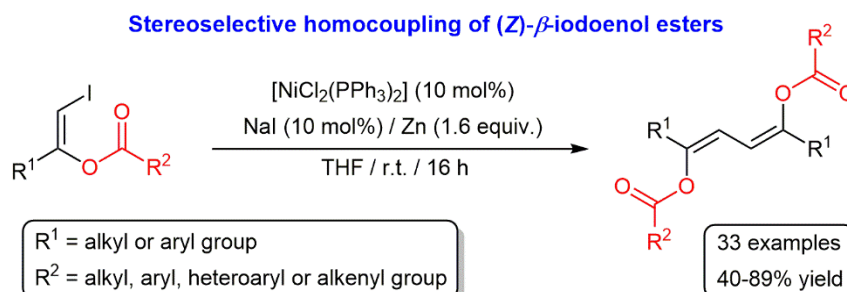


Nickel-Catalyzed Homocoupling of (*Z*)- β -Iodoenol Esters: Stereoselective Access to (*Z,Z*)-Buta-1,3-diene-1,4-diyl Diesters

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

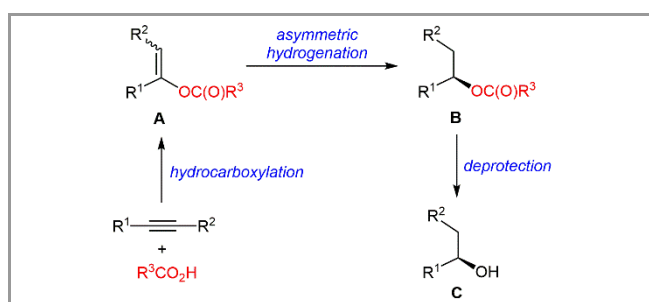


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Abstract A straightforward and broad scope procedure to obtain symmetrically substituted buta-1,3-diene-1,4-diyl diesters, based on the homocoupling of the corresponding (*Z*)- β -iodoenol esters, is presented. It involves the use of a catalytic system composed of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (10 mol%), NaI (10 mol%) and excess of Zn dust. The reactions proceed in THF at r.t. with exquisite preservation of the stereochemistry of the C=C bond of the starting iodo-olefins, 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

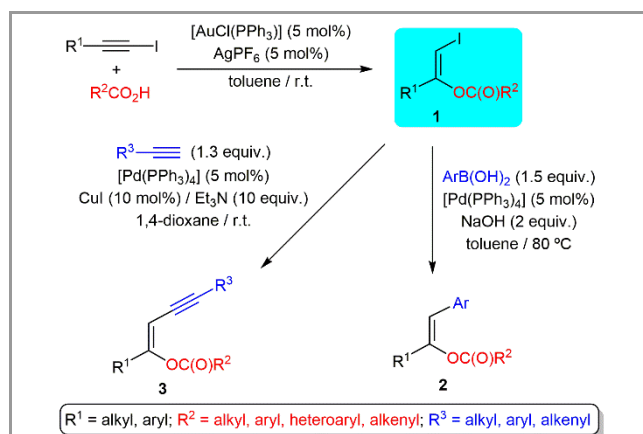
Enol esters **A** are an important class of compounds widely employed as substrates and intermediates in organic chemistry.¹ In particular, much attention has been devoted to the asymmetric hydrogenation of these molecules, since the resulting saturated esters **B** can be easily converted into synthetically 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 substrates 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 -aryl-vinyl 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**.

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, featuring only one of them the same stereochemistry as compounds **4** (Figure 1).⁸

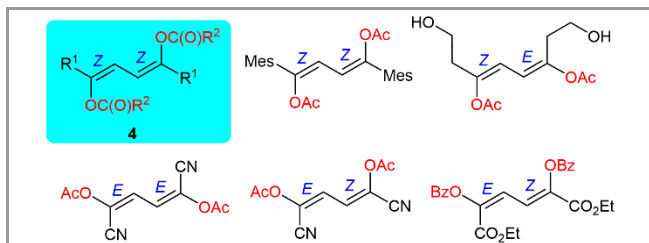
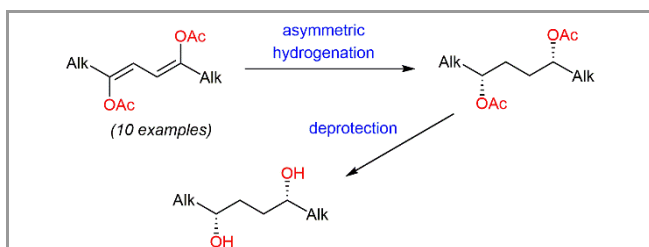


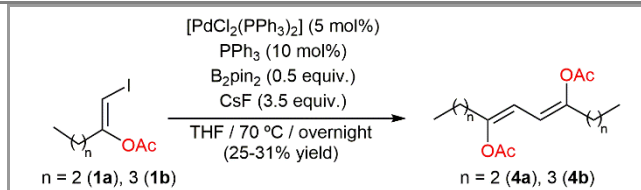
Figure 1 The generic structure of compounds **4** and that of related buta-1,3-dienes reported in the literature.

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.

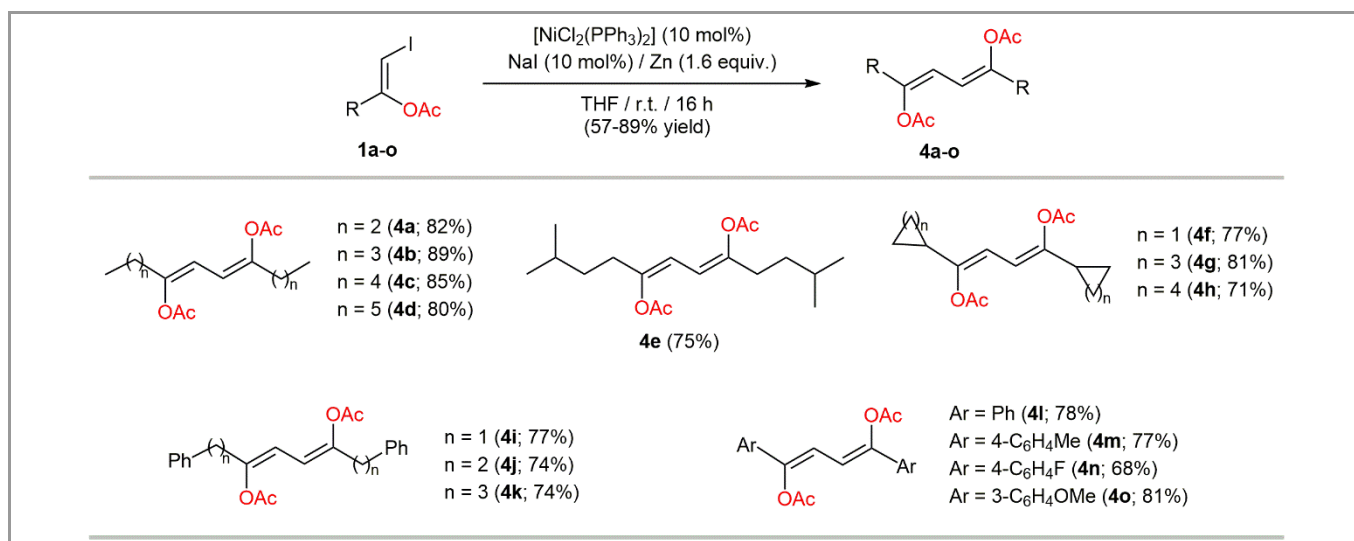
The use of stoichiometric or catalytic amounts of zero-valent nickel complexes for homocoupling reactions of alkenyl halides is well documented, and this methodology is the one that led to the best results in the present case.¹³ Thus, as shown in Table 1, the treatment of a THF solution of (*Z*)-1-iodopent-1-en-2-yl acetate (**1a**) with 30 mol% of $[NiCl_2(PPh_3)_2]$, in the presence of Zn powder (2 equiv.) as the reductant and nBu_4NI (1 equiv.) as an additive to assist the reduction of Ni(II) to Ni(0),^{13cf} for 16 h resulted in the clean formation of the desired diene **4a**, which was isolated in 67% yield after appropriate chromatographic work-up (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**.^{13cf} Alternative nickel sources, *i.e.* $NiCl_2$ 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 nBu_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).

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

| Entry | $[NiCl_2(PPh_3)_2]$ | Iodide salt | Zn | Yield ^b |
|----------------|---------------------|----------------------|----------|--------------------|
| 1 | 30 mol% | nBu_4NI (1 equiv.) | 2 equiv. | 67% |
| 2 | 10 mol% | nBu_4NI (1 equiv.) | 2 equiv. | 65% |
| 3 | 5 mol% | nBu_4NI (1 equiv.) | 2 equiv. | 33% |
| 4 | 10 mol% | ---- | 2 equiv. | 27% |
| 5 | 10 mol% | nBu_4NI (1 equiv.) | ---- | 0% |
| 6 | ---- | nBu_4NI (1 equiv.) | 2 equiv. | 0% |
| 7 ^c | 10 mol% | nBu_4NI (1 equiv.) | 2 equiv. | 63% |
| 8 ^d | 10 mol% | nBu_4NI (1 equiv.) | 2 equiv. | 48% |
| 9 ^e | 10 mol% | nBu_4NI (1 equiv.) | 2 equiv. | 62% |
| 10 | 10 mol% | KI (1 equiv.) | 2 equiv. | 75% |
| 11 | 10 mol% | NaI (1 equiv.) | 2 equiv. | 84% |

| | | | | |
|-----------------|---------|---------------|------------|-----|
| 12 | 10 mol% | Nal (50 mol%) | 2 equiv. | 84% |
| 13 | 10 mol% | Nal (10 mol%) | 2 equiv. | 83% |
| 14 | 10 mol% | Nal (10 mol%) | 1.6 equiv. | 82% |
| 15 ^f | 10 mol% | Nal (10 mol%) | 1.6 equiv. | 65% |
| 16 ^g | 10 mol% | Nal (10 mol%) | 1.6 equiv. | 47% |

^a Reactions performed under Ar atmosphere for 16 h employing 1 mmol of **1a** and 5 mL of anhydrous THF. ^b Isolated yield after chromatographic work-up is given. ^c Reaction performed in the presence of free PPh₃ (20 mol%). ^d Reaction performed employing NiCl₂ instead of [NiCl₂(PPh₃)₂]. ^e Reaction performed employing [NiCl₂(glyme)] instead of [NiCl₂(PPh₃)₂]. ^f Reaction performed in toluene. ^g Reaction performed in CH₂Cl₂.



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

With the optimized reaction conditions in hand (entry 14 in Table 1), the scope of the process was next explored. In this regard, the behaviour of a series of (*Z*)- β -iodoenol acetates **1b-h** was firstly 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 obtained 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 ¹³C NMR spectra confirmed the equivalence of the two CH=CR(OAc) units of **4a-o**, with singlet signals at $\delta_{\text{H}} = 5.58$ –6.64 ppm and $\delta_{\text{C}} = 107.3$ –110.7 (=CH) and 146.9–154.0 (=C) ppm 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 on a 1 mmol scale, we would like to remark that 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%).

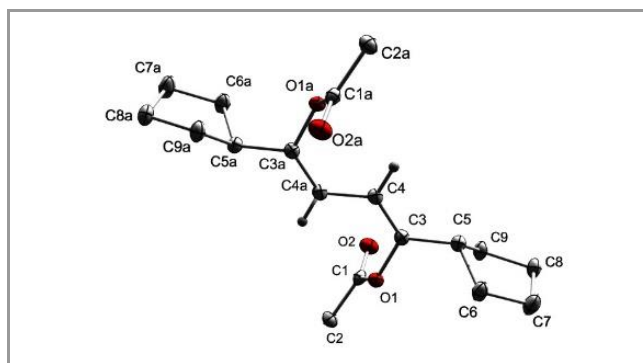
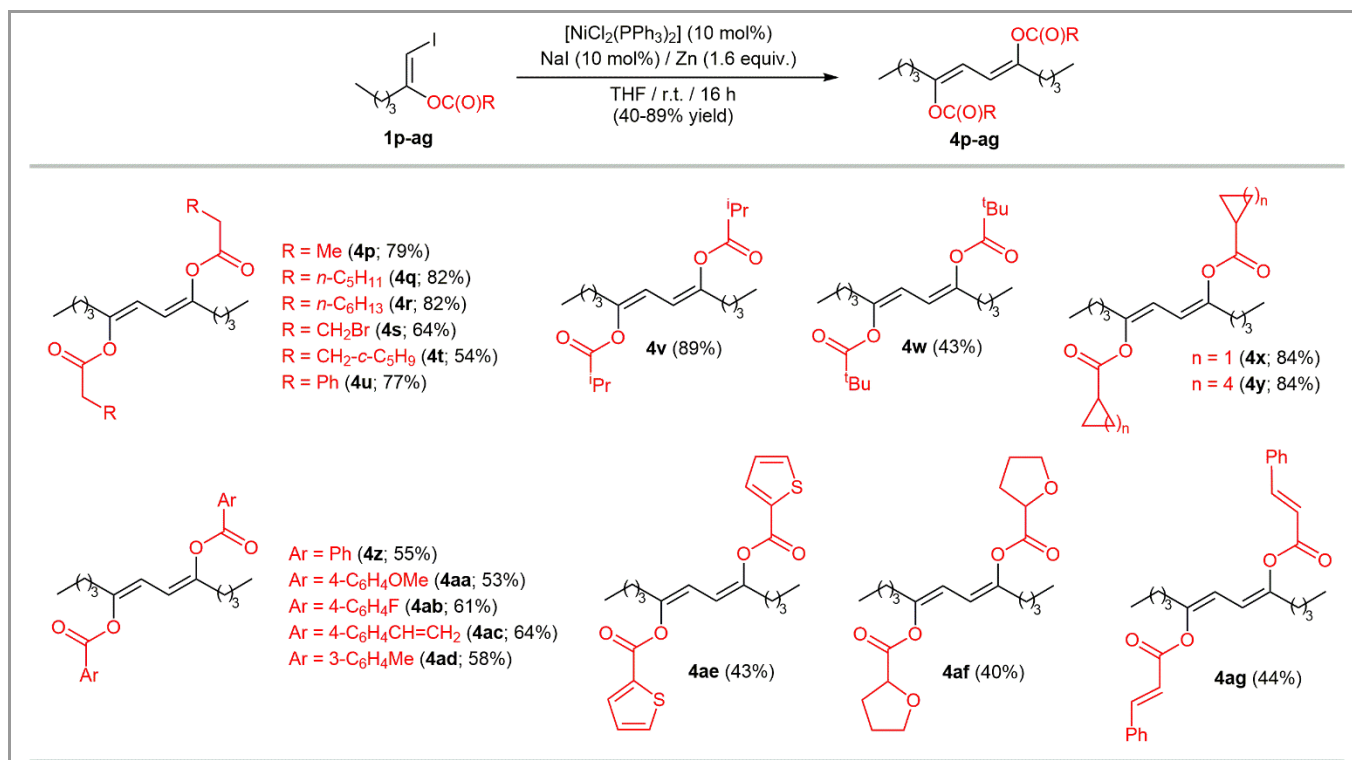


Figure 2 ORTEP-type view of the structure of diene **4g** showing the crystallographic labelling scheme. Hydrogen atoms, except those on C(4) and C(4a), have been omitted for clarity. Those atoms labelled with “a” are generated by symmetry. Thermal ellipsoids are drawn at 30% probability level. Selected 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)–C(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).

Concerning the mechanism of the present homocoupling process, we assume that it proceeds through the reaction pathway proposed by Takagi and co-workers (Scheme 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 $[\text{NiCl}_2(\text{PPh}_3)_2]$ 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 undergo reductive elimination to form the final diene product. In this disproportionation step, $[\text{NiI}_2(\text{PPh}_3)_2]$ is also generated and reduced by the Zn powder to ensure the catalytic cycle.



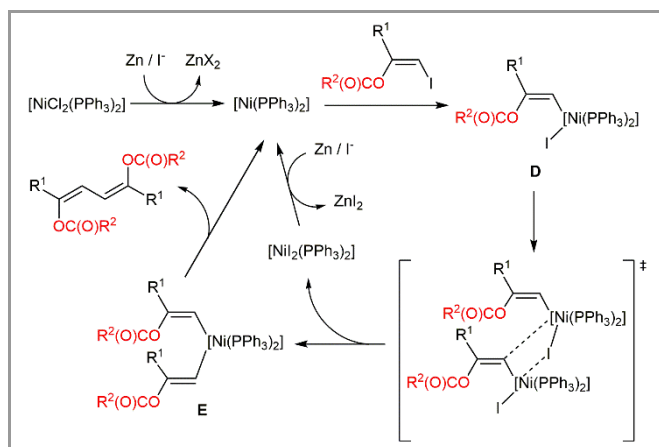
Scheme 6 Nickel-catalyzed homocoupling of (*Z*)- β -iodoenol esters **1**: Scope of the process concerning the nature of the carboxylate group. Isolated yields after column chromatography are given.

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 the 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 is in the present case taking place at the disproportionation stage. Although we have not a conclusive explanation for this, we suspect that a potential interaction/coordination of the ester groups to Ni could be responsible of 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 $[\text{NiCl}_2(\text{PPh}_3)_2]$, NaI and Zn dust. Exquisite preservation of the stereochemistry of the C=C bond of the starting iodoolefins was in all the cases observed, the reactions leading to the 1,3-diene products in a complete stereospecific manner, and with isolated yields ranging from 40% to 89%.

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All reactions were performed under argon atmosphere using standard Schlenk-type techniques. Solvents were distilled under argon with sodium-benzophenone-ketyl (for Et₂O and THF) or sodium (for hexanes). The (*Z*)- β -iodoenol ester **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 file. $[\text{NiCl}_2(\text{PPh}_3)_2]$ 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 Perkin-Elmer 1720-XFT spectrometer. NMR spectra were obtained on Bruker DPX-300 or AV-400 spectrometers. ¹³C{¹H} and ¹H chemical shifts were referenced to the residual signal of deuterated solvent. All data are reported in ppm downfield from (CH₃)₄Si. For ¹⁹F{¹H} NMR spectra, the chemical shifts were referenced to the CFCl₃ 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.

General Procedure for the Synthesis of (Z,Z)-Buta-1,3-diene-1,4-diyl diesters 4

A suspension of [NiCl₂(PPh₃)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 room temperature 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 further stirred 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/diethyl ether (10:1) as eluent, to provide the desired products **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 (CDCl₃, 300 MHz): δ = 5.61 (s, 2 H, =CH), 2.21 (t, *J* = 7.5 Hz, 4 H, CH₂), 2.15 (s, 6 H, CH₃), 1.53-1.41 (m, 4 H, CH₂), 0.88 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₁₄H₂₂O₄Na: 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 (CDCl₃, 400 MHz): δ = 5.64 (s, 2 H, =CH), 2.26 (t, *J* = 7.2 Hz, 4 H, CH₂), 2.19 (s, 6 H, CH₃), 1.44-1.40 (m, 4 H, CH₂), 1.35-1.31 (m, 4 H, CH₂), 0.90 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₁₆H₂₇O₄: 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 (CDCl₃, 300 MHz): δ = 5.65 (s, 2 H, =CH), 2.27 (t, *J* = 7.2 Hz, 4 H, CH₂), 2.21 (s, 6 H, CH₃), 1.48-1.43 (m, 4 H, CH₂), 1.32-1.29 (m, 8 H, CH₂), 0.90 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₁₈H₃₀O₄Na: 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 (CDCl₃, 400 MHz): δ 5.63 (s, 2 H, =CH), 2.25 (t, *J* = 7.6 Hz, 4 H, CH₂), 2.19 (s, 6 H, CH₃), 1.44-1.41 (m, 4 H, CH₂), 1.27 (br, 12 H, CH₂), 0.88 (t, *J* = 6.0 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₀H₃₄O₄Na: 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 (CDCl₃, 300 MHz): δ = 5.64 (s, 2 H, =CH), 2.27 (t, *J* = 7.5 Hz, 4 H, CH₂), 2.21 (s, 6 H, CH₃), 1.59-1.53 (m, 2 H, CH), 1.38-1.30 (m, 4 H, CH₂), 0.89 (d, *J* = 6.6 Hz, 12 H, CH₃).

¹³C NMR (CDCl₃, 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 C₁₈H₃₀O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.66 (s, 2 H, =CH), 2.21 (s, 6 H, CH₃), 1.65-1.56 (m, 2 H, CH), 0.72-0.66 (m, 4 H, CH₂), 0.61-0.58 (m, 4 H, CH₂).

¹³C NMR (CDCl₃, 75 MHz): δ = 168.6, 149.8, 108.3, 20.6, 14.3, 5.7.

HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₁₄H₁₈O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.64 (s, 2 H, =CH), 2.75-2.64 (m, 2 H, CH), 2.20 (s, 6 H, CH₃), 1.81 (br, 4 H, CH₂), 1.66-1.46 (m, 12 H, CH₂).

¹³C NMR (CDCl₃, 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 C₁₈H₂₆O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.58 (s, 2 H, =CH), 2.22 (s, 6 H, CH₃), 2.19-2.14 (m, 2 H, CH), 1.89-1.66 (m, 10 H, CH₂), 1.32-1.08 (m, 10 H, CH₂).

¹³C NMR (CDCl₃, 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 C₂₀H₃₀O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.33-7.21 (m, 10 H, Ar-H), 5.68 (s, 2 H, =CH), 3.63 (s, 4 H, CH₂), 2.06 (s, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₂H₂₂O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.38-7.19 (m, 10 H, Ar-H), 5.67 (s, 2 H, =CH), 2.81 (t, *J* = 7.8 Hz, 4 H, CH₂), 2.62 (t, *J* = 7.8 Hz, 4 H, CH₂), 2.13 (s, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₄H₂₆O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.35-7.20 (m, 10 H, Ar-H), 5.70 (t, *J* = 4.3 Hz, 2 H, =CH), 2.67 (t, *J* = 7.4 Hz, 4 H, CH₂), 2.38-2.35 (m, 4 H, CH₂), 2.22 (s, 6 H, CH₃), 1.85-1.82 (m, 4 H, CH₂).

¹³C NMR (CDCl₃, 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 C₂₆H₃₀O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.50-7.36 (m, 10 H, Ar-H), 6.59 (s, 2 H, =CH), 2.38 (s, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₀H₁₈O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.38 (d, *J* = 8.1 Hz, 4 H, Ar-H), 7.19 (d, *J* = 8.1 Hz, 4 H, Ar-H), 6.53 (s, 2 H, =CH), 2.38 (s, 12 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₂H₂₂O₄Na: 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.

¹H NMR (DMSO-*d*₆, 300 MHz): δ 7.67 (br, 4 H, Ar-H), 7.24 (br, 4 H, Ar-H), 6.64 (s, 2 H, =CH), 2.43 (s, 6 H, CH₃).

¹³C 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.

¹⁹F NMR (DMSO-*d*₆, 282 MHz): δ -112.4.

HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₂₀H₁₆O₄F₂Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.31 (t, *J* = 8.0 Hz, 2 H, Ar-H), 7.10 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.01 (d, *J* = 2.1 Hz, 2 H, Ar-H), 6.89 (dd, *J* = 8.0 and 2.1 Hz, 2 H, Ar-H), 6.57 (s, 2 H, =CH), 3.85 (s, 6 H, OCH₃), 2.38 (s, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₂H₂₂O₆Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.62 (s, 2 H, =CH), 2.47 (q, *J* = 7.5 Hz, 4 H, CH₂), 2.25 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.46-1.28 (m, 8 H, CH₂), 1.21 (t, *J* = 7.5 Hz, 6 H, CH₃), 0.89 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₁₈H₃₁O₄: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.64 (s, 2 H, =CH), 2.46 (t, *J* = 7.5 Hz, 4 H, CH₂), 2.27 (t, *J* = 6.9 Hz, 4 H, CH₂), 1.77-1.67 (m, 4 H, CH₂), 1.46-1.34 (m, 20 H, CH₂), 0.93-0.89 (m, 12 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₆H₄₆O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.64 (s, 2 H, =CH), 2.46 (t, *J* = 7.2 Hz, 4 H, CH₂), 2.27 (t, *J* = 6.9 Hz, 4 H, CH₂), 1.77-1.67 (m, 4 H, CH₂), 1.46-1.32 (m, 24 H, CH₂), 0.91 (t, *J* = 6.9 Hz, 12 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₈H₅₀O₄Na: 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.

¹H NMR (CDCl₃, 400 MHz): δ 5.74 (s, 2 H, =CH), 3.65 (t, *J* = 6.4 Hz, 4 H, CH₂Br), 3.08 (t, *J* = 6.4 Hz, 4 H, CH₂CH₂Br), 2.27 (t, *J* = 7.6 Hz, 4 H, CH₂), 1.46-1.40 (m, 4 H, CH₂), 1.35-1.29 (m, 4 H, CH₂), 0.89 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₁₈H₂₈O₄Br₂Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.63 (s, 2 H, =CH), 2.47 (t, *J* = 7.8 Hz, 4 H, CH₂), 2.26 (t, *J* = 6.9 Hz, 4 H, CH₂), 1.82-1.15 (m, 30 H, CH₂ + CH), 0.90 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₈H₄₆O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 7.37-7.30 (m, 10 H, Ar-H), 5.30 (s, 2 H, =CH), 3.72 (s, 4 H, CH₂), 2.11 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.25-1.21 (m, 8 H, CH₂), 0.86 (t, *J* = 6.6 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₈H₃₄O₄Na: 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.

¹H NMR (CDCl₃, 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, CH₂), 1.43-1.32 (m, 8 H, CH₂), 1.28 (d, *J* = 6.9 Hz, 12 H, CH₃), 0.90 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₀H₃₄O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.63 (s, 2 H, =CH), 2.25 (t, *J* = 6.9 Hz, 4 H, CH₂), 1.45-1.31 (m, 8 H, CH₂), 1.27 (s, 18 H, CH₃), 0.90 (t, *J* = 6.9 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₂H₃₈O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.65 (s, 2 H, =CH), 2.27 (t, *J* = 6.9 Hz, 4 H, CH₂), 1.75-1.72 (m, 2 H, CH), 1.46-1.30 (m, 8 H, CH₂), 1.13-1.10 (m, 4 H, CH₂), 0.99-0.95 (m, 4 H, CH₂), 0.91 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₀H₃₀O₄Na: 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.

¹H NMR (CDCl₃, 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, CH₂), 2.03-1.99 (m, 4 H, CH₂), 1.79-1.32 (m, 24 H, CH₂), 0.90 (t, *J* = 6.9 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₆H₄₂O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 8.18 (d, *J* = 7.5 Hz, 4 H, Ar-H), 7.68-7.51 (m, 6 H, Ar-H), 5.86 (s, 2 H, =CH), 2.38 (t, *J* = 7.3 Hz, 4 H, CH₂), 1.49-1.44 (m, 4 H, CH₂), 1.36-1.29 (m, 4 H, CH₂), 0.86 (t, *J* = 7.0 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₆H₃₀O₄Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 8.12 (d, *J* = 8.9 Hz, 4 H, Ar-H), 7.01 (d, *J* = 8.9 Hz, 4 H, Ar-H), 5.83 (s, 2 H, =CH), 3.92 (s, 6 H, OCH₃), 2.36 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.50-1.40 (m, 4 H, CH₂), 1.38-1.26 (m, 4 H, CH₂), 0.86 (t, *J* = 6.9 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₈H₃₄O₆Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 8.18 (dd, *J* = 8.4 and 5.4 Hz, 4 H, Ar-H), 7.20 (t, *J* = 8.4 Hz, 4 H, Ar-H), 5.81 (s, 2 H, =CH), 2.36 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.47-1.40 (m, 4 H, CH₂), 1.38-1.28 (m, 4 H, CH₂), 0.86 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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.

¹⁹F NMR (CDCl₃, 282 MHz): δ -104.6.

HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₂₆H₂₈O₄F₂Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 8.12 (d, *J* = 8.4 Hz, 4 H, Ar-H), 7.55 (d, *J* = 8.4 Hz, 4 H, Ar-H), 6.81 (dd, *J* = 17.4 and 11.1 Hz, 2 H, =CH), 5.93 (d, *J* = 17.4 Hz, 2 H, =CH₂), 5.84 (s, 2 H, =CH), 5.45 (d, *J* = 11.1 Hz, 2 H, =CH₂), 2.37 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.50-1.43 (m, 4 H, CH₂), 1.40-1.26 (m, 4 H, CH₂), 0.86 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₃₀H₃₅O₄: 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.

¹H NMR (CDCl₃, 300 MHz): δ 8.01–7.98 (m, 4 H, Ar-H), 7.49–7.40 (m, 4 H, Ar-H), 5.88 (s, 2 H, =CH), 2.48 (s, 6 H, CH₃), 2.40 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.51–1.46 (m, 4 H, CH₂), 1.38–1.31 (m, 4 H, CH₂), 0.88 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₈H₃₄O₄Na: 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.

¹H NMR (CDCl₃, 400 MHz): δ 7.93 (dd, *J* = 4.0 and 1.2 Hz, 2 H, Thienyl-H), 7.66 (dd, *J* = 5.2 and 1.2 Hz, 2 H, Thienyl-H), 7.18 (dd, *J* = 5.2 and 4.0 Hz, 2 H, Thienyl-H), 5.85 (s, 2 H, =CH), 2.38 (t, *J* = 7.2 Hz, 4 H, CH₂), 1.50–1.45 (m, 4 H, CH₂), 1.43–1.28 (m, 4 H, CH₂), 0.87 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₂H₂₆O₄S₂Na: 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.

¹H NMR (CDCl₃, 300 MHz): δ 5.64 (s, 2 H, =CH), 4.60 (dd, *J* = 8.1 and 5.1 Hz, 2 H, OCH), 4.07–3.95 (m, 4 H, OCH₂), 2.41–2.29 (m, 2 H, OCHCH₂), 2.27 (t, *J* = 7.2 Hz, 4 H, CH₂), 2.12–2.09 (m, 2 H, OCH₂CH₂), 2.02–1.96 (m, 4 H, CH₂), 1.42–1.30 (m, 8 H, CH₂), 0.88 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₂₂H₃₅O₆: 395.2428; found: 395.2430.

(*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 (CDCl₃, 300 MHz): δ 7.83 (d, *J* = 15.9 Hz, 2 H, =CH), 7.61 (br, 4 H, Ar-H), 7.45 (br, 6 H, Ar-H), 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, CH₂), 1.53–1.29 (m, 8 H, CH₂), 0.90 (t, *J* = 7.2 Hz, 6 H, CH₃).

¹³C NMR (CDCl₃, 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 C₃₀H₃₄O₄Na: 481.2349; found: 481.2347.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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