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Nickel-Catalyzed Homocoupling of (*Z*)-β-Iodoenol Esters: Stereoselective Access to (*Z*,*Z*)-Buta-1,3-diene-1,4-diyl Diesters

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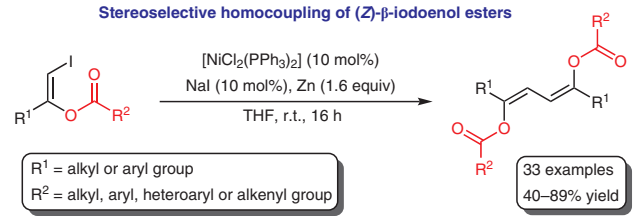
Dedicated to Prof. Pablo Espinet on the occasion of his 70th birthday



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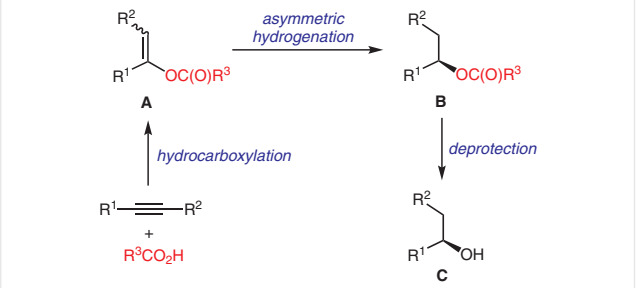
Abstract A straightforward and broad-scope procedure to obtain symmetrically substituted buta-1,3-diene-1,4-diyl diesters, based on the homocoupling of the corresponding (*Z*)-β-iodoenol esters, is presented. It involves the use of a catalytic system composed of $[NiCl_2(PPh_3)_2]$ (10 mol%), NaI (10 mol%), and excess of Zn dust. The reactions proceed in THF at room temperature with exquisite preservation of the stereochemistry of the C=C bond of the starting iodoolefins, thus leading to the final dienes as the corresponding *Z*,*Z*-stereoisomers exclusively.

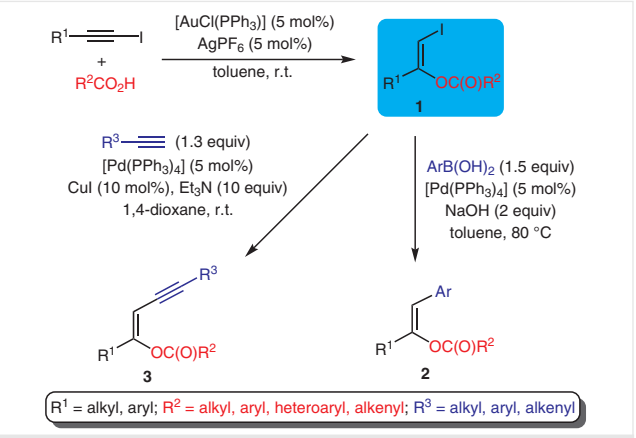
Key words homocoupling reactions, nickel, iodoalkenes, buta-1,3-dienes, enol esters, diesters

Enol esters **A** are an important class of compounds widely employed as substrates and intermediates in organic chemistry.[1] In particular, much attention has been devoted to the asymmetric hydrogenation of these molecules, since the resulting saturated esters **B** can be easily converted into synthetically relevant chiral alcohols **C** through a trivial deacylation process (Scheme 1).[2]



Scheme 1 Synthesis and asymmetric hydrogenation of enol esters

Among the different methods currently available for the synthesis of enol esters **A**,[3] the addition of carboxylic acids to alkynes catalyzed by transition metal complexes is probably the most versatile and appealing one, due to its complete atom economy and substrate availability (Scheme 1).[4,5] In this regard, in the context of our studies on this type of hydrocarboxylation processes,[6] we recently developed a wide scope procedure for the synthesis of (*Z*)-β-iodoenol esters **1** through the regio- and stereoselective intermolecular addition of carboxylic acids to iodoalkynes catalyzed by gold(I) (Scheme 2).[6d,f,g] Compounds **1** proved to be useful starting materials for the preparation of a large variety of stereochemically defined β-arylvinyl esters **2**[6d,g] and enynyl esters **3**[6f] via Suzuki and Sonogashira cross-coupling reactions, respectively (Scheme 2). In addition, in collaboration with Pizzano's group (IIQ-Seville), we also studied the asymmetric hydrogenation of **2** using Rh catalysts, which allowed the access to the corresponding chiral homobenzylic esters with high enantioselectivity levels.[6d,g]



Scheme 2 Synthesis and palladium-catalyzed C–C couplings of (*Z*)-β-iodoenol esters **1**

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In this work, the synthetic utility of the (*Z*)-β-iodoenol esters **1** is further demonstrated with their successful involvement in homocoupling reactions to generate symmetrically substituted (*Z*,*Z*)-buta-1,3-diene-1,4-diyl diesters **4** (Figure 1).[7] This type of conjugated dienes are scarcely represented in the literature. In fact, to the best of our knowledge, only five examples are currently known, with only one of them featuring the same stereochemistry as compounds **4** (Figure 1).[8]

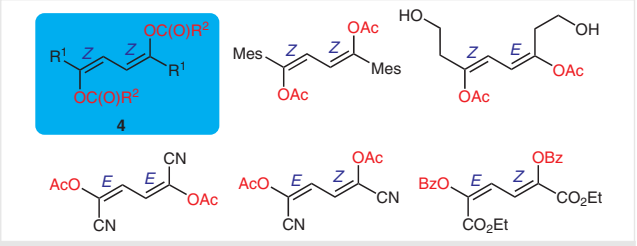
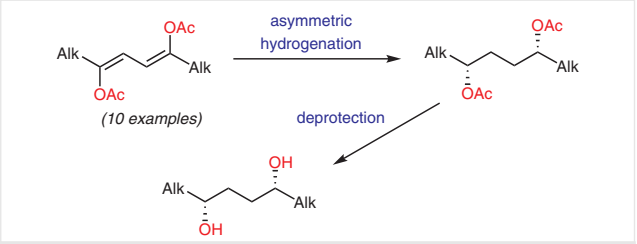


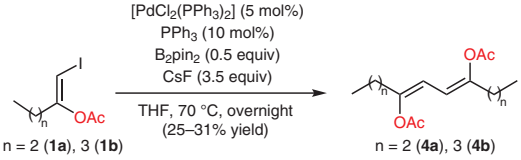
Figure 1 The generic structure of compounds **4** and that of related buta-1,3-dienes reported in the literature

On the other hand, we would like also to stress that, as we have very recently communicated employing a small family of alkyl-substituted diacetates (Scheme 3), the asymmetric hydrogenation of dienes **4** can open new routes for the synthesis of C_2 symmetric 1,4-diols, key building blocks in the preparation of a broad range of chiral heterocycles.[9] Herein, a full report on the preparation of (*Z*,*Z*)-buta-1,3-diene-1,4-diyl diesters **4** is presented.



Scheme 3 Access to C_2 symmetric 1,4-diols from (*Z*,*Z*)-buta-1,3-diene-1,4-diyl diacetates

Initial attempts to promote the homocoupling of the (*Z*)-β-iodoenol esters **1** with copper(I) thiophene-2-carboxylate (CuTC),[10] a reagent with proven effectiveness in reductive homocoupling reactions of aryl, heteroaryl, and alkenyl halides,[11] failed. Thus, regardless of the stoichiometry, solvent, and temperature employed, the starting iodoolefins were recovered unchanged. Different palladium-based methodologies described in the literature were also tested with little success.[12] Among them, only the one developed by Eddarir and Rolando led to the desired 1,3-dienes.[12b] However, as shown in Scheme 4 for the representative substrates **1a**,**b**, the yields were very low and all attempts to improve them by changing the reaction parameters (solvent, temperature, time, and amounts of reagents) were unsuccessful.



Scheme 4 Pd-catalyzed homocoupling of the (*Z*)-β-iodoenol esters **1a**,**b**. B_2pin_2 = bis(pinacolato)diboron.

The use of stoichiometric or catalytic amounts of zerovalent nickel complexes for homocoupling reactions of alkenyl halides is well documented, and this methodology is the one that led to the best results in the present case.[13] Thus, as shown in Table 1, the treatment of a THF solution of (*Z*)-1-iodopent-1-en-2-yl acetate (**1a**) with 30 mol% of $[NiCl_2(PPh_3)_2]$, in the presence of Zn powder (2 equiv) as the reductant and Bu_4NI (1 equiv) as an additive to assist the reduction of Ni(II) to Ni(0),[13c,f] for 16 hours resulted in the clean formation of the desired diene **4a**, which was isolated in 67% yield after appropriate chromatographic workup (Table 1, entry 1). Interestingly, the reaction gives **4a** as the corresponding *Z*,*Z*-isomer exclusively, indicating that *Z* → *E* isomerization of the starting iodoolefin does not take place along the process.[13f] Reduction of the nickel loading to 10 mol% led practically to the same result (entry 2), while the use of only 5 mol% of $[NiCl_2(PPh_3)_2]$ resulted in a significant decrease in the effectiveness of the process (entry 3). Additional experiments also revealed the need to include the three components of the catalytic system for the reaction to proceed efficiently (entries 4–6). On the other hand, as shown in entry 7, the addition of extra PPh_3 to the reaction medium did not lead to significant changes in the yield of **4a**.[13c,f] Alternative nickel sources, for example, $NiCl_2$ and $[NiCl_2(glyme)]$, were also explored and resulted less effective than $[NiCl_2(PPh_3)_2]$ (entries 8, 9). On the contrary, the use of inorganic iodide sources instead of Bu_4NI allowed to improve the yield of **4a** (entries 10, 11). In particular, the best results were obtained with NaI, which led to **4a** in >80% yield even when only 10 mol% was added to the reaction medium (entries 11–14). As shown in entry 14, under these conditions, it was also possible to reduce the quantity of Zn employed (82% yield). Finally, other solvents, such as toluene or CH_2Cl_2, were also screened but resulted less effective (entries 15, 16 vs entry 14).

With the optimized reaction conditions in hand (Table 1, entry 14), the scope of the process was next explored. In this regard, the behavior of a series of (*Z*)-β-iodoenol acetates **1b–o** was first investigated (Scheme 5). Thus, as observed for **1a**, other iodoolefins containing alkyl and cycloalkyl substituents **1b–h** could be successfully converted into the corresponding buta-1,3-diene-1,4-diyl diacetates **4b–h** in high yields (71–89%). Good results were also ob-

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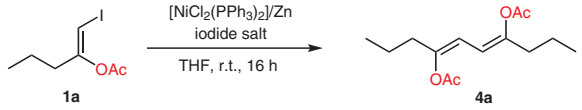
Table 1 Nickel-Catalyzed Homocoupling of the (*Z*)-β-Iodoenol Acetate **1a**: Optimization of the Reaction Conditions[a]



Entry	$[NiCl_2(PPh_3)_2]$ (mol%)	Iodide salt	Zn (equiv)	Yield (%)[b]
1	30	Bu_4NI (1 equiv)	2	67
2	10	Bu_4NI (1 equiv)	2	65
3	5	Bu_4NI (1 equiv)	2	33
4	10	–	2	27
5	10	Bu_4NI (1 equiv)	–	0
6	–	Bu_4NI (1 equiv)	2	0
7[c]	10	Bu_4NI (1 equiv)	2	63
8[d]	10	Bu_4NI (1 equiv)	2	48
9[e]	10	Bu_4NI (1 equiv)	2	62
10	10	KI (1 equiv)	2	75
11	10	NaI (1 equiv)	2	84
12	10	NaI (50 mol%)	2	84
13	10	NaI (10 mol%)	2	83
14	10	NaI (10 mol%)	1.6	82
15[f]	10	NaI (10 mol%)	1.6	65
16[g]	10	NaI (10 mol%)	1.6	47

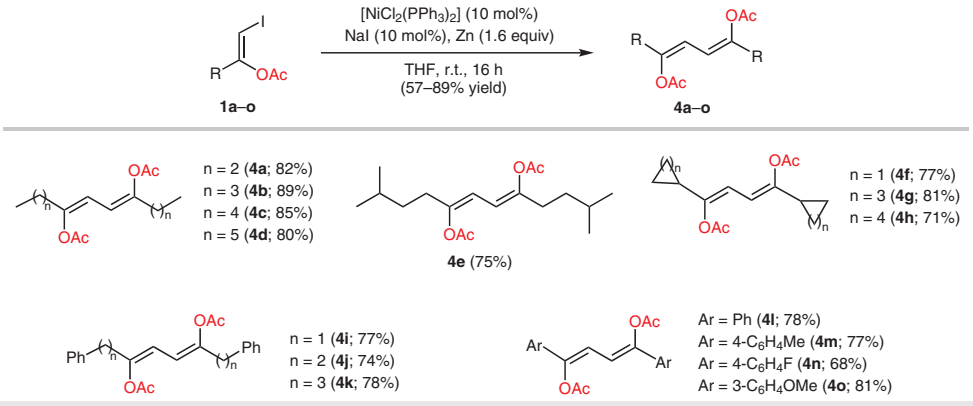
[a] Reactions performed under argon atmosphere for 16 h employing 1 mmol of **1a** and 5 mL of anhyd THF.
[b] Isolated yield after chromatographic workup is given.
[c] Reaction performed in the presence of free PPh_3 (20 mol%).
[d] Reaction performed employing $NiCl_2$ instead of $[NiCl_2(PPh_3)_2]$.
[e] Reaction performed employing $[NiCl_2(glyme)]$ instead of $[NiCl_2(PPh_3)_2]$.
[f] Reaction performed in toluene.
[g] Reaction performed in CH_2Cl_2.

tained employing substrates bearing phenyl-substituted alkyl groups (**1i–k**) and those generated by addition of acetic acid to aromatic iodoalkynes (**1l–o**), the resulting dienes **4i–o** being isolated in 68–81% yield. Remarkably, all these homocoupling reactions proceeded with complete preservation of the stereochemistry of the C=C bond of the starting iodoolefins **1**, leading to compounds **4** as the corresponding *Z*,*Z*-stereoisomers exclusively. In this regard, the ^1H and ^{13}C NMR spectra confirmed the equivalence of the two CH=CR(OAc) units of **4a–o**, with singlet signals at δ = 5.58–6.64 and δ = 107.3–110.7 (=CH) and 146.9–154.0 (=C) being characteristic fingerprints of the symmetrically substituted 1,3-dienic units (see details in the Experimental Section). In addition, the molecular structure of (*Z*,*Z*)-1,4-dicyclopentylbuta-1,3-diene-1,4-diyl diacetate (**4g**) was also determined by X-ray diffraction analysis, for which good quality crystals could be obtained by slow diffusion of hexane into a saturated solution of the compound in ethyl acetate.[14] An ORTEP-type drawing of the molecule, along with selected bonding parameters, is shown in Figure 2. The C(3)–C(4) and C(4)–C(4a) bond lengths observed [1.330(2) and 1.449(3) Å, respectively] fit well with those of the parent unsubstituted 1,3-butadiene molecule (C=C = 1.341 Å and C–C = 1.463 Å).[15]

On the other hand, although all the reactions collected in Scheme 5 were systematically carried out on a 1 mmol scale, they can be scaled up without major problems. As a representative example, a reaction conducted with (*Z*)-1-iodooct-1-en-2-yl acetate (**1d**) on a 10 mmol scale (2.96 g) allowed the preparation of 1.32 g (78% yield) of (*Z*,*Z*)-hexadeca-7,9-diene-7,10-diyl diacetate (**4d**).

Finally, in order to assess in more detail the scope of the process, the homocoupling of a series of (*Z*)-1-iodohex-1-en-2-yl esters **1p–ag**, featuring different aliphatic, aromatic, heteroaromatic, heterocyclic and α,β-unsaturated substituents on the carboxylate unit, was explored under identical experimental conditions (Scheme 6). To our delight, the catalytic reaction proved to be broadly applicable, and the novel 1,3-dienes **4p–ag** could be synthesized with complete stereoselectivity in moderate to good yields (40–89%).

Concerning the mechanism of the present homocoupling process, we assume that it proceeds through the reaction pathway proposed by Takagi and co-workers (Scheme



Scheme 5 Nickel-catalyzed homocoupling of (*Z*)-β-iodoenol acetates **1a–o**. Isolated yields after column chromatography are given.

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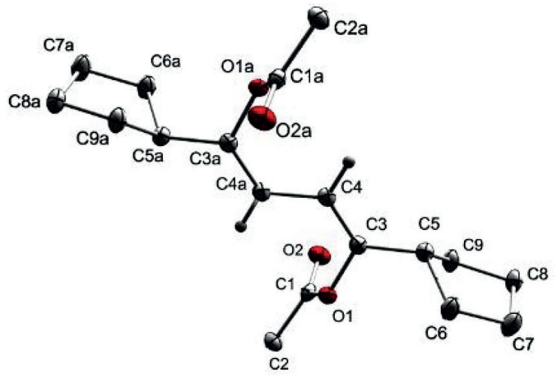
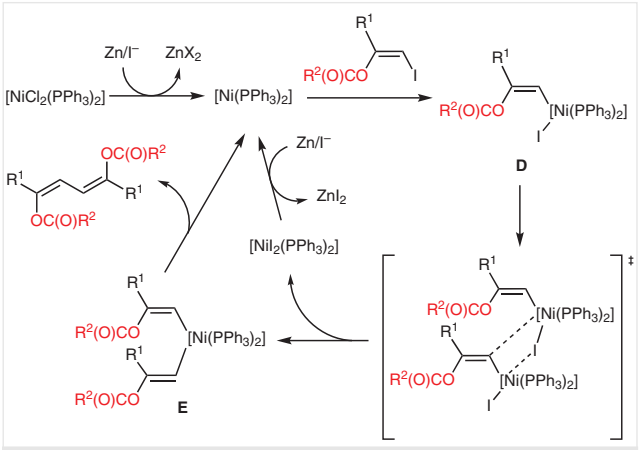


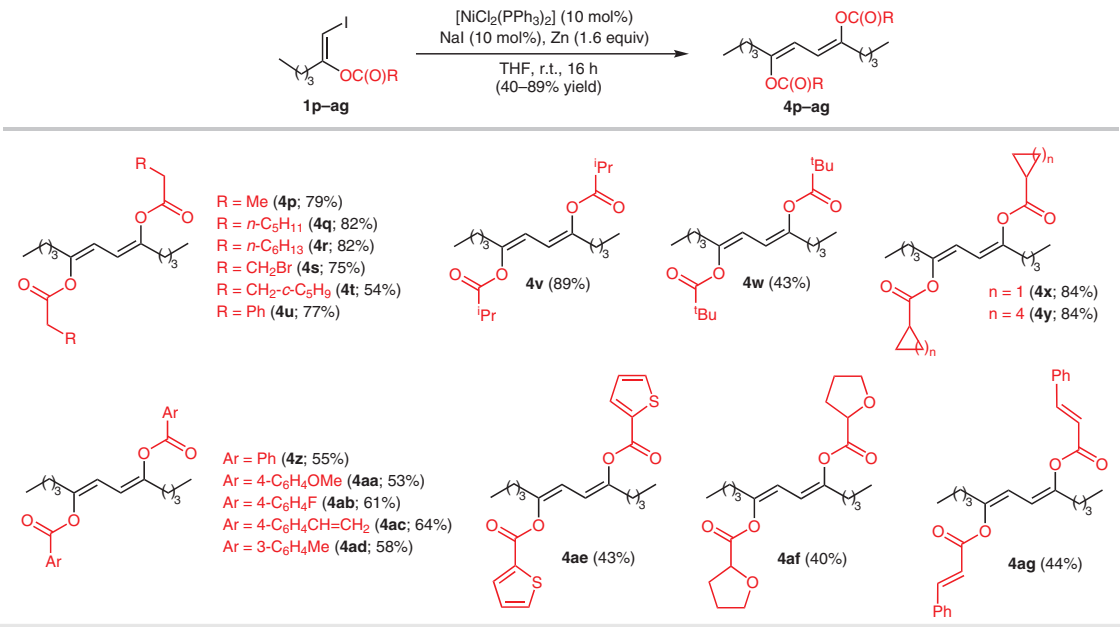
Figure 2 ORTEP-type view of the structure of diene **4g** showing the crystallographic labeling scheme. Hydrogen atoms, except those on C(4) and C(4a), have been omitted for clarity. The atoms labeled with 'a' are generated by symmetry. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): C(1)–O(1) 1.365(2), C(1)–O(2) 1.199(2), C(1)–C(2) 1.488(2), C(3)–O(1) 1.410(2), C(3)–C(4) 1.330(2), C(3)–C(5) 1.493(2), C(4)–C(4a) 1.449(3). Selected bond angles (°): O(1)–C(1)–O(2) 122.7(2), O(1)–C(1)–C(2) 110.7(2), O(2)–C(1)-–(2) 126.6(2), C(1)–O(1)–C(3) 117.9(1), O(1)–C(3)–C(4) 119.3(1), O(1)–C(3)–C(5) 114.3(1), C(3)–C(5)–C(6) 114.5(1), C(3)–C(5)–C(9) 116.1(1), C(3)–C(4)–C(4a) 125.3(2).

7).[16] It would involve the oxidative addition of the β-iodoenol ester to in situ formed Ni(0)-phosphine species generated by reduction of $[NiCl_2(PPh_3)_2]$ with Zn, a process that is facilitated by the NaI present in the reaction medium. Subsequent disproportionation of intermediate **D** thus formed, would generate the corresponding bis(alkenyl)-Ni(II) derivative **E**, which undergoes reductive elimination to form the final diene product. In this disproportionation step, $[NiI_2(PPh_3)_2]$ is also generated and reduced by the Zn powder to ensure the catalytic cycle.



Scheme 7 Proposed mechanism for the homocoupling process

Regarding the stereoselectivity of the process, as discussed by Takagi and co-workers,[16] both the oxidative addition and reductive elimination steps are known to proceed with retention of configuration of the alkenyl group. The exclusive formation of the *Z*,*Z*-stereoisomers implies that, unlike what is usually observed with other alkenyl halides,[13,16] no isomerization of the C=C bond takes place in the present case at the disproportionation stage. Although we have no conclusive explanation for this, we suspect that



Scheme 6 Nickel-catalyzed homocoupling of (*Z*)-β-iodoenol esters **1**: Scope of the process concerning the nature of the carboxylate group. Isolated yields after column chromatography are given.

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a potential interaction/coordination of the ester groups to Ni could be responsible for the high stereoselectivity observed.

In summary, we have developed a general and inexpensive protocol for the preparation of buta-1,3-diene-1,4-diyl diesters, a family of underrepresented conjugated dienes, from readily accessible (*Z*)-β-iodoenol esters. The catalytic homocoupling of the latter proceeded cleanly, and under mild conditions, in the presence of zero-valent nickel species generated in situ by combining $[NiCl_2(PPh_3)_2]$, NaI, and Zn dust. Exquisite preservation of the stereochemistry of the C=C bond of the starting iodoolefins was observed in all the cases, and the reactions lead to the 1,3-diene products in a completely stereospecific manner with isolated yields ranging from 40% to 89%.

All reactions were performed under an argon atmosphere using standard Schlenk-type techniques. Solvents were distilled under argon with Na-benzophenone-ketyl (for Et_2O and THF) or Na (for hexanes). The (*Z*)-β-iodoenol esters **1** were synthesized by hydrocarboxylation of the corresponding iodoalkyne as previously described by us (Scheme 2).[6f] Characterization data for compounds **1o–y**,**aa–ag**, not previously reported, have been included in the Supporting Information. $[NiCl_2(PPh_3)_2]$ was prepared by following the method described in the literature.[17] All other reagents were purchased from commercial suppliers and used as received. IR spectra were recorded on a PerkinElmer 1720-XFT spectrophotometer. NMR spectra were obtained on Bruker DPX-300 or AV-400 spectrometer. $^{13}C\{^1H\}$ and ^1H chemical shifts were referenced to the residual signal of deuterated solvent. All data are reported in ppm downfield from $(CH_3)_4Si$. For $^{19}F\{^1H\}$ NMR spectra, the chemical shifts were referenced to the $CFCl_3$ standard. All NMR measurements were carried out at 25 °C. HRMS data were obtained on a ESI-q-TOF Bruker Impact II mass spectrometer. For column chromatography, Merck silica gel 60 (230–400 mesh) was employed.

(*Z*,*Z*)-Buta-1,3-diene-1,4-diyl Diesters 4; General Procedure

A suspension of $[NiCl_2(PPh_3)_2]$ (0.065 g, 0.1 mmol), NaI (0.015 g, 0.1 mmol), and Zn dust (0.105 g, 1.6 mmol) in THF (5 mL) was stirred at r.t. for 30 min. After this time, a solution of the corresponding (*Z*)-β-iodoenol ester **1** (1 mmol) in THF (2 mL) was added and the resulting mixture was stirred further at r.t. for 16 h. The solvent was then removed under reduced pressure, and the crude reaction mixture directly purified by flash column chromatography over silica gel, using hexanes/Et_2O (10:1) as eluent, to provide the respective desired product **4**.

(*Z*,*Z*)-Deca-4,6-diene-4,7-diyl Diacetate (4a)

White solid; yield: 0.104 g (0.409 mmol, 82%); mp 61–63 °C.

IR (KBr): 2960, 2872, 1750, 1645, 1435, 1376, 1260, 1200, 1112, 1038, 1010, 942, 820, 721, 610, 577, 541, 500, 461 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 5.61 (s, 2 H, =CH), 2.21 (t, *J* = 7.5 Hz, 4 H, CH_2), 2.15 (s, 6 H, CH_3), 1.53–1.41 (m, 4 H, CH_2), 0.88 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.5, 149.6, 109.2, 35.6, 20.7, 19.9, 13.5.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{14}H_{22}O_4Na$: 277.1410; found: 277.1406.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Diacetate (4b)

White solid; yield: 0.126 g (0.446 mmol, 89%); mp 57–59 °C.

IR (KBr): 2954, 2870, 1760, 1647, 1430, 1371, 1200, 1099, 1024, 933, 878, 831, 785, 735, 692, 611, 573, 504, 490 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.64 (s, 2 H, =CH), 2.26 (t, *J* = 7.2 Hz, 4 H, CH_2), 2.19 (s, 6 H, CH_3), 1.44–1.40 (m, 4 H, CH_2), 1.35–1.31 (m, 4 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.9, 109.0, 33.3, 28.7, 22.1, 20.8, 13.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{27}O_4$: 283.1904; found: 283.1908.

(*Z*,*Z*)-Tetradeca-6,8-diene-6,9-diyl Diacetate (4c)

White solid; yield: 0.132 g (0.425 mmol, 85%); mp 60–62 °C.

IR (KBr): 2959, 2873, 1745, 1646, 1466, 1428, 1374, 1201, 1102, 1046, 1015, 934, 880, 853, 815, 730, 610, 576, 489 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 5.65 (s, 2 H, =CH), 2.27 (t, *J* = 7.2 Hz, 4 H, CH_2), 2.21 (s, 6 H, CH_3), 1.48–1.43 (m, 4 H, CH_2), 1.32–1.29 (m, 8 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.9, 109.1, 33.6, 31.2, 26.3, 22.4, 20.8, 14.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{30}O_4Na$: 333.2036; found: 333.2034.

(*Z*,*Z*)-Hexadeca-7,9-diene-7,10-diyl Diacetate (4d)

White solid; yield: 0.135 g (0.399 mmol, 80%); mp 48–51 °C.

IR (KBr): 2925, 2857, 1754, 1643, 1438, 1374, 1201, 1130, 1018, 933, 871, 809, 722, 622, 578, 554, 465 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.63 (s, 2 H, =CH), 2.25 (t, *J* = 7.6 Hz, 4 H, CH_2), 2.19 (s, 6 H, CH_3), 1.44–1.41 (m, 4 H, CH_2), 1.27 (br, 12 H, CH_2), 0.88 (t, *J* = 6.0 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.9, 109.1, 33.6, 31.6, 28.7, 26.6, 22.5, 20.8, 14.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{34}O_4Na$: 361.2349; found: 361.2351.

(*Z*,*Z*)-2,11-Dimethyldodeca-5,7-diene-5,8-diyl Diacetate (4e)

White solid; yield: 0.116 g (0.373 mmol, 75%); mp 65–67 °C.

IR (KBr): 2952, 2864, 1747, 1650, 1470, 1441, 1372, 1261, 1216, 1131, 1098, 1017, 935, 906, 856, 810, 767, 671, 614, 590, 543, 478 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2 H, =CH), 2.27 (t, *J* = 7.5 Hz, 4 H, CH_2), 2.21 (s, 6 H, CH_3), 1.59–1.53 (m, 2 H, CH), 1.38–1.30 (m, 4 H, CH_2), 0.89 (d, *J* = 6.6 Hz, 12 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 150.1, 108.9, 35.6, 31.6, 27.6, 22.4, 20.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{30}O_4Na$: 333.2036; found: 333.2040.

(*Z*,*Z*)-1,4-Dicyclopropylbuta-1,3-diene-1,4-diyl Diacetate (4f)

White solid; yield: 0.096 g (0.383 mmol, 77%); mp 53–55 °C.

IR (KBr): 3095, 3019, 2929, 1751, 1635, 1559, 1436, 1374, 1261, 1194, 1156, 1043, 1008, 932, 885, 802, 656, 613, 574, 502 cm^{-1}.

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^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.66 (s, 2 H, =CH), 2.21 (s, 6 H, CH_3), 1.65–1.56 (m, 2 H, CH), 0.72–0.66 (m, 4 H, CH_2), 0.61–0.58 (m, 4 H, CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.8, 108.3, 20.6, 14.3, 5.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{18}O_4Na$: 273.1097; found: 273.1100.

(*Z*,*Z*)-1,4-Dicyclopentylbuta-1,3-diene-1,4-diyl Diacetate (4g)

White solid; yield: 0.124 g (0.405 mmol, 81%); mp 60–62 °C.

IR (KBr): 2961, 2870, 1751, 1638, 1436, 1376, 1207, 1137, 1017, 950, 890, 857, 822, 720, 640, 571, 538, 432 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2 H, =CH), 2.75–2.64 (m, 2 H, CH), 2.20 (s, 6 H, CH_3), 1.81 (br, 4 H, CH_2), 1.66–1.46 (m, 12 H, CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.7, 152.4, 107.8, 44.1, 30.5, 24.8, 20.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{26}O_4Na$: 329.1723; found: 329.1726.

(*Z*,*Z*)-1,4-Dicyclohexylbuta-1,3-diene-1,4-diyl Diacetate (4h)

White solid; yield: 0.119 g (0.356 mmol, 71%); mp 57–59 °C.

IR (KBr): 2950, 2873, 1753, 1635, 1440, 1377, 1215, 1200, 1140, 1009, 964, 901, 845, 811, 743, 654, 592, 555, 449 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.58 (s, 2 H, =CH), 2.22 (s, 6 H, CH_3), 2.19–2.14 (m, 2 H, CH), 1.89–1.66 (m, 10 H, CH_2), 1.32–1.08 (m, 10 H, CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.7, 154.0, 107.3, 42.0, 30.6, 26.0, 25.9, 20.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{30}O_4Na$: 357.2036; found: 357.2035.

(*Z*,*Z*)-1,6-Diphenylhexa-2,4-diene-2,5-diyl Diacetate (4i)

White solid; yield: 0.135 g (0.385 mmol, 77%); mp 102–104 °C.

IR (KBr): 3070, 3026, 2952, 1748, 1635, 1494, 1455, 1436, 1364, 1202, 1151, 1114, 1014, 943, 877, 794, 751, 705, 633, 594, 564, 472 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33–7.21 (m, 10 H, ArH), 5.68 (s, 2 H, =CH), 3.63 (s, 4 H, CH_2), 2.06 (s, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.5, 149.2, 136.6, 129.2, 128.5, 126.8, 110.7, 39.9, 20.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}O_4Na$: 373.1410; found: 373.1415.

(*Z*,*Z*)-1,8-Diphenylocta-3,5-diene-3,6-diyl Diacetate (4j)

White solid; yield: 0.140 g (0.370 mmol, 74%); mp 97–99 °C.

IR (KBr): 3061, 3023, 2898, 1737, 1651, 1602, 1495, 1431, 1372, 1358, 1266, 1220, 1102, 1026, 947, 857, 790, 741, 697, 608, 583, 556, 491 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38–7.19 (m, 10 H, ArH), 5.67 (s, 2 H, =CH), 2.81 (t, *J* = 7.8 Hz, 4 H, CH_2), 2.62 (t, *J* = 7.8 Hz, 4 H, CH_2), 2.13 (s, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.3, 140.9, 128.4, 128.3, 126.1, 109.6, 35.3, 33.1, 20.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{26}O_4Na$: 401.1723; found: 401.1725.

(*Z*,*Z*)-1,10-Diphenyldeca-4,6-diene-4,7-diyl Diacetate (4k)

White solid; yield: 0.158 g (0.388 mmol, 78%); mp 107–109 °C.

IR (KBr): 3023, 2944, 2860, 1746, 1644, 1602, 1498, 1462, 1369, 1204, 1121, 1018, 932, 882, 827, 798, 752, 701, 614, 576, 535, 498, 461 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.20 (m, 10 H, ArH), 5.70 (t, *J* = 4.3 Hz, 2 H, =CH), 2.67 (t, *J* = 7.4 Hz, 4 H, CH_2), 2.38–2.35 (m, 4 H, CH_2), 2.22 (s, 6 H, CH_3), 1.85–1.82 (m, 4 H, CH_2).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.4, 141.8, 128.5, 128.4, 125.9, 109.6, 35.1, 33.2, 28.2, 20.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{30}O_4Na$: 429.2036; found: 429.2040.

(*Z*,*Z*)-1,4-Diphenylbuta-1,3-diene-1,4-diyl Diacetate (4l)

Pale yellow solid; yield: 0.126 g (0.391 mmol, 78%); mp 170–172 °C.

IR (KBr): 3079, 2929, 1757, 1610, 1574, 1492, 1447, 1367, 1200, 1185, 1040, 1025, 860, 755, 687, 626, 569, 518, 442 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.50–7.36 (m, 10 H, ArH), 6.59 (s, 2 H, =CH), 2.38 (s, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 148.1, 134.6, 128.9, 128.7, 124.7, 110.4, 20.7.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{18}O_4Na$: 345.1097; found: 345.1098.

(*Z*,*Z*)-1,4-Bis(4-methylphenyl)buta-1,3-diene-1,4-diyl Diacetate (4m)

White solid; yield: 0.135 g (0.385 mmol, 77%); mp 175–177 °C.

IR (KBr): 3070, 3032, 2921, 1769, 1612, 1504, 1371, 1210, 1194, 1175, 1034, 1014, 882, 810, 664, 606, 564, 541, 469 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (d, *J* = 8.1 Hz, 4 H, ArH), 7.19 (d, *J* = 8.1 Hz, 4 H, ArH), 6.53 (s, 2 H, =CH), 2.38 (s, 12 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 147.9, 138.9, 131.8, 129.4, 124.6, 109.6, 21.3, 20.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}O_4Na$: 373.1410; found: 373.1412.

(*Z*,*Z*)-1,4-Bis(4-fluorophenyl)buta-1,3-diene-1,4-diyl Diacetate (4n)

Pale yellow solid; yield: 0.122 g (0.340 mmol, 68%); mp 164–166 °C.

IR (KBr): 3070, 2933, 1760, 1614, 1503, 1365, 1230, 1188, 1157, 1041, 913, 878, 836, 820, 753, 609, 566, 533 cm^{-1}.

^{1}H NMR (DMSO-d_6, 300 MHz): δ = 7.67 (br, 4 H, ArH), 7.24 (br, 4 H, ArH), 6.64 (s, 2 H, =CH), 2.43 (s, 6 H, CH_3).

^{13}C NMR (DMSO-d_6, 101 MHz): δ = 169.4, 162.8 (d, *J* = 247.0 Hz), 146.9, 130.9 (d, *J* = 2.8 Hz), 127.4 (d, *J* = 8.2 Hz), 116.1 (d, *J* = 21.8 Hz), 110.5, 21.1.

^{19}F NMR (DMSO-d_6, 282 MHz): δ = –112.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{16}O_4F_2Na$: 381.0909; found: 381.0913.

(*Z*,*Z*)-1,4-Bis(3-methoxyphenyl)buta-1,3-diene-1,4-diyl Diacetate (4o)

White solid; yield: 0.155 g (0.405 mmol, 81%); mp 189–191 °C.

IR (KBr): 3076, 2941, 2839, 1761, 1600, 1575, 1482, 1438, 1372, 1298, 1259, 1210, 1187, 1033, 917, 842, 781, 682, 580, 506 cm^{-1}.

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^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31 (t, *J* = 8.0 Hz, 2 H, ArH), 7.10 (d, *J* = 8.0 Hz, 2 H, ArH), 7.01 (d, *J* = 2.1 Hz, 2 H, ArH), 6.89 (dd, *J* = 8.0, 2.1 Hz, 2 H, ArH), 6.57 (s, 2 H, =CH), 3.85 (s, 6 H, OCH_3), 2.38 (s, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 168.6, 159.8, 147.9, 136.1, 129.8, 117.3, 113.9, 110.9, 110.6, 55.3, 20.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{22}O_6Na$: 405.1309; found: 405.1311.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Dipropionate (4p)

White solid; yield: 0.123 g (0.396 mmol, 79%); mp 55–57 °C.

IR (KBr): 2984, 2939, 2872, 1749, 1645, 1454, 1413, 1364, 1303, 1151, 1130, 931, 869, 822, 807, 731, 558 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.62 (s, 2 H, =CH), 2.47 (q, *J* = 7.5 Hz, 4 H, CH_2), 2.25 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.46–1.28 (m, 8 H, CH_2), 1.21 (t, *J* = 7.5 Hz, 6 H, CH_3), 0.89 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.0, 149.7, 108.9, 33.3, 28.7, 27.5, 22.1, 13.8, 9.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{31}O_4$: 311.2217; found: 311.2219.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Diheptanoate (4q)

Colorless oil; yield: 0.173 g (0.409 mmol, 82%).

IR (film): 2956, 2930, 2860, 1752, 1643, 1467, 1433, 1379, 1210, 1127, 1049, 937, 829, 727 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2 H, =CH), 2.46 (t, *J* = 7.5 Hz, 4 H, CH_2), 2.27 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.77–1.67 (m, 4 H, CH_2), 1.46–1.34 (m, 20 H, CH_2), 0.93–0.89 (m, 12 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 149.8, 109.0, 34.3, 33.4, 31.4, 28.8, 28.7, 25.1, 22.5, 22.1, 14.0, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{46}O_4Na$: 445.3288; found: 445.3287.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Dioctanoate (4r)

White solid; yield: 0.185 g (0.410 mmol, 82%); mp 47–49 °C.

IR (KBr): 2927, 2871, 1742, 1641, 1468, 1418, 1380, 1321, 1271, 1224, 1154, 1123, 938, 877, 842, 770, 720, 580, 481 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2 H, =CH), 2.46 (t, *J* = 7.2 Hz, 4 H, CH_2), 2.27 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.77–1.67 (m, 4 H, CH_2), 1.46–1.32 (m, 24 H, CH_2), 0.91 (t, *J* = 6.9 Hz, 12 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 149.8, 109.0, 34.3, 33.4, 31.7, 29.1, 28.9, 28.7, 25.1, 22.6, 22.1, 14.0, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{50}O_4Na$: 473.3601; found: 473.3595.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(3-bromopropanoate) (4s)

White solid; yield: 0.175 g (0.374 mmol, 75%); mp 66–68 °C.

IR (KBr): 2960, 2941, 2874, 1747, 1643, 1467, 1427, 1336, 1285, 1217, 1132, 1109, 952, 884, 816, 668, 580, 548 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.74 (s, 2 H, =CH), 3.65 (t, *J* = 6.4 Hz, 4 H, CH_2Br), 3.08 (t, *J* = 6.4 Hz, 4 H, CH_2CH_2Br), 2.27 (t, *J* = 7.6 Hz, 4 H, CH_2), 1.46–1.40 (m, 4 H, CH_2), 1.35–1.29 (m, 4 H, CH_2), 0.89 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 168.1, 149.8, 109.3, 37.7, 33.3, 28.7, 25.8, 22.1, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{28}Br_2O_4Na$: 489.0247; found: 489.0247.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(3-cyclopentylpropanoate) (4t)

White solid; yield: 0.121 g (0.271 mmol, 54%); mp 54–56 °C.

IR (KBr): 2951, 2868, 1740, 1649, 1467, 1420, 1381, 1355, 1303, 1262, 1153, 1130, 999, 930, 883, 829, 731, 563, 441 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.63 (s, 2 H, =CH), 2.47 (t, *J* = 7.8 Hz, 4 H, CH_2), 2.26 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.82–1.15 (m, 30 H, CH_2 + CH), 0.90 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.5, 149.8, 109.0, 39.6, 33.6, 33.3, 32.4, 31.3, 28.7, 25.1, 22.1, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{46}O_4Na$: 469.3288; found: 469.3287.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(2-phenylacetate) (4u)

White solid; yield: 0.167 g (0.384 mmol, 77%); mp 56–58 °C.

IR (KBr): 2951, 2848, 1733, 1652, 1454, 1327, 1298, 1231, 1118, 1052, 944, 876, 809, 717, 692, 550, 479 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37–7.30 (m, 10 H, ArH), 5.30 (s, 2 H, =CH), 3.72 (s, 4 H, CH_2), 2.11 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.25–1.21 (m, 8 H, CH_2), 0.86 (t, *J* = 6.6 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.1, 149.8, 133.7, 129.3, 128.7, 127.3, 108.9, 41.6, 33.1, 28.5, 22.1, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{34}O_4Na$: 457.2349; found: 457.2347.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(2-methylpropanoate) (4v)

Colorless oil; yield: 0.151 g (0.446 mmol, 89%).

IR (film): 2959, 2934, 2874, 1753, 1644, 1469, 1386, 1343, 1233, 1182, 1120, 1095, 1052, 935, 828, 748 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2 H, =CH), 2.70 (sept, *J* = 6.9 Hz, 2 H, CH), 2.27 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.43–1.32 (m, 8 H, CH_2), 1.28 (d, *J* = 6.9 Hz, 12 H, CH_3), 0.90 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 174.7, 149.7, 108.8, 34.1, 33.2, 28.6, 22.1, 19.0, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{34}O_4Na$: 361.2349; found: 361.2345.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(2,2-dimethylpropanoate) (4w)

Colorless oil; yield: 0.079 g (0.215 mmol, 43%).

IR (film): 2959, 2933, 2873, 1747, 1645, 1480, 1462, 1396, 1369, 1263, 1114, 1029, 938, 843, 761 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.63 (s, 2 H, =CH), 2.25 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.45–1.31 (m, 8 H, CH_2), 1.27 (s, 18 H, CH_3), 0.90 (t, *J* = 6.9 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 176.1, 149.7, 108.8, 39.1, 33.1, 28.5, 27.2, 22.0, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{38}O_4Na$: 389.2662; found: 389.2655.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Dicyclopropanecarboxylate (4x)

White solid; yield: 0.140 g (0.418 mmol, 84%); mp 64–67 °C.

IR (KBr): 2940, 2870, 1734, 1646, 1456, 1445, 1382, 1307, 1266, 1143, 1124, 1098, 1029, 932, 848, 824, 737, 695, 633, 557, 473 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.65 (s, 2 H, =CH), 2.27 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.75–1.72 (m, 2 H, CH), 1.46–1.30 (m, 8 H, CH_2), 1.13–1.10 (m, 4 H, CH_2), 0.99–0.95 (m, 4 H, CH_2), 0.91 (t, *J* = 7.2 Hz, 6 H, CH_3).

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^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.5, 149.7, 109.0, 33.3, 28.7, 22.1, 13.8, 12.8, 8.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{30}O_4Na$: 357.2036; found: 357.2034.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Dicyclohexanecarboxylate (4y)

White solid; yield: 0.176 g (0.420 mmol, 84%); mp 79–81 °C.

IR (KBr): 2929, 2858, 2669, 1749, 1643, 1451, 1376, 1311, 1241, 1211, 1152, 1117, 1018, 937, 896, 870, 831, 743, 694, 612, 547, 488 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.63 (s, 2 H, =CH), 2.50–2.43 (m, 2 H, CH), 2.25 (t, *J* = 6.3 Hz, 4 H, CH_2), 2.03–1.99 (m, 4 H, CH_2), 1.79–1.32 (m, 24 H, CH_2), 0.90 (t, *J* = 6.9 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.7, 149.7, 108.9, 43.2, 33.3, 29.1, 28.6, 25.7, 25.4, 22.1, 13.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{42}O_4Na$: 441.2975; found: 441.2976.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Dibenzoate (4z)

White solid; yield: 0.112 g (0.275 mmol, 55%); mp 159–161 °C.

IR (KBr): 2955, 2926, 2861, 1724, 1652, 1600, 1452, 1284, 1257, 1238, 1174, 1108, 1064, 1025, 865, 800, 702, 682, 622 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.18 (d, *J* = 7.5 Hz, 4 H, ArH), 7.68–7.51 (m, 6 H, ArH), 5.86 (s, 2 H, =CH), 2.38 (t, *J* = 7.3 Hz, 4 H, CH_2), 1.49–1.44 (m, 4 H, CH_2), 1.36–1.29 (m, 4 H, CH_2), 0.86 (t, *J* = 7.0 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.3, 150.2, 133.5, 130.1, 129.5, 128.6, 109.6, 33.5, 28.8, 22.2, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{30}O_4Na$: 429.2036; found: 429.2039.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(4-methoxybenzoate) (4aa)

White solid; yield: 0.124 g (0.266 mmol, 53%); mp 170–172 °C.

IR (KBr): 2956, 2931, 2872, 1717, 1644, 1605, 1511, 1461, 1321, 1288, 1253, 1165, 1103, 1074, 1028, 844, 766, 694, 599 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.12 (d, *J* = 8.9 Hz, 4 H, ArH), 7.01 (d, *J* = 8.9 Hz, 4 H, ArH), 5.83 (s, 2 H, =CH), 3.92 (s, 6 H, OCH_3), 2.36 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.50–1.40 (m, 4 H, CH_2), 1.38–1.26 (m, 4 H, CH_2), 0.86 (t, *J* = 6.9 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.1, 163.8, 150.1, 132.2, 121.9, 113.8, 109.6, 55.5, 33.5, 28.8, 22.2, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{34}O_6Na$: 489.2253; found: 489.2248.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(4-fluorobenzoate) (4ab)

White solid; yield: 0.135 g (0.305 mmol, 61%); mp 165–167 °C.

IR (KBr): 3079, 2954, 2930, 2872, 1728, 1646, 1603, 1507, 1414, 1280, 1234, 1156, 1104, 1072, 1011, 858, 839, 764, 686, 597 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.18 (dd, *J* = 8.4, 5.4 Hz, 4 H, ArH), 7.20 (t, *J* = 8.4 Hz, 4 H, ArH), 5.81 (s, 2 H, =CH), 2.36 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.47–1.40 (m, 4 H, CH_2), 1.38–1.28 (m, 4 H, CH_2), 0.86 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.1 (d, *J* = 254.9 Hz), 163.3, 150.1, 132.6 (d, *J* = 9.4 Hz), 125.6, 115.8 (d, *J* = 22.0 Hz), 109.5, 33.4, 28.8, 22.1, 13.8.

^{19}F NMR ($CDCl_3$, 282 MHz): δ = –104.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{28}F_2O_4Na$: 465.1848; found: 465.1845.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(4-vinylbenzoate) (4ac)

White solid; yield: 0.147 g (0.320 mmol, 64%); mp 140–142 °C.

IR (KBr): 2953, 2929, 2871, 1721, 1646, 1606, 1466, 1406, 1256, 1236, 1177, 1104, 1076, 1016, 932, 855, 780, 709, 599 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.12 (d, *J* = 8.4 Hz, 4 H, ArH), 7.55 (d, *J* = 8.4 Hz, 4 H, ArH), 6.81 (dd, *J* = 17.4, 11.1 Hz, 2 H, =CH), 5.93 (d, *J* = 17.4 Hz, 2 H, =CH_2), 5.84 (s, 2 H, =CH), 5.45 (d, *J* = 11.1 Hz, 2 H, =CH_2), 2.37 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.50–1.43 (m, 4 H, CH_2), 1.40–1.26 (m, 4 H, CH_2), 0.86 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.9, 150.2, 142.5, 135.9, 130.4, 128.6, 126.3, 116.9, 109.5, 33.5, 28.8, 22.2, 13.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{30}H_{35}O_4$: 459.2530; found: 459.2528.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(3-methylbenzoate) (4ad)

White solid; yield: 0.126 g (0.290 mmol, 58%); mp 162–164 °C.

IR (KBr): 2956, 2928, 2871, 1726, 1611, 1466, 1422, 1286, 1262, 1184, 1107, 916, 882, 810, 778, 737, 679, 622 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.01–7.98 (m, 4 H, ArH), 7.49–7.40 (m, 4 H, ArH), 5.88 (s, 2 H, =CH), 2.48 (s, 6 H, CH_3), 2.40 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.51–1.46 (m, 4 H, CH_2), 1.38–1.31 (m, 4 H, CH_2), 0.88 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.5, 150.2, 138.5, 134.3, 130.6, 129.5, 128.5, 127.2, 109.6, 33.5, 28.8, 22.2, 21.3, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{28}H_{34}O_4Na$: 457.2349; found: 457.2348.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(thiophene-2-carboxylate) (4ae)

White solid; yield: 0.090 g (0.215 mmol, 43%); mp 92–94 °C.

IR (KBr): 2954, 2928, 2861, 1725, 1643, 1519, 1467, 1413, 1359, 1242, 1217, 1101, 1063, 861, 820, 777, 743, 711, 603, 541 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 (dd, *J* = 4.0, 1.2 Hz, 2 H, Thienyl-H), 7.66 (dd, *J* = 5.2, 1.2 Hz, 2 H, Thienyl-H), 7.18 (dd, *J* = 5.2, 4.0 Hz, 2 H, Thienyl-H), 5.85 (s, 2 H, =CH), 2.38 (t, *J* = 7.2 Hz, 4 H, CH_2), 1.50–1.45 (m, 4 H, CH_2), 1.43–1.28 (m, 4 H, CH_2), 0.87 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 101 MHz): δ = 159.8, 149.9, 134.4, 133.3, 132.9, 128.0, 109.7, 33.4, 28.8, 22.2, 13.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{26}O_4S_2Na$: 441.1165; found: 441.1160.

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl Bis(tetrahydrofuran-2-carboxylate) (4af)

Colorless oil; yield: 0.079 g (0.200 mmol, 40%).

IR (film): 2956, 2932, 2873, 1767, 1645, 1466, 1348, 1245, 1154, 1129, 1084, 964, 930, 883, 839, 744 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2 H, =CH), 4.60 (dd, *J* = 8.1, 5.1 Hz, 2 H, OCH), 4.07–3.95 (m, 4 H, OCH_2), 2.41–2.29 (m, 2 H, OCHCH_2), 2.27 (t, *J* = 7.2 Hz, 4 H, CH_2), 2.12–2.09 (m, 2 H, OCH_2CH_2), 2.02–1.96 (m, 4 H, CH_2), 1.42–1.30 (m, 8 H, CH_2), 0.88 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 171.0, 149.6, 109.0, 76.5, 69.5, 33.1, 30.4, 28.6, 25.3, 22.1, 13.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{35}O_6$: 395.2428; found: 395.2430.

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(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl (*E*,*E*)-Bis(3-phenylacrylate) (4ag)

White solid; yield: 0.101 g (0.220 mmol, 44%); mp 115–117 °C.

IR (KBr): 2960, 2931, 2859, 1722, 1634, 1579, 1467, 1423, 1326, 1308, 1271, 1141, 1112, 979, 860, 766, 706, 680, 566, 481 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 7.83 (d, *J* = 15.9 Hz, 2 H, =CH), 7.61 (br, 4 H, ArH), 7.45 (br, 6 H, ArH), 6.58 (d, *J* = 15.9 Hz, 2 H, =CH), 5.80 (s, 2 H, =CH), 2.36 (t, *J* = 6.9 Hz, 4 H, CH_2), 1.53–1.29 (m, 8 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.6, 150.0, 146.3, 134.2, 130.7, 129.0, 128.3, 117.2, 109.4, 33.5, 28.8, 22.2, 13.9.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{30}H_{34}O_4Na$: 481.2349; found: 481.2347.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610709.

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