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An Interrupted Vinylogous Iso-Nazarov Reaction: Cycloisomerization of Conjugated Trienones to Cyclopenta[*b*]furan Derivatives

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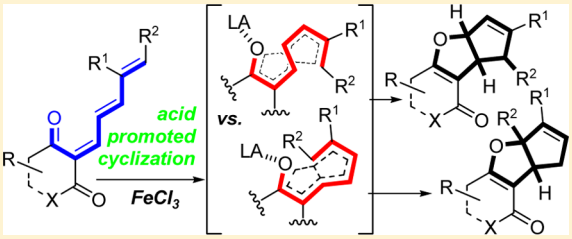
Supporting Information

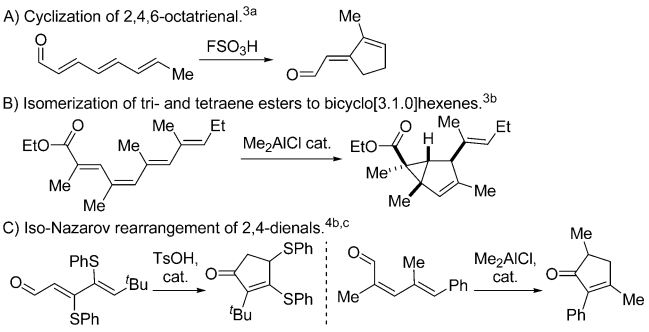
ABSTRACT: Iron(III) chloride-catalyzed cyclopentannulation of π-conjugated 1,3-dicarbonyl compounds is described. An interrupted vinylogous iso-Nazarov reaction of trienones was established in which cyclopenta[*b*]furan derivatives are obtained as single diastereomers.



INTRODUCTION

Cycloisomerization reactions are powerful synthetic tools for the construction of polycyclic compounds. Polyunsaturated molecules have been privileged substrates in a vast number of transition-metal-catalyzed and/or electrophile-promoted cycloisomerizations affording five-membered-ring systems.[1] As far as conjugated precursors are concerned, the acid-catalyzed ring closure of cross-conjugated ketones, the Nazarov reaction, has particularly witnessed an outstanding evolution since its discovery, gaining substantial acceptance as an efficient strategy for pentannulation.[2] To the best of our knowledge, however, only few examples of acid-promoted isomerizations of linearly conjugated π-extended carbonyl systems have been reported (Scheme 1A,B).[3] These are related to the iso-Nazarov reaction

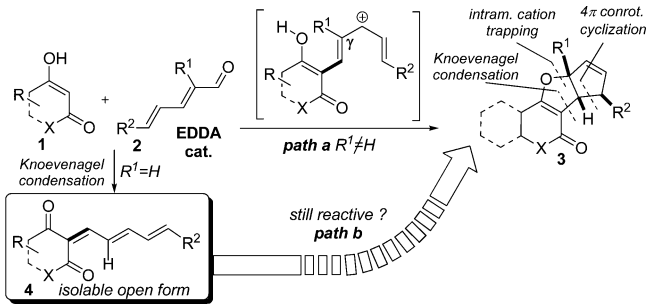
Scheme 1. Acid Activation of Linearly-Conjugated π-Extended Carbonyl Moieties (Ts = 4-Toluenesulfonyl)



of lower vinylogues (Scheme 1C), in which a cyclopentenone is formed via initial conrotatory 4π-electrocyclization of 1-oxypentadienyl cation intermediates.[4]

Our studies of the preparation of extended π-conjugated carbonyl systems via Knoevenagel condensation of 1,3-dicarbonyl substrates (**1**) and α,β,γ,δ-unsaturated aldehydes (**2**) revealed that, depending on the substitution pattern and/or electronic properties, products of type **3** can be obtained via cycloisomerization of a primary, nonisolable, coupled intermediate (Scheme 2, path a).[5] In this manner, a novel stereoselective

Scheme 2. Developed Domino Reaction (EDDA = Ethylenediammonium Diacetate)



annulation cascade for the synthesis of the cyclopenta[*b*]furan motif, which is present in many biologically active molecules,[6] was established.

On the basis of our previous research, in which a novel interrelation between cationic species and stability/reactivity of polyene systems has been disclosed, an intriguing question arose as to whether electrophilic activation of isolable polyunsaturated 1,3-dicarbonyl substrates of type **4** could trigger the pentadienyl−cyclopentenyl cation rearrangement/intramolecular cation trapping sequence as a viable cycloisomerization pathway for the assembly of cyclopenta[*b*]furans (Scheme 2, path b).

In this paper we report the successful realization of such an approach, resulting in a new heterocycloisomerization for the stereoselective synthesis of cyclopenta[*b*]furans from simple

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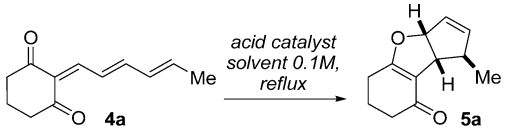
polyene substrates. From a fundamental chemistry viewpoint, the reactivity displayed by linearly conjugated carbonyl compounds is closely related to Nazarov-based reactions of cross-conjugated ones, expanding the chemistry of cationic 4π-electrocyclizations for the synthesis of five-membered-ring systems.

RESULTS AND DISCUSSION

Taking into account the fact that their specific polarization properties are greatly modulated by not only electronic but also steric factors, we selected unsubstituted polyene **4a** as a model substrate for our initial studies. The effect of Brønsted acids was first examined, and the results are collected in Table 1. While in the presence of mineral acids at room temperature compound **4a** rapidly decomposed to give a complex mixture of unidentified products (not shown), organic acids such as CSA and TFA fortunately were able to promote the desired rearrangement toward derivative **5a**, which was obtained as a single diastereomer, albeit in low yield (entries 1 and 2). To optimize suitable conditions for this reaction, several metallic and nonmetallic Lewis acids were screened. In this regard, $BF_3{\cdot}OEt_2$, $ZnCl_2$, $AuCl_3$, and $AlCl_3$ exhibited promising activities, furnishing the desired product **5a** in yields ranging from 65 to 80%, whereas $PtCl_2$, $CuCl_2$, and $Ti(O^iPr)_4$ proved to be ineffective in promoting the reaction, displaying low conversions of the starting materials and low yields of the isolated products (entries 3, 6, 8, and 9 vs 4, 5, and 7). We were eventually pleased to find that the best results were achieved by using inexpensive and environmentally friendly ferric chloride (entry 10). In regard to catalyst loading, in the presence of superstoichiometric amounts (3 equiv of $FeCl_3$) a rapid rearrangement of **4a** occurs at room temperature, leading selectively to compound **5a** in comparable yield to that using 0.5 equiv (entry 11). On the other hand, when the amount of promoter was further decreased, longer reaction times were observed along with deteriorated yields and conversions (entries 12 and 14). The use of other solvents such as toluene or THF provided faster transformations, although a concomitant drop in yield was also observed (entries 15 and 16). The presence of water was shown not to have a significant impact on the reaction, as the use of nondried distilled CH_2Cl_2 or hydrated catalyst ($FeCl_3{\cdot}6H_2O$) still allowed for the formation of **5a** in comparable yield to that obtained under anhydrous conditions (entries 12 vs 13 and 10 vs 17).

Table 1. Screening of Effective Reaction Conditions[a]



entry	catalyst (equiv)	solvent	t [h]	conv.[b]	yield
1	CSA (0.5)	CH_2Cl_2	8	95%	30%
2	TFA (0.5)	CH_2Cl_2	4	100%	56%
3	$BF_3{\cdot}OEt_2$ (2)	CH_2Cl_2[c]	2	100%	80%
4	$PtCl_2$ (0.5)	CH_2Cl_2	6	30%	6%
5	$CuCl_2$ (0.5)	CH_2Cl_2	>6	30%	traces
6	$ZnCl_2$ (0.5)	CH_2Cl_2	4	100%	83%
7	$Ti(O^iPr)_4$ (0.5)	CH_2Cl_2	6	20%	traces
8	$AuCl_3$ (0.5)	CH_2Cl_2	3	100%	65%
9	$AlCl_3$ (0.5)	CH_2Cl_2	1	91%	67%
10	$FeCl_3$ (0.5)	CH_2Cl_2	4	100%	88%
11	$FeCl_3$ (3)	CH_2Cl_2[c]	0.25	100%	85%
12	$FeCl_3$ (0.25)	CH_2Cl_2	6	82%	50%
13	$FeCl_3$ (0.25)	CH_2Cl_2[d]	6	72%	39%
14	$FeCl_3$ (0.05)	CH_2Cl_2	>50	77%	36%
15	$FeCl_3$ (0.5)	THF	1	100%	60%
16	$FeCl_3$ (0.5)	toluene	1	100%	73%
17	$FeCl_3.6H_2O$ (0.5)	CH_2Cl_2	6	95%	70%

[a]Optimization reactions were carried out with substrate **4a** (0.5 mmol). [b]Conversion based on isolated starting material recovered. [c]Reaction was run at room temperature. [d]Only distilled, nondried CH_2Cl_2 was used. Abbreviations: CSA, camphorsulfonic acid; TFA, trifluoroacetic acid; THF, tetrahydrofuran.

Having demonstrated the feasibility of introducing the key intramolecular cyclization for the assembly of cyclopenta[b]-furan derivatives, we next investigated the effects of polyene structural variations to delineate the scope and utility of the process (Table 2). Six-membered 1,3-dicarbonyl derivatives proved to be good substrates, affording the tricyclic scaffold in yields ranging from 75 to 85% (**5b–h**). Aryl or alkyl substitution was tolerated both at the end of the triene chain and on the cyclohexanedione ring. Acyclic β-diketones as well as β-keto esters participated in the reaction, although lower yields were obtained in these cases (**5i–k**). For the preparation of ester **5k**, the same yield was obtained starting from either the 2-*Z* or 2-*E* isomer of the corresponding polyunsaturated diastereomeric precursor. Remarkably, a different reactivity profile was found for branched trienediones **4l–n**, which were stable in the solid state but were found to gradually convert to corresponding cyclopenta[b]furan derivatives **5l–n** in deuterated chloroform solution. On the other hand, some substrates did not afford any of the desired cyclopenta[b]furan derivative. Five-membered dicarbonyl olefinic compounds, such as **4o** and **4p**, remained unaltered under several sets of experimental reaction conditions, as did substrates **4q** and **4r** in which one of triene double bonds is involved in an aromatic system. On the other hand, trienediones **4s** and **4t**, both bearing two substituents at the end of the polyene chain, underwent thorough decomposition under $FeCl_3$ treatment, resulting in complex mixtures.

A consistent stepwise mechanism for the synthesis of products **5** is depicted in Scheme 3. Lewis or Brønsted acid activation of conjugated substrate **4** generates bisallyl cation **A**, which after a conformational change to the "U form" undergoes a 4π-electrocyclization reaction in a conrotatory manner to give the new cyclopentenyl cation **B**. Intermediate **B** may be intramolecularly stabilized by a through-space interaction involving the assistance of the π bond of the enol moiety,[7] leading to a heavily localized allyl cation that would then be trapped by enolic oxygen to provide *cis*-fused cyclopenta[b]furan derivative **5** exclusively. In the case of ε-branched trienediones **4l–n**, the slow spontaneous conversion in deuterated chloroform may be due to traces of acid and could be explained by either a steric destabilization effect of the planar polyunsaturated form of substrate **4** exerted by the substituent or a stabilizing effect of the ε-substituent on cyclopentenyl cation intermediate **B**, which would then be tertiary allylic. Some attempts to trap cyclopentenyl cation **B** intermolecularly failed.[4d] On the other hand, experiments with deuterium -labeled substrates **4u** and **4v** supported this postulated mechanism (Scheme 3): the products **5u** and **5v** thus obtained retained the labels, with deuterium atoms located at the expected positions, ruling out either elimination or migration steps.

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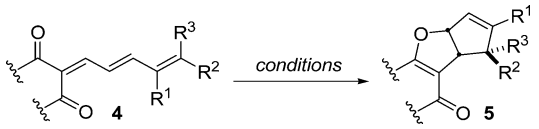
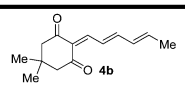
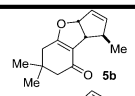
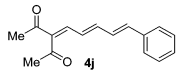
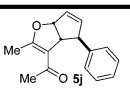
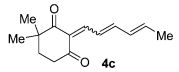
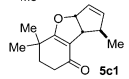
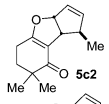
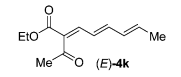
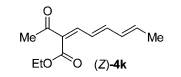
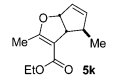
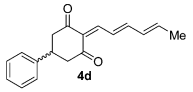
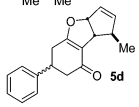
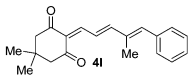
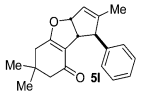
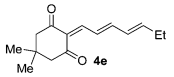
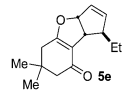
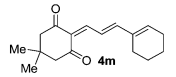
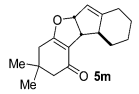
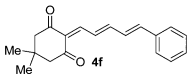
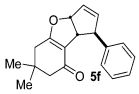
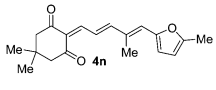
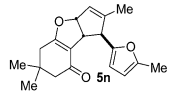
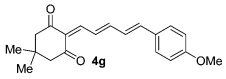
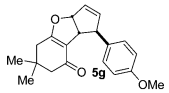
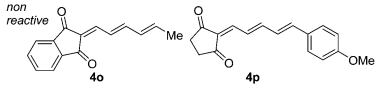
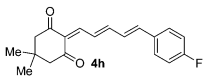
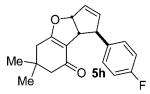
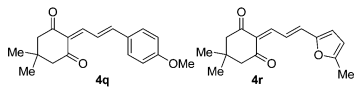
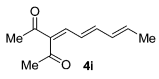
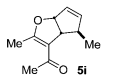
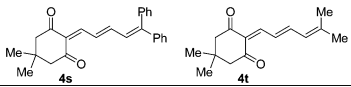
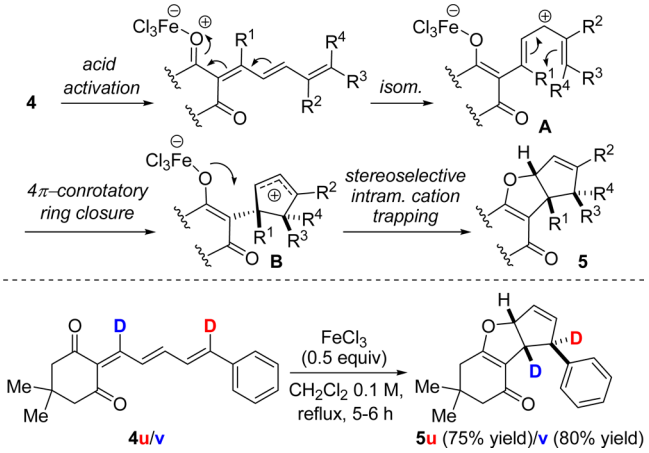
Table 2. Substrate Scope and Limitations[a]



substrate	t [h]	product	yield	substrate	t [h]	product	yield
 4b	3	 5b	80%	 4j	10	 5j	40%
 4c	4	 5c1  5c2	85%[b]	 (E)-4k  (Z)-4k	1 1	 5k	25%
 4d	4	 5d	80%[c]	 4l	d	 5l	60%
 4e	4	 5e	80%	 4m	d	 5m	65%
 4f	7	 5f	85%	 4n	d	 5n	60%
 4g	4	 5g	85%	non reactive  4o 4p			
 4h	3	 5h	75%	 4q 4r			
 4i	4	 5i	55%	decompose  4s 4t			

[a]Unless otherwise noted, the reactions were run with the corresponding substrate **4** (0.5 mmol) in CH_2Cl_2 (0.1 M) at reflux using $FeCl_3$ (0.5 equiv) as the catalyst. [b]Obtained as a separable mixture of **5c1** and **5c2** in a ratio of 0.6:1. [c]Obtained as an inseparable mixture of diastereomers. [d]Obtained via spontaneous isomerization of the substrate in $CDCl_3$.

Scheme 3. Proposed Mechanism for the Rearrangement and Labeling Experiments



Our results, in agreement with previous experimental observations (Scheme 1A,B), assert that the preferred initial event for 1-oxyheptatrienyl cations involves a five-atom, four-electron process at the end of the linear trienecarbonyl chain, which could be defined as a vinylogous iso-Nazarov path. The fate of the resulting cyclopentenyl cation intermediate, however, is highly dependent on the substrate structure, leading to two formal paths: nucleophilic capture or β-elimination. In connection with advances in Nazarov chemistry, the former can be defined as an interrupted reaction.[8] Nevertheless, while bicyclo[3.1.0]hexenes result when cyclopentenyl cations are trapped by enolic carbon−carbon double bonds (Scheme 1B),[9] the flexibility of the trienedicarbonyl system allows a hitherto-unknown outcome in which the enolic oxygen gets involved in the second cyclization step. On the other hand, (2-methylcyclopent-2-enylidene)acetaldehyde can be seen as the "normal" ("not interrupted") product of a vinylogous iso-Nazarov reaction (Scheme 1A).

As stated above, during our studies we verified net stability/reactivity differences between unsubstituted and alkyl-branched polyenic series. Indeed, when ε-branched compounds **4l** and **4m** were subjected to the developed $FeCl_3$ cycloisomerization protocol, the new tricyclic isomers **6l** and **6m** were found as main products instead of the expected **5l** and **5m** (Scheme 4). This alternative reaction course, which was found to be more

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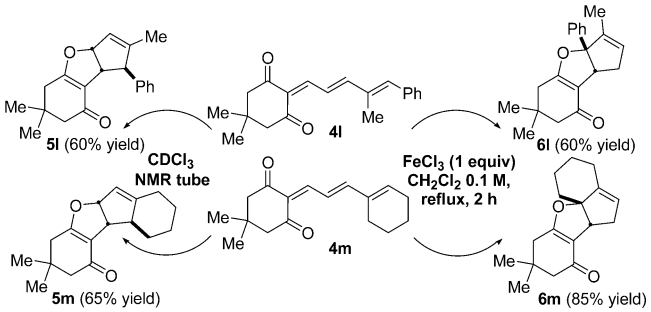
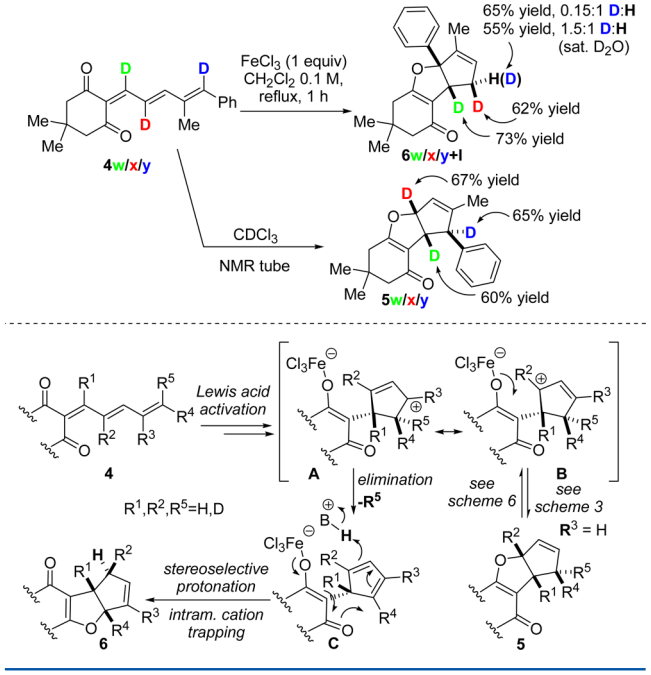
Scheme 4. Alternative Hard Lewis Acid-Promoted Cycloisomerization Pathway



efficient when an equimolar quantity of $FeCl_3$ was used, provided a new insight into this complex chemistry.

In order to clarify the origin of the observed alternative reaction course, the behavior of alkyl-branched deuterated substrates was examined. As shown in Scheme 5, in the presence of

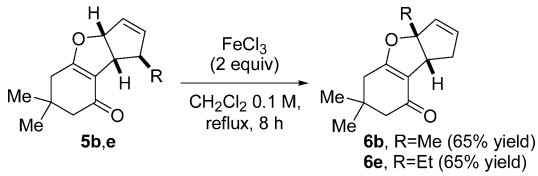
Scheme 5. Further Deuterium-Labeling Studies and Unified Mechanistic Proposal



iron(III), compounds **4w**, **4x**, and **4y** were isomerized to the corresponding rearranged products **6w**, **6x**, and **6y**, the latter obtained as a mixture of **6y** and unlabeled **6l** in a 0.15:1 ratio. This substantial loss of deuterium content could be partially prevented (the ratio raised to 1.5:1) when the reaction was conducted in deuterium oxide-saturated CH_2Cl_2. The fact that the deuterium label can be partially lost from substrate **4y** clearly suggests different mechanistic routes for the formation of cyclopenta[*b*]furans of types **5** and **6**, considering that compound **4u** (Scheme 3), which also bears a label at the end of the polyene chain, did not exhibit any loss upon $FeCl_3$-catalyzed rearrangement. It thus became apparent that the formation of isomers **6** may feature an elimination step, and on the basis of these findings a unified mechanistic proposal was elaborated (Scheme 5). After Lewis acid activation, alkyl substitution on ε-branched substrates (R^3 = alkyl) could result in a favored canonical structure **A** for the cyclopentenyl cation intermediate, which behaves more as a classical trivalent carbenium ion. This cationic center dictates a new tandem reactivity that involves the formation of cyclopentadiene intermediate **C**, which can be stereoselectively protonated in a 1,4-conjugated fashion to give isomers of type **6**, as suggested by the exchange of deuterium with the medium in the case of compound **4y**.

In addition, a control experiment showed that when cyclopenta[*b*]furans **5b** and **5e** were treated with superstoichiometric amounts of iron salt, tricyclic products of type **6** were produced, suggesting that the formation of "normal" or "rearranged" products could also be associated with the concepts of kinetic and thermodynamic control (Scheme 6).

Scheme 6. Rearrangement of Cyclopenta[*b*]furans



CONCLUSION

Our results have established an innovative approach for the assembly of cyclopenta[*b*]furan moieties based on an unusual carbocation chemistry developed from simple conjugated carbonyl polyenes. These studies significantly expand the scope of cationic cascades for the synthesis of five-membered-ring systems. The application of these methodologies beyond dicarbonyl polyene substrates, more detailed mechanistic studies, and the development of asymmetric versions of these transformations will be the focus of future work.

EXPERIMENTAL SECTION

All of the unsaturated aldehydes employed to prepare dicarbonyl substrates **4**, except most of the deuterated analogues, are either commercially available or have been previously prepared in the literature.[10−17] The unsaturated precursors **4a**, **4b**, **4f**, **4i**, **4l**, **4q**, and **5l** have been previously prepared by our group.[5,12] In the NMR data, the labels * and ** indicate that the labeled assignments are exchangeable.

General Procedure for the Preparation of Substrates 4 via Condensation of 1,3-Dicarbonyl Compounds and Unsaturated Aldehydes. A mixture of 1,3-dicarbonyl compound (1 mmol), unsaturated aldehyde (1 mmol, 1 equiv), and 1,2-ethylenediammonium diacetate (EDDA, 36 mg, 0.2 mmol) in CH_2Cl_2 (5.0 mL, 0.2 M) was heated at reflux until the aldehyde substrate was completely consumed (TLC monitoring, approximately 3−4 h). The solvent was then evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to afford the following compounds.

Substrate ***4c***. An inseparable mixture of diastereomers obtained as an orange solid (164 mg, 75%), mp 140.0 °C (dec.). IR (KBr): 2963, 2928, 1651, 1537, 1366, 1184, 1005 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75−7.52 (overlapping m, 4H), 7.05−6.90 (overlapping dd, 2H), 6.45−6.30 (overlapping m, 2H), 6.28−6.15 (overlapping m, 2H), 2.68−2.61 (overlapping t, 4H), 1.94−1.83 (overlapping m, 10H), 1.22−1.20 (overlapping s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.2 (C), 202.1 (C), 198.9 (C), 197.9 (C), 153.33 (CH), 153.26 (CH), 152.3 (CH), 152.2 (CH), 141.00 (CH), 140.97 (CH), 131.9 (2 × CH), 128.6 (C), 128.5 (C), 127.3 (CH), 127.2 (CH), 42.6 (C), 41.4 (C), 35.8 (CH_2), 34.5 (CH_2), 31.6 (CH_2), 31.5 (CH_2), 24.5 (2 × CH_3), 24.4 (2 × CH_3), 18.7 (2 × CH_3). HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{18}O_2Na$ $[M + Na]^+$ 241.1199, found 241.1190.

Substrate ***4d***. Obtained as an orange solid (133 mg, 50%), mp 121.5−122.0 °C. IR (KBr): 3061, 3028, 2961, 2905, 1686, 1645, 1570,

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1522, 1368, 1238, 1177, 1144, 1026 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83−7.64 (m, 2H), 7.41−7.18 (m, 5H), 7.11−6.95 (m, 1H), 6.41 (dd, J = 14.9 Hz, J = 10.9 Hz, 1H), 6.26 (dq, J = 14.9 Hz, J = 6.7 Hz, 1H), 3.38 (tt, J = 11.8 Hz, J = 4.0 Hz, 1H), 3.00−2.72 (m, 4H), 1.91 (bd, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.9 (C), 196.9 (C), 154.9 (CH), 152.6 (CH), 142.2 (CH), 142.0 (C), 132.2 (CH), 128.7 (2 × CH), 128.3 (C), 127.4 (CH), 126.9 (CH), 126.3 (2 × CH), 47.4 (CH_2), 45.8 (CH_2), 35.6 (CH), 19.0 (CH_3). HRMS (ESI) m/z: calcd for $C_{18}H_{18}O_2Na$ $[M + Na]^+$ 289.1199, found 289.1187.

Substrate ***4e***. Obtained as a yellow solid (174 mg, 75%), mp 51.0−52.0 °C. IR (KBr): 2961, 2951, 2932, 1642, 1576, 1530, 1375, 1237, 1181, 1029 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76−7.62 (m, 2H), 7.09−6.93 (m, 1H), 6.44−6.22 (m, 2H), 2.51 (bs, 4H), 2.25 (bquint, J = 7.1 Hz, 2H), 1.11−1.03 (overlapping signals, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7 (C), 197.7 (C), 154.4 (CH), 151.4 (CH), 148.3 (CH), 129.7 (CH), 127.9 (C), 127.6 (CH), 53.8 (CH_2), 52.1 (CH_2), 29.9 (C), 28.4 (2 × CH_3), 26.2 (CH_2), 12.6 (CH_3). HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1355, found 255.1344.

Substrate ***4g***. Obtained as a red solid (248 mg, 80%), mp 165.0−166.0 °C. IR (KBr): 2953, 2934, 1638, 1560, 1522, 1506, 1373, 1240, 1161 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, J = 14.1 Hz, J = 12.3 Hz, 1H), 7.71 (d, J = 12.4 Hz, 1H), 7.48−7.40 (m, 2H), 7.17 (ddd, J = 14.2 Hz, J = 9.1 Hz, J = 1.2 Hz, 1H), 7.01−6.86 (m, 4H), 3.83 (s, 3H), 2.52 (bs, 2H), 2.51 (bs, 2H), 1.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7 (C), 197.7 (C), 160.8 (C), 154.6 (CH), 151.0 (CH), 142.0 (CH), 129.1 (2 × CH), 128.8 (CH), 128.7 (C), 127.3 (C), 126.3 (CH), 114.3 (2 × CH), 55.2 (CH_3), 53.8 (CH_2), 52.1 (CH_2), 29.9 (C), 28.4 (2 × CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{23}O_3$ $[M + H]^+$ 311.1642, found 311.1638.

Substrate ***4h***. Obtained as a red solid (253 mg, 85%), mp 140.0−141.0 °C. IR (KBr): 3049, 2953, 2930, 1684, 1638, 1560, 1516, 1501, 1373, 1225, 1155, 1011 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (dd, J = 14.1 Hz, J = 12.3 Hz, 1H), 7.70 (d, J = 12.3 Hz, 1H), 7.51−7.43 (m, 2H), 7.21−6.86 (m, 5H), 2.55−2.52 (bs, 4H), 1.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8 (C), 197.8 (C), 163.3 (C, d, J = 250.9 Hz), 153.2 (CH), 150.4 (CH), 140.3 (CH), 132.2 (C, d, J = 3.3 Hz), 129.8 (CH), 129.1 (2 × CH, d, J = 8.2 Hz), 128.2 (C), 128.1 (CH, d, J = 2.2 Hz), 115.9 (2 × CH, d, J = 22.0 Hz), 53.9 (CH_2), 52.2 (CH_2), 30.0 (C), 28.4 (2 × CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{19}FO_2Na$ $[M + Na]^+$ 321.1261, found 321.1246.

Substrate ***4j***. Obtained as a yellow solid (228 mg, 95%), mp 89.5−90.0 °C. IR (KBr): 3065, 3030, 2995, 1699, 1645, 1599, 1587, 1558, 1379, 1248, 1151 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.46−7.40 (m, 2H), 7.38−7.24 (m, 3H), 7.13 (d, J = 11.6 Hz, 1H), 6.96−6.75 (m, 3H), 6.74−6.60 (m, 1H), 2.38 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.8 (C), 196.8 (C), 145.1 (CH), 142.4 (CH), 140.6 (C), 138.9 (CH), 135.9 (C), 128.8 (CH), 128.6 (2 × CH), 127.6 (CH), 127.2 (CH), 126.9 (2 × CH), 31.5 (CH_3), 26.1 (CH_3). HRMS (ESI) m/z: calcd for $C_{16}H_{16}O_2Na$ $[M + Na]^+$ 263.1042, found 263.1048.

*Substrates (2E)-***4k** *and (2Z)-***4k**. These substrates are unstable compounds; the stereochemistry assignment is based on NOEs. (2*E*)-**4k** was obtained as a pale-yellow liquid (73 mg, 35%). IR (film): 2984, 2937, 2915, 1714, 1594, 1371, 1228 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, J = 11.0 Hz, 1H), 6.75−6.56 (m, 2H), 6.27−6.15 (m, 1H), 6.05 (dq, J = 15.1 Hz, J = 6.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.85 (bdd, J = 6.7 Hz, J = 1.2 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.3, 165.3, 146.2, 145.3, 137.8, 131.3, 130.5, 124.9, 60.8, 31.0, 18.5, 14.0. (2*Z*)-**4k** was obtained as a pale-yellow liquid (73 mg, 35%). IR (film): 2984, 2939, 1720, 1688, 1593, 1380, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J = 11.4 Hz, 1H), 6.80−6.54 (m, 2H), 6.24 (ddq, J = 15.1 Hz, J = 10.3 Hz, J = 1.4 Hz, 1H), 6.08 (dq, J = 15.1 Hz, J = 6.8 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.87 (bd, J = 6.7 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.3, 166.3, 146.4, 144.8, 138.1, 131.34, 131.31, 125.0, 61.0, 27.7, 18.6, 14.0.

Substrate ***4m***. Obtained as a yellow solid (194 mg, 75%), mp 96.0−97.0 °C. IR (KBr): 2947, 2926, 2907, 1684, 1653, 1578, 1541, 1366, 1178 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78−7.64 (m, 2H), 7.09−6.95 (m, 1H), 6.29 (bt, J = 3.6 Hz, 1H), 2.51 (bs, 4H), 2.36−2.21 (m, 4H), 1.77−1.57 (m, 4H), 1.07 (bs, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8 (C), 197.9 (C), 157.9 (CH), 152.6 (CH), 142.0 (CH), 137.5 (C), 127.6 (C), 122.8 (CH), 53.8 (CH_2), 52.2 (CH_2), 29.9 (C), 28.4 (2 × CH_3), 26.9 (CH_2), 24.2 (CH_2), 21.82 (CH_2), 21.77 (CH_2). HRMS (ESI) m/z: calcd for $C_{17}H_{22}O_2Na$ $[M + Na]^+$ 281.1512, found 281.1508.

Substrate ***4n***. Obtained as a dark-red solid (239 mg, 80%), mp 121.0−122.0 °C. IR (KBr): 2953, 2922, 1638, 1570, 1520, 1356, 1177 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (dd, J = 14.4 Hz, J = 12.4 Hz, 1H), 7.77 (d, J = 12.2 Hz, 1H), 7.15 (d, J = 14.6 Hz, 1H), 6.57 (s, 1H), 6.53 (d, J = 2.9 Hz, 1H), 6.13 (d, J = 2.7 Hz, 1H), 2.52 (s, 4H), 2.37 (s, 3H), 2.24 (s, 3H), 1.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.9 (C), 197.9 (C), 159.6 (CH), 155.0 (C), 151.8 (CH), 151.4 (C), 132.5 (C), 127.9 (CH), 126.9 (C), 124.9 (CH), 116.6 (CH), 109.1 (CH), 53.9 (CH_2), 52.2 (CH_2), 30.0 (C), 28.4 (2 × CH_3), 13.9 (CH_3), 13.8 (CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{22}NaO_3$ $[M + Na]^+$ 321.1461, found 321.1458.

Substrate ***4o***. Obtained as a yellow solid (67 mg, 30%), mp 139.0−140.0 °C. IR (KBr): 3022, 2994, 2960, 2933, 1719, 1683, 1599, 1587, 1366, 1219, 991 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.00−7.87 (m, 2H), 7.84−7.65 (m, 3H), 7.46 (d, J = 12.3 Hz, 1H), 6.95 (dd, J = 14.7 Hz, J = 10.9 Hz, 1H), 6.42 (dd, J = 14.8 Hz, J = 10.9 Hz, 1H), 6.23 (dq, J = 14.8 Hz, J = 6.8 Hz, 1H), 1.91 (d, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2 (C), 189.8 (C), 151.7 (CH), 144.7 (CH), 141.8 (C), 141.2 (CH), 140.5 (C), 134.7 (CH), 134.5 (CH), 131.9 (CH), 126.8 (C), 125.3 (CH), 122.7 (CH), 122.5 (CH), 18.9 (CH_3). HRMS (ESI) m/z: calcd for $C_{15}H_{12}O_2Na$ $[M + Na]^+$ 247.0729, found 247.0721.

Substrate ***4p***. Obtained as a dark-red solid (54 mg, 20%), mp 189.0 °C (dec.). IR (KBr): 3046, 3005, 2966, 2918, 1661, 1539, 1165 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (dd, J = 14.3 Hz, J = 12.5 Hz, 1H), 7.50−7.40 (m, 3H), 7.30−7.20 (m, 1H), 7.08−6.96 (m, 2H), 6.95−6.86 (m, 2H), 3.85 (s, 3H), 2.68 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.7, 203.1, 161.3, 156.3, 148.2, 144.1, 129.5, 128.6, 127.1, 126.2, 126.0, 114.5, 55.3, 34.8, 34.1. HRMS (ESI) m/z: calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1172, found 269.1163.

Substrate ***4r***. Obtained as an orange to red solid (233 mg, 90%), mp 96.5−97.5 °C. IR (KBr): 2953, 2941, 2926, 2868, 1684, 1636, 1607, 1545, 1474, 1354, 1263, 1138, 1020 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (dd, J = 15.0 Hz, J = 12.5 Hz, 1H), 7.74 (d, J = 12.5 Hz, 1H), 7.04 (d, J = 15.1 Hz, 1H), 6.68 (d, J = 3.4 Hz, 1H), 6.15 (d, J = 3.3 Hz, 1H), 2.53 (bs, 2H), 2.52 (bs, 2H), 2.39 (s, 3H), 1.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7, 197.8, 157.6, 151.11, 151.08, 138.6, 127.4, 122.3, 118.9, 110.0, 53.9, 52.2, 30.0, 28.4, 14.0. HRMS (ESI) m/z: calcd for $C_{16}H_{19}O_3$ $[M + H]^+$ 259.1329, found 259.1336.

Substrate ***4s***. Obtained as an orange solid (214 mg, 60%), mp 140.0 °C (dec.). IR (KBr): 3074, 3055, 3019, 2949, 1684, 1647, 1560, 1555, 1518, 1354, 1234, 1177 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (dd, J = 13.3 Hz, J = 12.5 Hz, 1H), 7.58 (d, J = 12.4 Hz, 1H), 7.47−7.40 (m, 3H), 7.36−7.31 (m, 5H), 7.25−7.18 (m, 2H), 7.15−7.02 (m, 2H), 2.52 (bs, 2H), 2.50 (bs, 2H), 1.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8 (C), 197.8 (C), 152.7 (C), 152.1 (CH), 151.0 (CH), 140.8 (C), 138.3 (C), 130.7 (CH), 130.4 (2 × CH), 129.1 (CH), 128.5 (CH), 128.35 (2 × CH), 128.29 (2 × CH), 128.2 (2 × CH), 127.7 (C), 127.5 (CH), 53.9 (CH_2), 52.2 (CH_2), 30.0 (C), 28.4 (2 × CH_3). HRMS (ESI) m/z: calcd for $C_{25}H_{25}O_2$ $[M + H]^+$ 357.1849, found 357.1838.

Substrate ***4t***. Obtained as an orange solid (174 mg, 75%), mp 96.0−97.0 °C. IR (KBr): 3057, 2955, 2928, 2903, 1684, 1637, 1570, 1526, 1339, 1238, 1190 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78−7.63 (m, 2H), 7.40−7.22 (m, 1H), 6.23 (bd, J = 11.6 Hz, 1H), 2.51 (s, 4H), 1.94 (bs, 6H), 1.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.6 (C), 197.8 (C), 152.1 (CH), 150.7 (CH), 149.8 (C), 127.3 (CH), 127.2 (C), 126.5 (CH), 53.8 (CH_2), 52.1 (CH_2), 29.9 (C), 28.4 (2 × CH_3), 26.9 (CH_3), 19.1 (CH_3). HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1350, found 255.1355.

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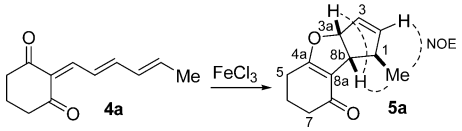
General Procedure for the Rearrangement of Conjugated 1,3-Dicarbonyl Substrates 4. To a solution of dicarbonyl substrate **4** (0.5 mmol) in CH_2Cl_2 (5.0 mL, 0.1 M) was added anhydrous $FeCl_3$ (41.7 mg, 0.25 mmol, 0.5 equiv). The mixture was refluxed until the dicarbonyl substrate was completely consumed (TLC monitoring; see Tables 1 and 2). The solvent was then evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) to afford the following compounds.

Cyclopenta[b]furan ***5a***.



Obtained as a colorless to pale-yellow solid (84 mg, 88%), mp 46.5–47.0 °C. IR (film): 2961, 2941, 2893, 1640, 1622, 1400, 1179 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.02 (dd, J = 5.6 Hz, J = 2.2 Hz, 1H, 2-H), 5.82 (dt, J = 8.6 Hz, J = 1.8 Hz, 1H, 3a-H), 5.74 (dt, J = 5.6 Hz, J = 2.0 Hz, 1H, 3-H), 3.27 (dq, J = 8.5 Hz, J = 1.8 Hz, 1H, 8b-H), 2.84 (qquint, J = 7.3 Hz, J = 1.9 Hz, 1H, 1-H), 2.39 (td, J = 6.4 Hz, J = 1.6 Hz, 2H, 5-H), 2.32 (t, J = 6.3 Hz, 2H, 7-H), 2.00 (quint, J = 6.4 Hz, 2H, 6-H), 1.18 (d, J = 7.3 Hz, 3H, 1-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.3 (C, C-8), 175.4 (C, C-4a), 143.9 (CH, C-2), 126.1 (CH, C-3), 117.0 (C, C-8a), 95.1 (CH, C-3a), 49.3 (CH, C-8b), 46.5 (CH, C-1), 36.5 (CH_2, C-7), 23.8 (CH_2, C-5), 21.52 (CH_3, C1-CH_3), 21.47 (CH_2, C-6). HRMS (ESI) m/z: calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1067, found 191.1068.

Cyclopenta[b]furan ***5b***. Obtained as a colorless to pale-yellow solid (87 mg, 80%), mp 42.5–43.0 °C. IR (film): 2959, 2910, 2897, 1649, 1634, 1401, 1207, 1037 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.02 (dd, J = 5.6 Hz, J = 2.2 Hz, 1H), 5.84 (dt, J = 8.5 Hz, J = 2.0 Hz, 1H), 5.74 (dt, J = 5.6 Hz, J = 2.0 Hz, 1H), 3.29 (dq, J = 8.5 Hz, J = 1.8 Hz, 1H), 2.84 (qquint, J = 7.1 Hz, J = 2.2 Hz, 1H), 2.25 (d, J = 1.6 Hz, 2H), 2.20 (bs, 2H), 1.18 (d, J = 7.3 Hz, 3H), 1.08 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5 (C), 174.2 (C), 143.8 (CH), 126.2 (CH), 115.4 (C), 95.3 (CH), 50.9 (CH_2), 49.0 (CH), 46.4 (CH), 37.6 (CH_2), 33.7 (C), 28.5 (CH_3), 28.3 (CH_3), 21.5 (CH_3). HRMS (ESI) m/z: calcd for $C_{14}H_{18}O_2Na$ $[M + Na]^+$ 241.1199, found 241.1198.

Cyclopenta[b]furans ***5c1*** *and* ***5c2***. These products are regioisomers; their assignment is based on coupling between the carbonyl carbon and the *gem*-dimethyl groups in the HMBC spectra. **5c1** was obtained as a colorless liquid (35 mg, 32%). IR (film): 2963, 2926, 1651, 1620, 1396, 1159 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.00 (ddm, J = 5.6 Hz, J = 2.4 Hz, 1H), 5.79 (dtd, J = 8.5 Hz, J = 2.1 Hz, J = 0.7 Hz, 1H), 5.72 (dt, J = 5.6 Hz, J = 2.0 Hz, 1H), 3.25 (dd, J = 8.5 Hz, J = 1.8 Hz, 1H), 2.82 (qquint, J = 7.0 Hz, J = 2.2 Hz, 1H), 2.37 (bt, J = 6.6 Hz, 2H), 1.80 (bt, J = 6.2 Hz, 2H), 1.21 (s, 3H), 1.16 (d, J = 7.2 Hz, 3H), 1.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8 (C), 180.8 (C), 143.6 (CH), 126.0 (CH), 114.6 (C), 94.6 (CH), 49.4 (CH), 46.3 (CH), 36.7 (CH_2), 34.3 (CH_2), 32.4 (C), 24.8 (CH_3), 24.7 (CH_3), 21.5 (CH_3). HRMS (ESI) m/z: calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1374. **5c2** was obtained as a colorless liquid (58 mg, 53%). IR (film): 2957, 2926, 1632, 1400, 1192 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.98 (dd, J = 5.6 Hz, J = 2.2 Hz, 1H), 5.79 (dt, J = 8.7 Hz, J = 2.1 Hz, 1H), 5.71 (dt, J = 5.6 Hz, J = 2.0 Hz, 1H), 3.21 (dq, J = 8.5 Hz, J = 1.5 Hz, 1H), 2.75 (qquint, J = 7.0 Hz, J = 2.0 Hz, 1H), 2.38 (tm, J = 6.4 Hz, 2H), 1.80 (t, J = 6.3 Hz, 2H), 1.15 (d, J = 7.0 Hz, 3H), 1.08 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.3 (C), 173.2 (C), 144.0 (CH), 126.2 (CH), 115.2 (C), 95.3 (CH), 49.5 (CH), 46.7 (CH), 40.5 (C), 35.5 (CH_2), 24.3 (2 × CH_3), 21.44 (CH_3), 21.39 (CH_2). HRMS (ESI) m/z: calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1383.

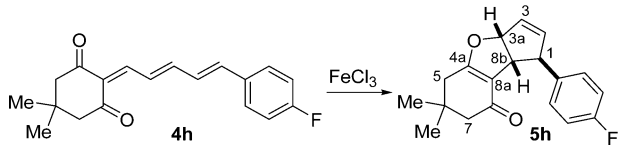
Cyclopenta[b]furans ***5d***. Obtained as a colorless solid (106 mg, 80%), mp 70.0–71.0 °C. The diastereomeric ratio could not be determined because all of the signals overlap. IR (KBr): 3059, 3028, 2955, 2922, 1647, 1628, 1400, 1198, 1034 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37–7.29 (overlapping m, 4H), 7.28–7.20 (overlapping m, 6H), 6.08–6.02 (overlapping m, 2H), 5.92–5.84 (overlapping m, 2H), 5.80–5.72 (overlapping m, 2H), 3.47–3.27 (overlapping m, 4H), 2.95–2.83 (overlapping m, 2H), 2.67–2.54 (overlapping m, 8H), 1.23–1.17 (overlapping m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8 (C), 193.7 (C), 174.7 (C), 174.6 (C), 144.0 (CH, CH), 142.6 (C, C), 128.6 (2 × CH, 2 × CH), 126.8 (CH, CH), 126.6 (2 × CH, 2 × CH), 126.2 (CH), 126.0 (CH), 117.1 (C), 116.6 (C), 95.8 (CH), 95.6 (CH), 49.20 (CH), 49.17 (CH), 46.8 (CH), 46.1 (CH), 44.1 (CH_2), 43.7 (CH_2), 40.3 (CH), 40.0 (CH), 31.45 (CH_2), 31.39 (CH_2), 21.6 (CH_3), 21.5 (CH_3). HRMS (ESI) m/z: calcd for $C_{18}H_{18}O_2Na$ $[M + Na]^+$ 289.1199, found 289.1186.

Cyclopenta[b]furan ***5e***. Obtained as a colorless liquid (93 mg, 80%). IR (film): 2960, 2931, 1653, 1632, 1401, 1202, 1039 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.09–6.01 (m, 1H), 5.84–5.74 (m, 2H), 3.34 (dm, J = 8.4 Hz, 1H), 2.81–2.71 (m, 1H), 2.24 (bs, 2H), 2.19 (bs, 2H), 1.67–1.38 (m, 2H), 1.08 (bs, 3H), 1.06 (bs, 3H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C), 174.2 (C), 141.7 (CH), 127.0 (CH), 115.3 (C), 95.0 (CH), 52.9 (CH), 51.0 (CH_2), 46.9 (CH), 37.7 (CH_2), 33.7 (C), 28.7 (CH_2), 28.6 (CH_3), 28.3 (CH_3), 11.3 (CH_3). HRMS (ESI) m/z: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1355, found 255.1353.

Cyclopenta[b]furan ***5f***. Obtained as a pale-yellow liquid (119 mg, 85%). IR (film): 3061, 3028, 2959, 2929, 1630, 1401 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.33–7.28 (m, 4H), 7.25–7.17 (m, 1H), 6.15 (dd, J = 5.7 Hz, J = 2.4 Hz, 1H), 6.02 (dt, J = 5.7 Hz, J = 2.0 Hz, 1H), 5.94 (bdt, J = 8.4 Hz, J = 2.2 Hz, 1H), 4.09 (quint, J = 2.1 Hz, 1H), 3.58 (dq, J = 8.3 Hz, J = 1.7 Hz, 1H), 2.29 (bs, 2H), 2.25 (bs, 2H), 1.11 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C), 174.3 (C), 143.5 (C), 139.8 (CH), 129.0 (CH), 128.4 (2 × CH), 127.2 (2 × CH), 126.4 (CH), 115.2 (C), 95.0 (CH), 56.7 (CH), 2 × 51.1 (CH, CH_2), 37.8 (CH_2), 33.9 (C), 28.7 (CH_3), 28.3 (CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{20}O_2Na$ $[M + Na]^+$ 303.1355, found 303.1354.

Cyclopenta[b]furan ***5g***. Obtained as a pale-yellow solid (132 mg, 85%), mp 109.5–110.5 °C. IR (KBr): 3069, 3003, 2951, 1632, 1508, 1398, 1244, 1030 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25–7.18 (m, 2H), 6.88–6.81 (m, 2H), 6.13 (ddm, J = 5.6 Hz, J = 2.3 Hz, 1H), 6.00 (dt, J = 5.6 Hz, J = 2.0 Hz, 1H), 5.92 (dm, J = 8.5 Hz, 1H), 4.03 (quint, J = 2.0 Hz, 1H), 3.78 (s, 3H), 3.52 (dm, J = 8.5 Hz, 1H), 2.28 (bs, 2H), 2.24 (s, 2H), 1.10 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C), 174.2 (C), 158.1 (C), 140.0 (CH), 135.6 (C), 128.6 (CH), 128.1 (2 × CH), 115.2 (C), 113.7 (2 × CH), 95.0 (CH), 55.9 (CH), 55.1 (CH_3), 51.2 (CH), 51.0 (CH_2), 37.7 (CH_2), 33.8 (C), 28.6 (CH_3), 28.3 (CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{22}O_3K$ $[M + K]^+$ 349.1200, found 349.1192.

Cyclopenta[b]furan ***5h***.



Obtained as a colorless liquid (112 mg, 75%). IR (film): 2957, 2930, 1632, 1506, 1402, 1221 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–7.23 (m, 2H, Ar–H), 7.03–6.93 (m, 2H, Ar–H), 6.13 (bdd, J = 5.7 Hz, J = 2.4 Hz, 1H, 2-H), 6.03 (dt, J = 5.7 Hz, J = 1.9 Hz, 1H, 3-H), 5.92 (dm, J = 8.3 Hz, 1H, 3a-H), 4.05 (quint, J = 2.0 Hz, 1H, 1-H), 3.52 (dq, J = 8.3 Hz, J = 1.7 Hz, 1H, 8b-H), 2.29 (d, J = 1.5 Hz, 2H, 5-H), 2.25 (s, 2H, 7-H), 1.10 (s, 3H, 6-CH_3), 1.09 (s, 3H, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C, C-8), 174.4 (C, C-4a), 161.5 (C, d, J = 244.8 Hz, C–F), 139.6 (CH, C-2), 139.2 (C, d, J = 2.7 Hz, Ar), 129.2 (CH, C-3), 128.2 (2 × CH, d, J = 7.7 Hz, Ar), 115.1 (C, C-8a), 115.0 (2 × CH, d, J = 20.9 Hz, Ar), 94.9 (CH, C-3a), 56.0 (CH, C-1), 51.2 (CH, C-8b), 51.0 (CH_2, C-7), 37.7 (CH_2, C-5), 33.9 (C, C-6), 28.6 (CH_3, C6-CH_3), 28.3 (CH_3, C6-CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{20}FO_2$ $[M + H]^+$ 299.1442, found 299.1443.

Cyclopenta[b]furan ***5i***. Obtained as a colorless liquid (49 mg, 55%). IR (film): 2957, 2926, 1666, 1614, 1587, 1379, 1205 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.00 (dm, J = 5.5 Hz, 1H), 5.73 (dm, J = 5.7 Hz, 1H), 5.65 (dm, J = 9.0 Hz, 1H), 3.38 (dm, J = 9.0 Hz, 1H), 2.74 (qquint, J = 7.1 Hz, J = 2.2 Hz, 1H), 2.25 (bs, 3H), 2.19 (bs, 3H),

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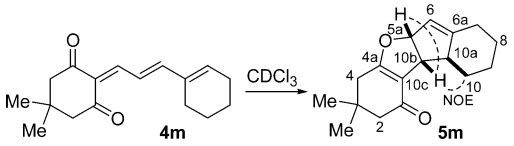
1.18 (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3 (C), 166.5 (C), 143.0 (CH), 126.9 (CH), 117.3 (C), 91.5 (CH), 53.0 (CH), 48.3 (CH), 29.3 (CH_3), 21.6 (CH_3), 15.2 (CH_3). HRMS (ESI) m/z: calcd for $C_{11}H_{14}O_2Na$ $[M + Na]^+$ 201.0886, found 201.0883.

Cyclopenta[b]furan ***5j***. Obtained as a pale-yellow liquid (48 mg, 40%). IR (film): 3030, 2957, 1655 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.28 (m, 2H), 7.27−7.17 (m, 3H), 6.06 (bdd, J = 5.6 Hz, J = 2.2 Hz, 1H), 5.97 (dt, J = 5.6 Hz, J = 1.9 Hz, 1H), 5.79 (bd, J = 8.8 Hz, 1H), 3.94 (quint, J = 1.9 Hz, 1H), 3.74 (bd, J = 8.8 Hz, 1H), 2.23 (overlapping signals, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.2, 166.6, 143.4, 140.0, 128.8, 128.5, 127.3, 126.5, 117.1, 91.4, 59.0, 55.0, 29.6, 15.3. HRMS (ESI) m/z: calcd for $C_{16}H_{16}O_2Na$ $[M + Na]^+$ 263.1042, found 263.1051.

Cyclopenta[b]furan ***5k***. Obtained as a colorless liquid (26 mg, 25%). IR (film): 2958, 2927, 1701, 1640, 1381, 1204, 1081 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.00 (ddd, J = 5.6 Hz, J = 2.3 Hz, J = 0.6 Hz, 1H), 5.73 (dt, J = 5.6 Hz, J = 2.0 Hz, 1H), 5.65 (dtd, J = 8.9 Hz, J = 2.2 Hz, J = 0.8 Hz, 1H), 4.27−4.09 (m, 2H), 3.31 (dm, J = 8.9 Hz, 1H), 2.80 (qquint, J = 7.1 Hz, J = 2.2 Hz, 1H), 2.17 (d, J = 1.4 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H), 1.15 (d, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8 (C), 166.3 (C), 143.1 (CH), 127.0 (CH), 106.1 (C), 91.6 (CH), 59.2 (CH_2), 52.4 (CH), 48.3 (CH), 21.4 (CH_3), 14.3 (CH_3), 14.1 (CH_3). HRMS (ESI) m/z: calcd for $C_{12}H_{17}O_3$ $[M + H]^+$ 209.1172, found 209.1168.

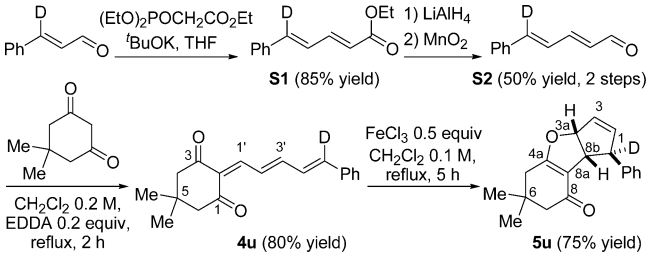
Spontaneous Cycloisomerization of Compounds 4m and 4n in $CDCl_3$. *Cyclopenta[b]furan* ***5m***.



Leaving compound **4m** (77 mg, 0.3 mmol) in $CDCl_3$ for 2 weeks at room temperature afforded compound **5m** as a colorless to pale-yellow solid in 65% yield (50 mg) after flash column chromatography (silica gel, eluting with petroleum ether/ethyl acetate). Mp: 98.0−99.0 °C. IR (KBr): 2922, 2851, 1647, 1624, 1404, 1213, 1032 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.72 (dtd, J = 8.8 Hz, J = 2.2 Hz, J = 0.6 Hz, 1H, 5a-H), 5.42 (q, J = 1.8 Hz, 1H, 6-H), 3.31 (dq, J = 8.8 Hz, J = 1.8 Hz, 1H, 10b-H), 2.50 (dm, J = 13.2 Hz, 1H, 7-H$_\beta$), 2.42−2.31 (m, 2H, 10a-H, 10-H$_\alpha$), 2.25 (d, J = 1.3 Hz, 2H, 4-H), 2.20 (s, 2H, 2-H), 1.97 (btd, J = 13.2 Hz, J = 5.4 Hz, 1H, 7-H$_\alpha$), 1.90−1.79 (m, 1H, 8-H$_\alpha$), 1.79−1.69 (m, 1H, 9-H$_\beta$), 1.37 (qt, J = 13.3 Hz, J = 3.3 Hz, 1H, 9-H$_\alpha$), 1.17 (qt, J = 12.9 Hz, J = 3.8 Hz, 1H, 8-H$_\beta$), 1.08 (s, 3H, 3-CH_3), 1.07 (s, 3H, 3-CH_3), 0.98 (qd, J = 13.1 Hz, J = 3.4 Hz, 1H, 10-H$_\beta$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5 (C, C-1), 174.8 (C, C-4a), 156.5 (C, C-6a), 117.4 (CH, C-6), 115.7 (C, C-10c), 95.5 (CH, C-5a), 52.6 (CH, C-10a), 50.9 (CH_2, C-2), 48.0 (CH, C-10b), 37.8 (CH_2, C-4), 35.7 (CH_2, C-10), 33.7 (C, C-3), 29.1 (CH_2, C-7), 28.6 (CH_3, C3-CH_3), 28.4 (CH_3, C3-CH_3), 27.3 (CH_2, C-8), 25.5 (CH_2, C-9). HRMS (ESI) m/z: calcd for $C_{17}H_{23}O_2$ $[M + H]^+$ 259.1693, found 259.1688.

Cyclopenta[b]furan ***5n***. Leaving compound **4n** (60 mg, 0.2 mmol) in $CDCl_3$ for 2 months at room temperature afforded compound **5n** as a colorless to pale-yellow liquid in 60% yield (36 mg) after flash column chromatography (silica gel, eluting with petroleum ether/ethyl acetate). IR (film): 2957, 2920, 1620, 1402, 1215 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.00 (d, J = 2.9 Hz, 1H), 5.89 (dm, J = 8.2 Hz, 1H), 5.85 (d, J = 2.2 Hz, 1H), 5.58−5.54 (m, 1H), 3.84 (bs, 1H), 3.78 (bd, J = 8.3 Hz, 1H), 2.27 (bs, 2H), 2.25−2.19 (overlapping signals, 5H), 1.69 (s, 3H), 1.09 (s, 3H), 1.07 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3 (C), 174.7 (C), 153.3 (C), 150.8 (C), 148.1 (C), 123.8 (CH), 114.7 (C), 106.6 (CH), 105.9 (CH), 95.0 (CH), 53.5 (CH), 51.0 (CH_2), 48.7 (CH), 37.8 (CH_2), 33.8 (C), 28.9 (CH_3), 28.2 (CH_3), 15.2 (CH_3), 13.5 (CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{22}NaO_3$ $[M + Na]^+$ 321.1461, found 321.1467.

Deuterium Labeling Experiments: Substitution at Unbranched Dienal C-5.



Ester ***S1***. To a solution of ethyl diethylphosphonoacetate (1.35 mL, 6.8 mmol) in THF (14.0 mL) at 0 °C was added potassium *tert*-butoxide (0.94 g, 7.8 mmol). The mixture was stirred for 30 min at 0 °C, and then cinnamaldehyde-3-d[18] (0.89 g, 6.7 mmol) in THF (2.0 mL) was added. The mixture was stirred for 1 h at room temperature. The reaction was quenched with water, and the resulting mixture was extracted three times with Et_2O. The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. Flash column chromatography (silica gel, eluting with petroleum ether) afforded ester **S1** as a colorless liquid (1.16 g, 85% yield). IR (film): 3057, 3022, 2980, 2227, 1707, 1624, 1258, 1138 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51−7.24 (overlapping signals, 6H), 6.87 (bd, J = 11.2 Hz, 1H), 5.99 (d, J = 15.4 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 144.4, 135.9, 128.9, 128.7, 127.0, 126.0, 121.2, 60.2, 14.2, CD signal missing. HRMS (ESI) m/z: calcd for $C_{13}H_{13}DO_2Na$ $[M + Na]^+$ 226.0949, found 226.0956.

Aldehyde ***S2***. To a suspension of lithium aluminum hydride (0.10 g, 2.60 mmol) in Et_2O (4.5 mL) at 0 °C was added dropwise a solution of ester **S1** (0.45 g, 2.23 mmol) in Et_2O (2.4 mL). The mixture was stirred for 1 h at room temperature and then cooled to 0 °C. The mixture was then treated dropwise with an aqueous sodium hydroxide solution (0.45 g of NaOH in 0.45 mL of H_2O). After being stirred for 30 min, the mixture was diluted with Et_2O, filtered through Celite (Et_2O wash), and concentrated under reduced pressure. The residue was then dissolved in CH_2Cl_2 (4 mL) and hexanes (4 mL). To this stirred solution was added activated MnO_2 (1.84 g, 19 mmol). The reaction mixture was stirred for 4 h at room temperature and then filtered through Celite. The solid residue was washed with 30% ethyl acetate in hexanes solution. The combined filtrates were dried (Na_2SO_4) and concentrated under reduced pressure. Flash column chromatography of the residue (silica gel, eluting with 9:1 hexanes/ethyl acetate) afforded aldehyde **S2** as a pale-yellow liquid in 50% yield (177 mg) over two steps. IR (film): 3050, 3028, 2820, 2743, 2232, 1616, 1167, 1119 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.61 (d, J = 7.9 Hz, 1H), 7.54−7.44 (m, 2H), 7.42−7.30 (m, 3H), 7.25 (dd, J = 15.1 Hz, J = 11.1 Hz, 1H), 6.98 (bd, J = 11.0 Hz, 1H), 6.25 (dd, J = 15.1 Hz, J = 7.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3 (CH), 151.8 (CH), 141.9 (CD, t, J = 23.3 Hz), 135.3 (C), 131.4 (CH), 129.5 (CH), 128.7 (2 × CH), 127.3 (2 × CH), 125.9 (CH). HRMS (ESI) m/z: calcd for $C_{11}H_9DONa$ $[M + Na]^+$ 182.0687, found 182.0678.

Substrate ***4u***. Obtained in 80% yield (225 mg) as an orange to red solid using the general condensation protocol. Mp: 116.5−117.5 °C. IR (KBr): 3055, 3026, 2949, 2922, 1686, 1647, 1566, 1528, 1375, 1229 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (dd, J = 13.9 Hz, J = 12.3 Hz, 1H, 2′-H), 7.70 (d, J = 12.3 Hz, 1H, 1′-H), 7.52−7.44 (m, 2H, Ar−H), 7.40−7.25 (m, 3H, Ar−H), 7.23−7.02 (m, 2H, 3′-H, 4′-H), 2.524 (bs, 2H, 4-H*), 2.519 (bs, 2H, 6-H*), 1.07 (s, 6H, 5-CH_3, 5-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7 (C, C-1*), 197.6 (C, C-3*), 153.4 (CH, C-3′), 150.4 (CH, C-1′), 141.4 (CD, t, J = 23.5 Hz, C-5′), 135.8 (C, Ar), 129.7 (CH, C-2′), 129.3 (CH, Ar), 128.7 (2 × CH, Ar), 128.2 (CH, C-4′), 128.0 (C, C-2), 127.3 (2 × CH, Ar), 53.8 (CH_2, C-4**), 52.1 (CH_2, C-6**), 29.9 (C, C-5), 28.3 (2 × CH_3, C5-CH_3, C5-CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{20}DO_2$ $[M + H]^+$ 282.1599, found 282.1609.

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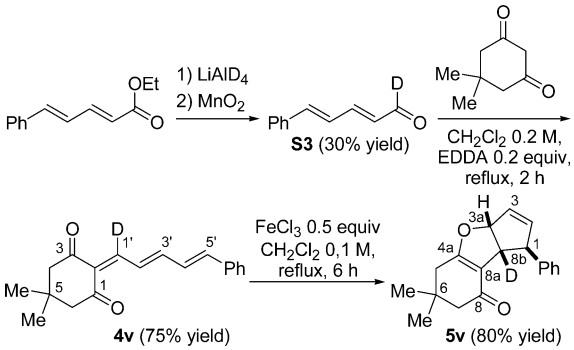
Cyclopenta[b]furan ***5u***. Obtained as a pale-yellow liquid in 75% yield (106 mg) using the general cycloisomerization protocol with $FeCl_3$ (0.5 equiv). IR (film): 3055, 3024, 2957, 1647, 1630, 1398, 1217 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34−7.26 (m, 4H, Ar−H), 7.25−7.16 (m, 1H, Ar−H), 6.14 (bd, J = 5.7 Hz, 1H, 2-H), 6.02 (dd, J = 5.7 Hz, J = 1.9 Hz, 1H, 3-H), 5.93 (dm, J = 8.4 Hz, 1H, 3a-H), 3.57 (dt, J = 8.3 Hz, J = 1.7 Hz, 1H, 8b-H), 2.29 (bd, J = 1.4 Hz, 2H, 5-H), 2.25 (bs, 2H, 7-H), 1.11 (s, 3H, 6-CH_3), 1.09 (s, 3H, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C, C-8), 174.3 (C, C-4a), 143.4 (C, Ar), 139.8 (CH, C-2), 129.0 (CH, C-3), 128.4 (2 × CH, Ar), 127.2 (2 × CH, Ar), 126.4 (CH, Ar), 115.2 (C, C-8a), 95.0 (CH, C-3a), 56.3 (CD, t, J = 21.0 Hz, C-1), 51.1 (CH_2, C-7), 51.0 (CH, C-8b), 37.8 (CH_2, C-5), 33.9 (C, C-6), 28.7 (CH_3, 6-CH_3), 28.3 (CH_3, 6-CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{20}DO_2$ $[M + H]^+$ 282.1599, found 282.1601.

Deuterium Labeling Experiments: Substitution at Unbranched Dienal C-1.

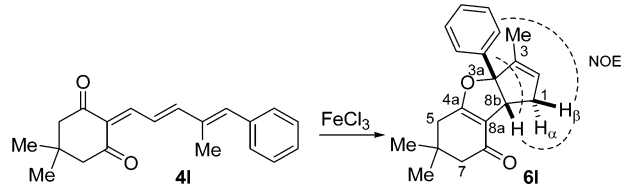


Aldehyde ***S3***. To a suspension of lithium aluminum deuteride (0.11 g, 2.6 mmol) in Et_2O (4.5 mL) at 0 °C was added dropwise a solution of ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate[19] (0.45 g, 2.25 mmol) in Et_2O (2.4 mL). The mixture was stirred for 15 min at room temperature and then cooled to 0 °C. The mixture was then treated dropwise with an aqueous sodium hydroxide solution (0.45 g of NaOH in 0.45 mL of H_2O). After being stirred for 30 min, the mixture was diluted with Et_2O, filtered through Celite (Et_2O wash), and concentrated under reduced pressure. The residue was then dissolved in CH_2Cl_2 (4 mL) and hexanes (4 mL). To this stirred solution was added activated MnO_2 (1.84 g, 19 mmol). The reaction mixture was stirred for 2 h at room temperature and then filtered through Celite. The solid residue was washed with 30% ethyl acetate in hexanes solution. The combined filtrates were dried (Na_2SO_4) and concentrated under reduced pressure. Flash column chromatography of the residue (silica gel, eluting with 9.8:0.2 hexanes/ethyl acetate) afforded aldehyde **S3** as a pale-yellow liquid (0.108 g, 0.68 mmol, 30% yield over two steps). IR (film): 3057, 3028, 2997, 2073, 1670, 1649, 1620, 1151 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.52−7.46 (m, 2H), 7.41−7.30 (m, 3H), 7.24 (ddd, J = 15.1 Hz, J = 7.3 Hz, J = 3.2 Hz, 1H), 7.04−6.91 (m, 2H), 6.25 (bd, J = 15.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.0 (CD, t, J = 26.3 Hz), 151.8, 142.2, 135.3, 131.3, 129.4, 128.7, 127.3, 126.0. HRMS (ESI) m/z: calcd for $C_{11}H_{10}DO$ $[M + H]^+$ 160.0867, found 160.0864.

Substrate ***4v***. Obtained in 75% yield (211 mg) as an orange solid using the general condensation protocol. Mp: 119.5−120.5 °C. IR (KBr): 3055, 3026, 2949, 1686, 1647, 1516, 1234 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 14.1 Hz, 1H, 2′-H), 7.51−7.46 (m, 2H, Ar−H), 7.41−7.29 (m, 3H, Ar−H), 7.23−7.02 (m, 2H, 3′-H, 4′-H), 6.94 (d, J = 14.8 Hz, 1H, 5′-H), 2.53 (bs, 2H, 4-H*), 2.52 (bs, 2H, 6-H*), 1.08 (s, 6H, 5-CH_3, 5-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8 (C, C-1*), 197.7 (C, C-3*), 153.5 (CH, C-3′), 150.1 (CD, t, J = 23.6 Hz, C-1′), 141.8 (CH, C-5′), 135.9 (C, Ar), 129.7 (CH, C-2′), 129.4 (CH, Ar), 128.8 (2 × CH, Ar), 128.3 (CH, C-4′), 128.0 (C, C-2), 127.4 (2 × CH, Ar), 53.9 (CH_2, C-4**), 52.2 (CH_2, C-6**), 29.9 (C, C-5), 28.4 (2 × CH_3, C5-CH_3, C5-CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{19}DO_2Na$ $[M + Na]^+$ 304.1418, found 304.1413.

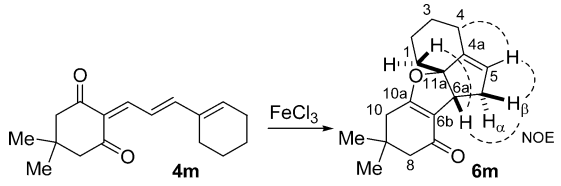
Cyclopenta[b]furan ***5v***. Obtained as a pale-yellow to colorless liquid in 80% yield (113 mg) using the general cycloisomerization protocol. IR (film): 3059, 2957, 1632, 1396, 1221, 1099 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34−7.26 (m, 4H, Ar−H), 7.24−7.16 (m, 1H, Ar−H), 6.14 (bdd, J = 5.7 Hz, J = 2.4 Hz, 1H, 2-H), 6.01 (dt, J = 5.7 Hz, J = 2.0 Hz, 1H, 3-H), 5.94−5.90 (m, 1H, 3a-H), 4.07 (q, J = 2.1 Hz, 1H, 1-H), 2.28 (s, 2H, 5-H), 2.24 (bs, 2H, 7-H), 1.10 (s, 3H, 6-CH_3), 1.08 (s, 3H, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C, C-8), 174.3 (C, C-4a), 143.4 (C, Ar), 139.8 (CH, C-2), 128.9 (CH, C-3), 128.3 (2 × CH, Ar), 127.1 (2 × CH, Ar), 126.4 (CH, Ar), 115.0 (C, C-8a), 94.9 (CH, C-3a), 56.6 (CH, C-1), 51.0 (CH_2, C-7), 50.7 (CD, t, J = 21.5 Hz, C-8b), 37.7 (CH_2, C-5), 33.8 (C, C-6), 28.6 (CH_3, C6-CH_3), 28.3 (CH_3, C6-CH_3). HRMS (ESI) m/z: calcd for $C_{19}H_{19}DO_2Na$ $[M + Na]^+$ 304.1418, found 304.1415.

Rearrangement of Branched Conjugated 1,3-Dicarbonyl Substrates Using $FeCl_3$. *Cyclopenta[b]furan* ***6l***.



Obtained as a colorless solid in 60% yield (88 mg) using the general cycloisomerization protocol (1 equiv of $FeCl_3$). Mp: 84.5−85.5 °C. IR (KBr): 3057, 3036, 2957, 2926, 1632, 1398, 1236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.39−7.32 (m, 2H, Ar−H), 7.30−7.21 (m, 3H, Ar−H), 5.73−5.70 (m, 1H, 2-H), 3.66 (dq, J = 7.7 Hz, J = 1.6 Hz, 1H, 8b-H), 2.86 (ddquint, J = 17.3 Hz, J = 7.7 Hz, J = 2.4 Hz, 1H, 1-H_β), 2.53 (dh, J = 17.3 Hz, J = 2.0 Hz, 1H, 1-H_α), 2.40 (bs, 2H, 5-H), 2.24 (dAB, J = 16.2 Hz, 1H, 7-H), 2.22 (dAB, J = 16.2 Hz, 1H, 7-H), 1.59 (td, J = 2.0 Hz, J = 1.8 Hz, 3H, 3-CH_3), 1.12 (s, 6H, 6-CH_3, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8 (C, C-8), 173.9 (C, C-4a), 141.8 (C, Ar), 139.5 (C, C-3), 129.9 (CH, C-2), 128.5 (2 × CH, Ar), 127.5 (CH, Ar), 124.4 (2 × CH, Ar), 115.9 (C, C-8a), 107.8 (C, C-3a), 51.2 (CH_2, C-7), 50.5 (CH, C-8b), 38.0 (CH_2, C-5), 37.0 (CH_2, C-1), 34.1 (C, C-6), 28.9 (CH_3, C6-CH_3), 28.5 (CH_3, C6-CH_3), 12.0 (CH_3, C3-CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{22}O_2Na$ $[M + Na]^+$ 317.1512, found 317.1504.

Cyclopenta[b]furan ***6m***.



Obtained as a pale-yellow liquid in 85% yield (110 mg) using the general cycloisomerization protocol (1 equiv of $FeCl_3$). IR (film): 2934, 2860, 1649, 1624, 1402, 1234, 1140 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.42 (q, J = 2.0 Hz, 1H, 5-H), 3.32 (dq, J = 8.0 Hz, J = 1.8 Hz, 1H, 6a-H), 2.70 (ddt, J = 17.1 Hz, J = 8.1 Hz, J = 2.3 Hz, 1H, 6-H_β), 2.48−2.28 (m, 2H, 6-H_α, 4-H), 2.26 (d, J = 1.4 Hz, 2H, 10-H), 2.24−2.06 (m, 2H, 1-H_α, 4-H), 2.20 (bs, 2H, 8-H), 1.93−1.66 (m, 3H, 2-H_α, 2-H_β, 3-H_α), 1.51 (td, J = 13.4 Hz, J = 4.6 Hz, 1H, 1-H_β), 1.29 (qt, J = 13.1 Hz, J = 4.1 Hz, 1H, 3-H_β), 1.09 (s, 3H, 9-CH_3), 1.07 (s, 3H, 9-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8 (C, C-7), 174.3 (C, C-10a), 141.3 (C, C-4a), 124.8 (CH, C-5), 115.8 (C, C-6b), 104.6 (C, C-11a), 50.8 (CH_2, C-8), 45.1 (CH, C-6a), 37.9 (CH_2, C-10), 37.3 (CH_2, C-6), 36.9 (CH_2, C-1), 33.7 (C, C-9), 28.5 (CH_3, C9-CH_3), 28.4 (CH_3, C9-CH_3), 26.5 (CH_2, C-3), 26.0 (CH_2, C-4), 22.1 (CH_2, C-2). HRMS (ESI) m/z: calcd for $C_{17}H_{23}O_2$ $[M + H]^+$ 259.1693, found 259.1688.

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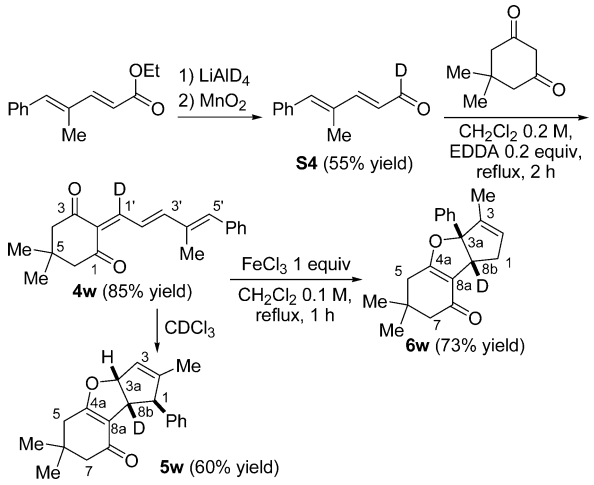
Deuterium Labeling Experiments: Substitution at Branched Dienal C-1.



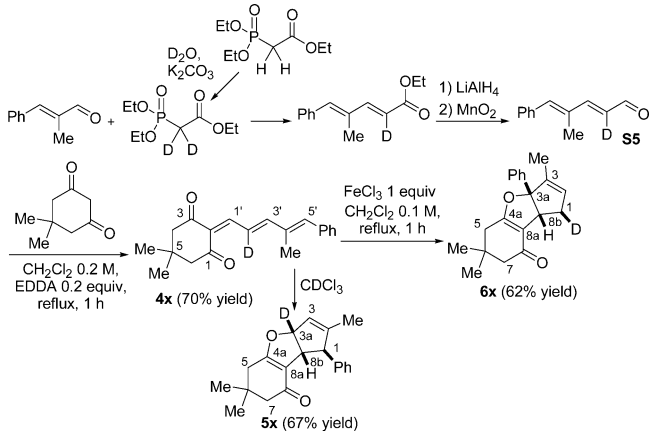
Aldehyde ***S4***. Obtained as a pale-yellow solid in 55% yield (0.214 g over two steps) from (2*E*,4*E*)-4-methyl-5-phenylpenta-2,4-dienoate[19] (0.487 g, 2.25 mmol) using the same reduction/oxidation protocol as for the preparation of aldehyde **S3**. Mp: 39.5−40.5 °C. IR (KBr): 3055, 3022, 2992, 2947, 2918, 2093, 1662, 1605, 1151 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44−7.25 (m, 6H), 6.94 (bs, 1H), 6.27 (d, J = 15.5 Hz, 1H), 2.08 (d, J = 1.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3 (CD, t, J = 26.4 Hz), 157.6, 140.5, 136.0, 134.2, 129.4, 128.2, 128.0, 127.9 (CHCD, t, J = 3.8 Hz), 13.6. HRMS (ESI) m/z: calcd for $C_{12}H_{12}DO$ $[M + H]^+$ 174.1023, found 174.1019.

Substrate ***4w***. Obtained in 85% yield (251 mg) as an orange solid using the general condensation protocol. Mp: 114.5−115.0 °C. IR (KBr): 2951, 2924, 1645, 1516, 1331, 1111 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J = 15.1 Hz, 1H, 2′-H), 7.41−7.26 (m, 5H, Ar−H), 7.22 (dd, J = 15.1 Hz, J = 0.8 Hz, 1H, 3′-H), 6.90 (bs, 1H, 5′-H), 2.53 (bs, 4H, 4-H, 6-H), 2.18 (d, J = 1.1 Hz, 3H, 4′-CH_3), 1.08 (s, 6H, 5-CH_3, 5-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.9 (C, C-1*), 197.8 (C, C-3*), 159.3 (CH, C-3′), 151.1 (CD, t, J = 23.7 Hz, C-1′), 141.0 (CH, C-5′), 136.45 (C, Ar), 136.37 (C, C-4′), 129.6 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.1 (CH, Ar), 127.9 (C, C-2), 125.4 (CH, C-2′), 53.9 (CH_2, C-4**), 52.2 (CH_2, C-6**), 30.0 (C, C-5), 28.4 (2 × CH_3, C5-CH_3, C5-CH_3), 13.9 (CH_3, C4′-CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{22}DO_2Na$ $[M + Na]^+$ 296.1755, found 296.1760.

Cyclopenta[b]furan ***6w***. Obtained as a colorless solid in 73% yield (108 mg) using the general cycloisomerization protocol (1 equiv of $FeCl_3$). Mp: 92.0−93.0 °C. IR (film): 3061, 2957, 2924, 2193, 1645, 1628, 1600, 1394, 1219, 1092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40−7.31 (m, 2H, Ar−H), 7.30−7.20 (m, 3H, Ar−H), 5.75−5.68 (m, 1H, 2-H), 2.85 (dquint, J = 17.2 Hz, J = 2.2 Hz, 1H, 1-H_β), 2.52 (dquint, J = 17.3 Hz, J = 2.1 Hz, 1H, 1-H_α), 2.41 (bs, 2H, 5-H), 2.23 (dAB, J = 16.4 Hz, 1H, 7-H), 2.22 (dAB, J = 16.4 Hz, 1H, 7-H), 1.59 (bq, J = 1.6 Hz, 3H, 3-CH_3), 1.12 (s, 6H, 6-CH_3, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7 (C, C-8), 173.8 (C, C-4a), 141.5 (C, Ar), 139.3 (C, C-3), 129.7 (CH, C-2), 128.4 (2 × CH, Ar), 127.3 (CH, Ar), 124.2 (2 × CH, Ar), 115.7 (C, C-8a), 107.5 (C, C-3a), 51.0 (CH_2, C-7), 50.0 (CD, t, J = 20.6 Hz, C-8b), 37.8 (CH_2, C-5), 36.7 (CH_2, C-1), 33.9 (C, C-6), 28.7 (CH_3, C6-CH_3), 28.3 (CH_3, C6-CH_3), 11.9 (CH_3, C3-CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{21}DO_2Na$ $[M + Na]^+$ 318.1575, found 318.1575.

Cyclopenta[b]furan ***5w***. Leaving substrate **4w** (59 mg, 0.2 mmol) in $CDCl_3$ for 5 weeks at room temperature afforded cyclopenta[*b*]-furan **5w** as a colorless to pale-yellow solid in 60% yield (35 mg) after flash column chromatography (silica gel, eluting with hexanes/ethyl acetate). Mp: 103.0−104.0 °C. IR (KBr): 3061, 3026, 2957, 2924, 2193, 1645, 1628, 1395, 1219, 1092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34−7.24 (m, 2H, Ar−H), 7.23−7.17 (m, 3H, Ar−H), 5.89 (bs, 1H, 3a-H), 5.67 (q, J = 1.6 Hz, 1H, 3-H), 3.83 (bs, 1H, 1-H), 2.30−2.21 (m, 4H, 5-H, 7-H), 1.65 (bs, 3H, 2-CH_3), 1.11 (s, 3H, 6-CH_3), 1.07 (s, 3H, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C, C-8), 174.4 (C, C-4a), 150.2 (C, C-2), 142.9 (C, Ar), 128.5 (2 × CH, Ar), 127.3 (2 × CH, Ar), 126.4 (CH, Ar), 124.2 (CH, C-3), 115.2 (C, C-8a), 95.0 (CH, C-3a), 60.3 (CH, C-1), 51.6 (CD, t, J = 21.5 Hz, C-8b), 51.1 (CH_2, C-7), 37.8 (CH_2, C-5), 33.8 (C, C-6), 28.9 (CH_3, C6-CH_3), 28.2 (CH_3, C6-CH_3), 15.4 (CH_3, C2-CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{22}DO_2$ $[M + H]^+$ 296.1755, found 296.1750.

Deuterium Labeling Experiments: Substitution at Branched Dienal C-2.



Aldehyde ***S5***.[20] Dry potassium carbonate (6.5 g, 45 mmol), deuterium oxide (7 mL), and ethyl diethylphosphonoacetate (3.3 g, 15 mmol) were vigorously stirred in a dry flask for 20 h at room temperature under a nitrogen atmosphere. Commercially available α-methylcinnamaldehyde (2.19 g, 15 mmol) was then introduced, and stirring was continued for 24 h. Extraction (Et_2O, 20 mL × 3) was performed after addition of water (10 mL). This crude ester was directly used to obtain aldehyde **S5** as a pale-yellow liquid (20% yield over three steps, 0.52 g) by means of the same reduction/oxidation protocol as for the preparation of **S2**. IR (film): 3059, 3027, 2996, 2981, 2951, 2821, 2728, 1672, 1599, 1584, 1132 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.45−7.23 (m, 6H), 6.96 (s, 1H), 2.10 (d, J = 1.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.9, 157.7, 140.7, 136.1, 134.3, 129.5, 128.3, 128.1, 13.7, the CD triplet signal overlapped with signals at 128.3 and 128.1 ppm. HRMS (ESI) m/z: calcd for $C_{12}H_{11}DONa$ $[M + Na]^+$ 196.0843, found 196.0843.

Substrate ***4x***. Obtained in 70% yield (207 mg) as an orange solid using the general condensation protocol. Mp: 109.0−110.0 °C. IR (KBr): 3065, 3055, 2951, 2866, 1684, 1645, 1526, 1364, 1144 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (bs, 1H, 1′-H), 7.43−7.34 (m, 4H, Ar−H), 7.34−7.24 (m, 1H, Ar−H), 7.21 (bs, 1H, 3′-H), 6.90 (bs, 1H, 5′-H), 2.53 (bs, 4H, 4-H, 6-H), 2.18 (bs, 3H, 4′-CH_3), 1.09 (s, 6H, 5-CH_3, 5-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8 (C, C-1*), 197.8 (C, C-3*), 159.2 (CH, C-3′), 151.4 (CH, C-1′), 141.0 (CH, C-5′), 136.5 (C, Ar), 136.4 (C, C-4′), 129.6 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.1 (CH, Ar), 128.0 (C, C-2), 125.3 (CD, t, J = 24.6 Hz, C-2′), 53.9 (CH_2, C-4**), 52.2 (CH_2, C-6**), 30.0 (C, C-5), 28.4 (2 × CH_3, C5-CH_3, C5-CH_3), 13.9 (CH_3, C4′-CH_3). HRMS (ESI) m/z: calcd for $C_{20}H_{21}DO_2Na$ $[M + Na]^+$ 318.1575, found 318.1568.

Cyclopenta[b]furan ***6x***. Obtained as a colorless liquid in 62% yield (92 mg) using the general cycloisomerization protocol (1 equiv of $FeCl_3$). IR (film): 3056, 2958, 2927, 2870, 1653, 1635, 1398, 1236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40−7.31 (m, 2H, Ar−H), 7.31−7.20 (m, 3H, Ar−H), 5.74−5.69 (m, 1H, 2-H), 3.65 (bs, 1H, 8b-H), 2.51 (bs, 1H, 1-H_α), 2.41 (d, J = 1.4 Hz, 2H, 5-H), 2.29−2.16 (m, 2H, 7-H), 1.61−1.57 (m, 3H, 3-CH_3), 1.12 (s, 6H, 6-CH_3, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7 (C, C-8), 173.8 (C, C-4a), 141.7 (C, Ar), 139.4 (C, C-3), 129.7 (CH, C-2), 128.4 (2 × CH, Ar), 127.3 (CH, Ar), 124.3 (2 × CH, Ar), 115.8 (C, C-8a), 107.7 (C, C-3a), 51.1 (CH_2, C-7), 50.3 (CH, C-8b), 37.8 (CH_2, C-5), 34.0 (C, C-6), 28.8 (CH_3, C6-CH_3), 28.4 (CH_3, C6-CH_3), 11.9 (CH_3, C3-CH_3), the CD signal was unclear in regard to multiplicity and was found as expected between the signals at 37.8 and 34.0 ppm.

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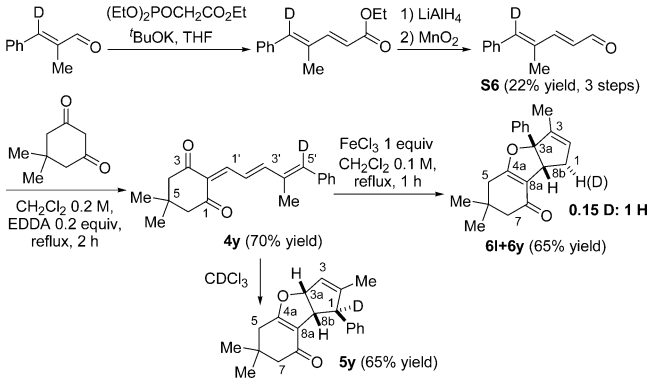
HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{21}DO_2Na$ $[M + Na]^+$ 318.1575, found 318.1575.

Cyclopenta[b]furan ***5x***. Leaving substrate **4x** (59 mg, 0.2 mmol) in $CDCl_3$ for 5 weeks at room temperature afforded compound **5x** as a pale-yellow solid in 67% yield (40 mg) after flash column chromatography (silica gel, eluting with hexanes/ethyl acetate). Mp: 89.0−90.0 °C. IR (KBr): 3061, 2957, 2924, 2203, 1645, 1630, 1394, 1238, 1140 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35−7.26 (m, 2H, Ar−H), 7.25−7.16 (m, 3H, Ar−H), 5.66 (quint, J = 1.5 Hz, 1H, 3-H), 3.83 (s, 1H, 1-H), 3.57 (s, 1H, 8b-H), 2.32−2.20 (m, 4H, 5-H, 7-H), 1.65 (bs, 3H, 2-CH_3), 1.11 (s, 3H, 6-CH_3), 1.08 (s, 3H, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C, C-8), 174.4 (C, C-4a), 150.3 (C, C-2), 143.0 (C, Ar), 128.5 (2 × CH, Ar), 127.3 (2 × CH, Ar), 126.4 (CH, Ar), 124.2 (CH, C-3), 115.3 (C, C-8a), 60.4 (CH, C-1), 51.9 (CH, C-8b), 51.1 (CH_2, C-7), 37.9 (CH_2, C-5), 33.8 (C, C-6), 28.9 (CH_3, C6-CH_3), 28.2 (CH_3, C6-CH_3), 15.4 (CH_3, C2-CH_3), CD signal missing. HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{22}DO_2$ $[M + H]^+$ 296.1755, found 296.1761.

Deuterium Labeling Experiments: Substitution at Branched Dienal C-5.



Aldehyde ***S6***. Obtained as a pale-yellow liquid in 22% yield over three steps (255 mg) from α-methylcinnamaldehyde-3-d[21] (6.7 mmol, 986 mg) using the same tandem Horner−Wadsworth−Emmons protocol/reduction/oxidation protocol for the preparation of **S2** without isolation of the ester intermediate. IR (film): 3053, 2916, 2812, 2731, 1666, 1607, 1304, 1130 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.65 (d, J = 7.7 Hz, 1H), 7.45−7.25 (overlapping signals, m, 5H; d, J = 15.5 Hz, 1H), 6.27 (dd, J = 15.5 Hz, J = 7.8 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8 (CH), 157.7 (CH), 140.2 (CD, t, J = 23.4 Hz), 136.0 (C), 134.1 (C), 129.4 (2 × CH), 128.3 (2 × CH), 128.11 (CH), 128.07 (CH), 13.7 (CH_3). HRMS (ESI) *m*/*z*: calcd for $C_{12}H_{12}DO$ $[M + H]^+$ 174.1024, found 174.1018.

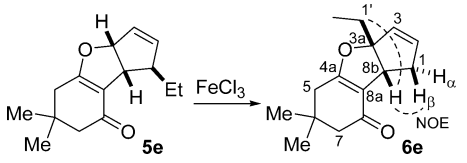
Substrate ***4y***. Obtained in 70% yield (207 mg) as a yellow to orange solid using the general condensation protocol. Mp: 108.0−109.0 °C. IR (KBr): 2952, 2945, 2925, 2866, 1688, 1646, 1568, 1531, 1366, 1174, 1146 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (dd, J = 14.8 Hz, J = 12.1 Hz, 1H, 2′-H), 7.77 (d, J = 12.1 Hz, 1H, 1′-H), 7.42−7.25 (m, 5H, Ar−H), 7.21 (d, J = 14.9 Hz, 1H, 3′-H), 2.53 (bs, 4H, 4-H, 6-H), 2.18 (s, 3H, 4′-CH_3), 1.08 (s, 6H, 5-CH_3, 5-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8 (C, C-1*), 197.7 (C, C-3*), 159.3 (CH, C-3′), 151.5 (CH, C-1′), 140.6 (CD, t, J = 23.3 Hz, C-5′), 136.3 (C, Ar), 136.2 (C, C-4′), 129.6 (2 × CH, Ar), 128.3 (2 × CH, Ar), 128.05 (CH, Ar), 127.98 (C, C-2), 125.5 (CH, C-2′), 53.9 (CH_2, C-4**), 52.2 (CH_2, C-6**), 29.9 (C, C-5), 28.4 (2 × CH_3, C5-CH_3, C5-CH_3), 13.9 (CH_3, C4′-CH_3). HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{21}DO_2Na$ $[M + Na]^+$ 318.1575, found 318.1576.

Cyclopenta[b]furans ***6l*** *and* ***6y***. An inseparable mixture of compounds **6l** and **6y** (**6l**:**6y** = 1:0.15) was obtained as a colorless liquid in 65% yield (96 mg) using the general cycloisomerization protocol (1 equiv of $FeCl_3$). IR (film): 3059, 3028, 2958, 2927, 1633, 1399, 1236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, described integration: major component **6l** 1H = 1H, minor component **6y** 1H = 0.15H): δ 7.39−7.32 (overlapping m, 2H, 0.3H), 7.30−7.21 (overlapping m, 3H, 0.45H), 5.73−5.70 (overlapping m, 1H, 0.15H), 3.66 (overlapping dq, J = 7.7 Hz, J = 1.7 Hz, 1H, 0.15H), 2.86 (overlapping ddquint, J = 17.3 Hz, J = 7.7 Hz, J = 2.4 Hz, 1H, 0.15H), 2.53 (dh, J = 17.3 Hz, J = 2.0 Hz, 1H), 2.40 (overlapping d, J = 1.6 Hz, 2H, 0.3H), 2.23 (overlapping dAB, J = 16.1 Hz, 1H, 0.15H), 2.22 (overlapping dAB, J = 16.1 Hz, 1H, 0.15H), 1.61−1.57 (overlapping signals, 3H, 0.45H), 1.12 (overlapping s, 6H, 0.9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6 (C, C), 173.8 (C, C), 141.6 (C, C), 139.4 (C), 139.3 (C), 129.8 (CH), 129.7 (CH), 128.4 (2 × CH, 2 × CH), 127.3 (CH, CH), 124.3 (2 × CH, 2 × CH), 115.7 (C, C), 107.6 (C, C), 51.0 (CH_2, CH_2), 50.4 (CH), 50.3 (CH), 37.8 (CH_2, CH_2), 36.8 (CH_2), 33.9 (C, C), 28.7 (CH_3, CH_3), 28.3 (CH_3, CH_3), 11.9 (CH_3, CH_3), CD signal was missing but could be found when the reaction was run using CH_2Cl_2 saturated with D_2O (**6l**:**6s** = 1:1.5). HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{22}DO_2$ $[M + H]^+$ 296.1755, found 296.1739.

Cyclopenta[b]furan ***5y***. Leaving compound **4y** (59 mg, 0.2 mmol) in $CDCl_3$ for 5 weeks at room temperature afforded compound **5y** as a pale-yellow solid in 65% yield (38 mg) after flash column chromatography (silica gel, eluting with hexanes/ethyl acetate). Mp: 94.5−95.5 °C. IR (KBr): 3062, 2958, 2925, 1646, 1630, 1396, 1213 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36−7.24 (m, 2H, Ar−H), 7.24−7.16 (m, 3H, Ar−H), 5.89 (bd, J = 8.3 Hz, 1H, 3a-H), 5.67 (bs, 1H, 3-H), 3.57 (bd, J = 8.4 Hz, 1H, 8b-H), 2.36−2.14 (m, 4H, 5-H, 7-H), 1.65 (bs, 3H, 2-CH_3), 1.11 (s, 3H, 6-CH_3), 1.07 (s, 3H, 6-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4 (C, C-8), 174.4 (C, C-4a), 150.2 (C, C-2), 142.9 (C, Ar), 128.5 (2 × CH, Ar), 127.2 (2 × CH, Ar), 126.4 (CH, Ar), 124.3 (CH, 3-H), 115.2 (C, C-8a), 95.1 (CH, C-3a), 60.0 (CD, t, J = 20.1 Hz, C-1), 51.9 (CH, C-8b), 51.1 (CH_2, C-7), 37.8 (CH_2, C-5), 33.8 (C, C-6), 28.9 (CH_3, C6-CH_3), 28.2 (CH_3, C6-CH_3), 15.4 (CH_3, C2-CH_3). HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{22}DO_2$ $[M + H]^+$ 296.1755, found 296.1746.

Rearrangement of Cyclopenta[*b*]furans. *Cyclopenta[b]furan* ***6b***. Obtained as a colorless solid in 65% yield (71 mg) using the general cycloisomerization protocol with cyclopenta[*b*]furan **5b** (0.5 mmol) as the substrate and $FeCl_3$ (2 equiv). Mp: 50.5−51.0 °C. IR (KBr): 2962, 2927, 1647, 1626, 1402, 1243, 1135, 1029 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.94 (dt, J = 5.5 Hz, J = 2.4 Hz, 1H), 5.68 (dt, J = 5.7 Hz, J = 2.3 Hz, 1H), 3.35 (dq, J = 7.7 Hz, J = 1.8 Hz, 1H), 2.78 (ddt, J = 17.8 Hz, J = 7.7 Hz, J = 2.2 Hz, 1H), 2.48 (dq, J = 17.8 Hz, J = 2.2 Hz, 1H), 2.24 (d, J = 1.2 Hz, 2H), 2.20 (bs, 2H), 1.56 (s, 3H), 1.09 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8 (C), 174.0 (C), 135.0 (CH), 131.8 (CH), 115.7 (C), 104.9 (C), 50.9 (CH_2), 46.4 (CH), 38.2 (CH_2), 37.9 (CH_2), 33.8 (C), 28.52 (CH_3), 28.47 (CH_3), 24.5 (CH_3). HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{18}O_2Na$ $[M + Na]^+$ 241.1199, found 241.1199.

Cyclopenta[b]furan ***6e***.



Obtained as a colorless liquid in 65% yield (75 mg) using the general cycloisomerization protocol with cyclopenta[*b*]furan **5e** (0.5 mmol) as the substrate and $FeCl_3$ (2 equiv). IR (film): 2961, 2928, 1651, 1630, 1402, 1232 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.99 (dt, J = 5.7 Hz, J = 2.3 Hz, 1H, 2-H), 5.67 (dt, J = 5.7 Hz, J = 2.1 Hz, 1H, 3-H), 3.43 (dm, J = 7.6 Hz, 1H, 8b-H), 2.72 (ddt, J = 17.7 Hz, J = 7.7 Hz, J = 2.1 Hz, 1H, 1-H_β), 2.48 (dq, J = 17.8 Hz, J = 2.1 Hz, 1H, 1-H_α), 2.25 (bs, 2H, 5-H), 2.20 (bs, 2H, 7-H), 1.96−1.74 (m, 2H, 1′-H), 1.08 (s, 3H, 6-CH_3), 1.07 (s, 3H, 6-CH_3), 0.91 (t, J = 7.4 Hz, 3H, 2′-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7 (C, C-8), 174.3 (C, C-4a), 135.7 (CH, C-2), 130.6 (CH, C-3), 115.8 (C, C-8a), 108.5 (C, C-3a), 50.9 (CH_2, C-7), 43.6 (CH, C-8b), 38.3 (CH_2, C-1), 37.8 (CH_2, C-5), 33.9 (C, C-6), 30.2 (CH_2, C-1′), 28.7 (CH_3, C6-CH_3), 28.3 (CH_3, C6-CH_3), 7.7 (CH_3, C-2′). HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{20}O_2Na$ $[M + Na]^+$ 255.1355, found 255.1353.

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■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all new compounds and 2D spectra for key structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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