 C), 141.80 (d), 145.26 (s), 158.63 (s), 202.01 (s) ppm. IR (neat): $\tilde{\nu}$ = 3065 (Ar−H), 3029 (Ar−H), 2926, 2854, 1765, 1680 (C=O), 1592, 1458, 1362, 1186, 1097, 944, 800, 752 cm^{-1}. MS (70 eV): m/z (%) = 882 (36) [M$^+$], 683 (36), 577 (29), 379 (80), 119 (58), 105 (100). $C_{58}H_{90}O_6$ (883.35). calcd. 882.67374, found 882.67336 (MS).

12. Transformation of 27b to 28b

$[Cl_2(PCy_3)_2Ru{=}CH{-}C{=}CPh_2]$ (16.1 mg, 20.1 μmol) was added to **27b** (143 mg, 401 μmol) in DCM (40 mL). The solution was stirred at room temperature until TLC demonstrated the complete consumption of the starting material. Evaporation of the solvent and column chromatography of the crude product on silica gel delivered **28b** (44.3 mg, 31%) as a colorless oil.

28b: R_f(H/EA, 10:1) = 0.29. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.20 (m, 16 H), 1.55−1.70 (m, 4 H), 1.92−2.01 (m, 4 H), 2.35−2.41 (m, 5 H), 2.58 (t, J = 6.7 Hz, 2 H), 5.28−5.32 (m, 2 H), 6.15 (br. s, 1 H), 6.39 (br. s, 1 H), 7.51 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.4/16.5, (25.7, 25.8, 26.2, 26.8, 26.9, 27.3, 27.6, 27.7, 27.9, 28.0, 28.3, 28.4, 28.5, 28.6, 28.7, 29.0, 29.2, 29.2, 29.3), 32.1/32.2, 44.6/44.8, 102.4/102.5, 120.2/120.6, 129.0/129.7, 130.2/130.3, 141.5/141.6, 145.2, 157.7/157.8, 202.5/202.3 ppm. $C_{24}H_{36}O_2$ (356.6).

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