Lithium Malonate Enolates as Precursors for Radical Reactions − Convenient Induction of Radical Cyclizations with either Radical or Cationic Termination

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Dedicated to Professor Dr. Henning Hopf on the occasion of his 60th birthday

Keywords: Carbocations / Electron transfer / Enolates / Oxygenation / Radicals

Lithium malonate enolates **4** or **13** are oxidized to the corresponding radicals by ferrocenium hexafluorophosphate (**1**) or $CuCl_2$ (**2**). Trapping by TEMPO (**5**) to produce **6**, dimerization to **7**, or radical 5-*exo* cyclizations are possible subsequent reaction steps following radical generation. The structure of the radical cyclization acceptor determines the outcome of the overall reaction sequence. Tertiary benzylic, alkyl, and α-alkoxy radicals are oxidized by **1**. The carbenium ions are stabilized by nucleophilic trapping or deprotonation to give compounds **14** and **18**. Secondary alkyl and vinyl radicals are not oxidized and, in the absence of trapping reagents, form radical-derived products. Radical 5-*exo* cyclization of **13** induced by $CuCl_2$ (**2**) was also efficient. At least for alkyl radicals, however, ligand transfer is the exclusive stabilization pathway, giving access to chloroalkylcyclopentane derivatives **21**. Radical scavenging studies revealed that malonyl radical trapping is slow, so that 5-*exo* cyclizations occurred. The cyclized radicals couple with TEMPO (**5**) to afford oxygenated cyclopentane derivatives **31**, depending on the rate of radical SET oxidation. The reaction behavior of compounds **14**, **22**, **23**, and **31** was investigated. Mechanistic issues are discussed and implications for synthetic planning are given.

Introduction

Sequential reactions are of rapidly growing importance in organic chemistry. Such reaction sequences allow time- and resource-efficient access to complex target structures from simple precursors.[1] Most of the strategies so far applied consist of domino processes, in which one intermediate type (anions *or* radicals *or* cations *or* carbenes) or pericyclic processes are involved [Equation (1)]. However, the success of the overall one-pot process will critically depend on the characteristic reactivity of the chosen intermediates.

$$M \longrightarrow [R^1\!* \longrightarrow R^2\!* \longrightarrow R^3\!* \longrightarrow R^4\!* \longrightarrow \cdots \longrightarrow R^n\!*] \longrightarrow P \qquad *\,=\,^{+}\ \textbf{or}\ \cdot\ \textbf{or}\ ^{-} \qquad (1)$$

Consequently, reaction sequences in which multiple intermediates of different oxidation states may be selectively generated and allowed to react are potentially much more attractive [Equation (2)].[2] This process amplifies the applicability of these intermediates and opens up complementary reaction channels in reaction sequences. Moreover, such heterointermediate reaction sequences may be planned either as overall oxidative processes or as overall reductive ones. The prerequisite for these sequences is the incorporation of selective electron transfer steps that induce the changes in the oxidation states.

$$M \rightleftharpoons [R^{1-} \rightleftharpoons R^{2-} \rightleftharpoons R^3\cdot \rightleftharpoons R^4\cdot \rightleftharpoons R^{5+} \rightleftharpoons R^{6+}] \rightleftharpoons P \qquad (2)$$

For reductive heterointermediate reaction sequences, SmI_2 has proven a valuable reagent.[3] Oxidative heterointermediate reaction sequences according to Equation (2), in contrast, are much less well developed, but oxidative radical reaction sequences of *neutral* carbonyl compounds employing $Mn(OAc)_3$ [4] or ceric ammonium nitrate (CAN)[5] are well established. A different picture emerges if carbanions, radicals, and carbenium ions are considered as intermediates in reaction sequences. In simple systems, enolate oxidation[6] followed by dimerization or oxygenation has been accomplished by use of reagents such as Cu^{II} [7] or Fe^{III} salts,[8] I_2,[9] $TiCl_4$,[10] or anodic oxidation.[11]

Other synthetic applications of α-carbonyl radicals generated by SET oxidation of enolates are rather rare. Schäfer and co-workers have studied anodic enolate oxidation/radical addition/SET oxidation/lactonization.[12] Kende demonstrated that equilibrium-generated β-diketone enolates may undergo SET oxidation by $K_3[Fe(CN)_6]$, followed by radical cyclization onto phenolates ultimately to form spiro[4,5]nonadienones.[13] This method, however, is limited to β-diketones as radical precursors; even malonates do not react under these conditions.

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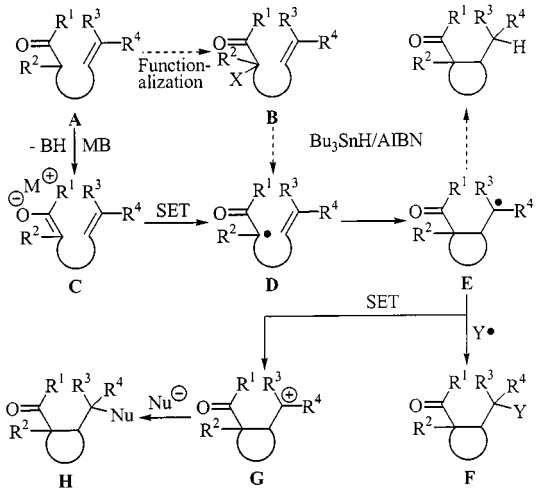


Scheme 1

On the basis of these results, reaction sequences according to Equation (2) should be feasible. The advantages of employing anionic intermediates **C** as precursors for radical reactions are clear (Scheme 1). The anionic precursor **C** is simply generated by deprotonation of **A**. In contrast, traditional Bu_3SnH-mediated radical chain reactions require precursors **B** that often actually originate from functionalization of **A** or **C**. Slow radical reaction steps **D** → **E**, which may not propagate chain reactions, especially at low temperature, are not a particular concern in processes starting from **C**. Finally, in contrast to radical chain reactions, removal of the ultimate radicals **E** can be achieved either by trapping with external reagents Y to form **F** or by further SET oxidation to produce a carbenium ion **G**, which may react with nucleophiles to give **H**. Opportunities for the synthesis of diversely functionalized products are hence much broader than those offered by tin hydride reactions.

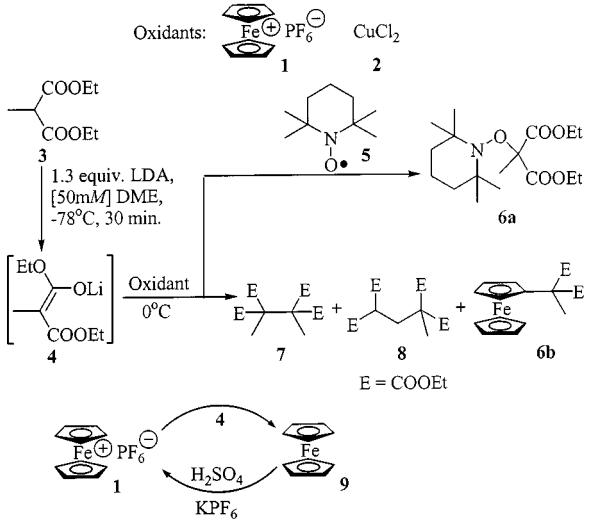
The most important potential advantage, however, is that anionic reactions can be combined with radical and cationic reactions, thus amplifying the applicability of intermediates.[14] Nevertheless, such reaction sequences require SET oxidation steps **C** → **D** and **E** → **G**, and so there is a need to devise reagents that promote these steps efficiently and predictably. An important prerequisite is that they should not interfere with the intermediates generated during the reaction sequence unless this is desired. No known oxidant fulfills these requirements perfectly. In anodic radical generation, high radical concentrations near the electrode sometimes produce unwanted side reactions such as dimerization or overoxidation. PET conditions often produce low yields of the desired products. Problems associated with chemical oxidation may include dependence on the reaction conditions and, more seriously, ligand transfer from the oxidant to radicals.

Here we report the results of investigations aimed at the development of techniques for the use of enolates **C** as precursors for radical 5-*exo* cyclizations.[15] SET oxidation of **C** gives α-carbonyl radicals **D**, which cyclize. The final radicals **E** may be trapped either by further SET oxidation, giving **G**, or by another radical Y· (Scheme 1). In this fundamental study, we chose malonates as starting materials, since they form robust enolates and they are not prochiral, thus avoiding the complicating problem of diastereomer formation during radical cyclization.[16] Malonate enolate SET oxidation is most conveniently induced by ferrocenium hexafluorophosphate[17] (**1**) and anhydrous $CuCl_2$ (**2**). An important issue is the termination of the cyclization reaction. Depending on the alkene cyclization acceptor and the oxidant, several functionalized structures can be obtained, mainly in good yield and with high chemoselectivity. The results of this study provide means for the generalization of oxidative reaction sequences incorporating anions, radicals, and cations in a predictable fashion. We also show that **1** is a conveniently accessible and *recyclable* SET oxidant for enolates and radicals, thus adding an environmental advantage to these cyclization reactions.

Results and Discussion

Initial Studies − SET Oxidation/Radical Trapping of Lithium Methylmalonate Enolate 4

To test the efficiency of the enolate → malonyl radical SET oxidation, diethyl methylmalonate (**3**) was chosen as a model substrate. Deprotonation of **3** by LDA in DME[18] at −78 °C gave enolate **4**. Two series of experiments were performed with **4**, to evaluate whether radical generation occurs and whether the oxidant undergoes ligand transfer sufficiently slowly to allow radical reactions (Scheme 2).



Scheme 2

In the first series, SET oxidation of **4** was performed with various oxidants at 0 °C in the presence of free radical TEMPO (**5**) (Table 1). In a control experiment (Entry 1), it was established that **5** did not itself act as an oxidant.[19] Oxidants **1** and **2** induced SET oxidation/oxygenation of **4**, efficiently providing piperidinyloxymethylmalonate **6a** as a colorless, crystalline solid, in 86% and 88% yields, respectively (Entries 2 and 3). Other common oxidants such as

Table 1. Evaluation of SET oxidants for oxidative radical generation from methylmalonate enolates

Entry	Oxidant[a]	**3** [%][b]	**6** [%]	**7** [%]	**8** [%]
1	**5**	95	–	–	–
2	**1**	–	**a** 86	–	–
3	**2**	–	**a** 88	–	–
4	$FeCl_3$	80	–	–	–
5	$K_3[Fe(CN)_6]$	72	–	–	–
6	**1**	–	**b** 3	21	26
7	**2**	8	–	74	–
8	$FeCl_3$	92	–	–	–
9	$K_3[Fe(CN)_6]$	84	–	–	–
10	$Fe(phen)_3(PF_6)_3$	35	–	10	7
11	$(p\text{-}BrC_6H_4)_3N{\cdot}PF_6$	50	–	–	–

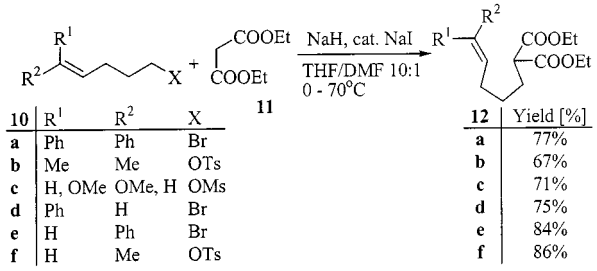
[a] The oxidant was added portionwise as a solid to a [50 mM] enolate solution at 0 °C in DME until consumption ceased. – [b] All yields are isolated yields.

anhydrous $FeCl_3$ or $K_3[Fe(CN)_6]$ did not oxidize **4** (Entries 4 and 5).

To assess the degree of involvement of ligand-derived products, enolate oxidation was conducted in the absence of efficient radical scavenger **5**. Oxidant **1** produced a separable mixture of the symmetrical and the unsymmetrical dimers **7** and **8**, in 21% and 26% yields, respectively (Entry 6), with 3% of ferrocenylmalonate **6b** also being isolated. In contrast, oxidation of **4** with $CuCl_2$ (**2**) gave only the symmetrical dimer **7**, in 74% yield, and 8% of **3** (Entry 7). Enolate oxidation/dimerization experiments with $FeCl_3$ and $K_3[Fe(CN)_6]$ paralleled those performed in the presence of TEMPO. Enolate oxidation failed to occur with either reagent, use of LDA or *n*BuLi as the base for deprotonation of **3** notwithstanding (Entries 8 and 9). Application of even stronger SET oxidants was not useful; Schmittel's $Fe(phen)_3(PF_6)_3$[20] was consumed quickly, but only 10% and 7% of dimers **7** and **8** were isolated, along with 35% of recovered **3** (Entry 10). Tris(*p*-bromophenyl)aminium hexafluorophosphate also reacted quickly, but only 50% of **3** was recovered, accompanied by tarry products (Entry 11). Significantly, ferrocene **9** was recovered almost quantitatively (by simple column chromatography, as the least polar component) from all oxidative reactions induced by **1** (Entries 2 and 6); it may be recycled to **1** in high yield by use of H_2SO_4 (Exp. Sect.).

2-(4-Pentenyl)malonate Enolates 13 as Radical 5-*exo* Cyclization Precursors

The results of the malonate enolate oxidation suggested only compounds **1** and **2** as suitable SET oxidants. If a radical 5-*exo* cyclization occurs as desired after malonyl radical generation, then the structure of the cyclized radical should have a profound influence on product formation, since it may either be trapped at the radical stage, or be further oxidized to a carbenium ion. To investigate these pathways, we therefore used several 5-substituted 4-pentenylmalonates **12**, which could be prepared in good yields by alkylation of diethyl malonate **11** with 4-pentenyl tosylates or 5-bromo-



10	R^1	R^2	X
a	Ph	Ph	Br
b	Me	Me	OTs
c	H, OMe	OMe, H	OMs
d	Ph	H	Br
e	H	Ph	Br
f	H	Me	OTs

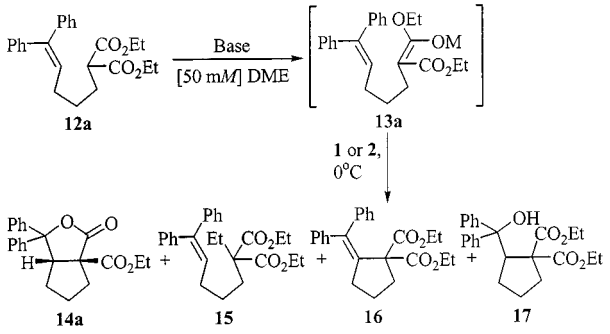
12	Yield [%]
a	77%
b	67%
c	71%
d	75%
e	84%
f	86%

Scheme 3

1-pentenes **10a**–**f**,[21,22] using NaH as the base in the presence of NaI (Scheme 3).

Oxidative Cyclizations of 5,5-Disubstituted 4-Pentenylmalonate Enolates

The enolates used in this study were obtained by deprotonation of malonate **12a** with various lithium bases such as LDA, LiHMDS, or *n*BuLi, at −78 °C for 30 min. Oxidative cyclizations of **13a** were generally performed in [50 mM] DME solution at 0 °C, by portionwise addition of the oxidants **1** or **2** until no more oxidant was consumed (Scheme 4, Table 2). For **1**, this could be monitored very easily by the disappearance of the blue color of the oxidant; the addition was complete when the blue-green color of the reaction mixture persisted for 30 min. For **2**, visual change was not a good indicator; reactions were complete when excess brown **2** remained suspended for a period of 1 h.



Scheme 4

Table 2. Oxidative cyclizations of malonate enolates **13a**

Entry	Base	Oxidant	**12a** [%]	**14a** [%]	**15** [%]	**16** [%]	**17** [%]
1	LDA[a]	**1**	–	64	12	–	–
2	LiHMDS[b]	**1**	–	57	6	–	–
3	BuLi[c]	**1**	13	54	–	–	–
4	NaH[d]	**1**	60	trace	–	–	–
5	LDA	**2**	–	69	–	11	–
6	BuLi[c]	**2**[e]	20	62	–	–	4
7	NaH[d]	**2**	58	31	–	–	–
8	BuLi[c]	[f]	50	32	–	–	–

[a] 1.3 equiv. – [b] 1.13 equiv. – [c] 1.0 equiv. – [d] 1.5 equiv., deprotonation and attempted oxidation at 0 °C. – [e] In addition, 7% of a compound corresponding to 2-chloro-2-(5,5-diphenyl-4-pentenyl)-malonate was detected in the reaction mixture, but could not be obtained pure. – [f] $Fe(phen)_3(PF_6)_3$ as oxidant.

Oxidative cyclization of **13a** generated with 1.3 equiv. of LDA and induced by **1** provided the bicyclic lactone **14a** as single diastereomer in 64% yield, accompanied by 12% of the acyclic ethylmalonate **15** (Entry 1). Increasing the amount of LDA had no influence on the reaction outcome. Deprotonation with LiHMDS or BuLi and oxidative cyclization under identical conditions proceeded similarly, also giving **14a** and **15** (Entries 2 and 3). At −25 °C, the reactions were considerably slower, resulting in only a 26% yield of **14a** after 5 h. The sodium enolate generated from **12a** and NaH at 0 °C, however, was not oxidized by compound **1**, with 60% of **12a** being recovered unchanged (Entry 4).

Addition of $CuCl_2$ (**2**) to enolate **13a** generated with LDA provided 69% of **14a** and 11% of 2-diphenylmethylenecyclopentanedicarboxylate **16**, while no malonate **15** was formed (Entry 5). The enolate generated with BuLi similarly provided 62% of **14a**, 4% of alcohol **17**, and 7% of a 2-chloromalonate (Entry 6). Oxidative cyclization of the sodium enolate was also inefficient with $CuCl_2$ (Entry 7), affording only 31% of **14a** and 58% of recovered **12a**. In a final experiment, oxidative cyclization of BuLi-generated **13a** in the presence of 2.5 equiv. $Fe(phen)_3(PF_6)_3$ gave only 32% of **14a**, with 50% of **12a** being recovered (Entry 8).

The constitution of the bicyclic lactone **14a** was unambiguously proven by X-ray crystal structure analysis (Figure 1). The ring junction stereochemistry is clearly shown to be *cis*. The ethoxycarbonyl group and the phenyl ring on the β-face of the butyrolactone ring are disposed in pseudoaxial manner. The butyrolactone ring adopts an envelope conformation (mean deviation from planarity for C6−O1−C7−C1 = 0.7 pm, with C5 38.4 pm out of the envelope plane). The conformation of the cyclopentane fragment is a half chair, with C2 situated 32.8 pm above the plane defined by C1−C5−C4, and C3 located 34.2 pm below it. The distance between the ethoxycarbonyl group and the phenyl ring is shown to be relatively short, amounting to 368.7 pm for the closest contact. The crystal packing shows weak nonclassical hydrogen bonds O2···H10B−C10 and O3···H19−C19, with interatomic distances and angles of 256 pm/349.9(3) pm/161.6° and 273 pm/365.4(3) pm/165.9°, respectively. This results in a chain arrangement of **14a** parallel to the *y* axis.

The structure of **14a** in solution should be similar. In comparison to other derivatives, the ethoxy group suffers a strong high-field shift in the ^1H NMR spectrum, since it is

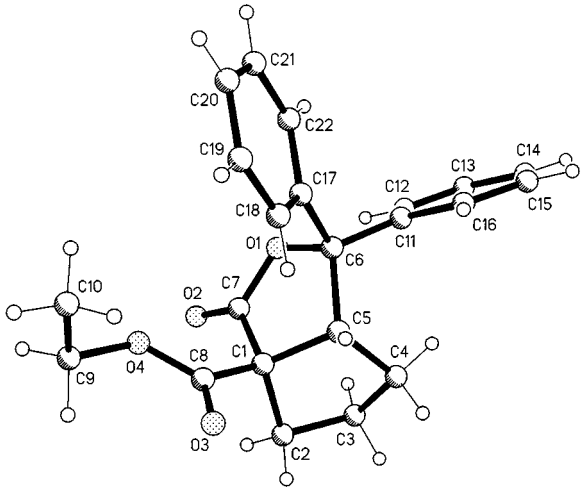
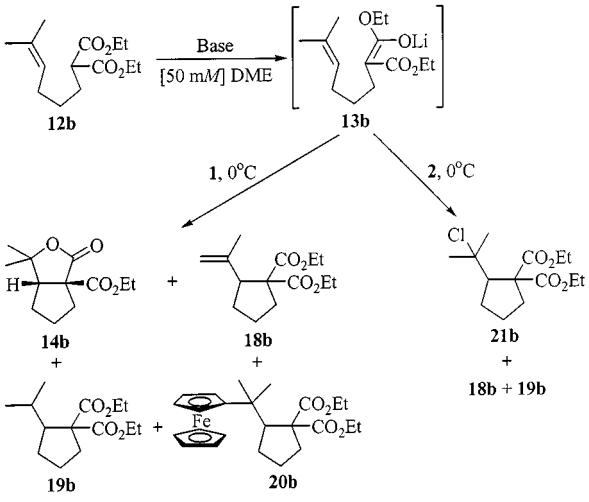


Figure 1. X-ray crystal structure analysis of lactone **14a**



Scheme 5

situated close to the shielding region of the phenyl ring (cf. 368.7 pm in the solid state, vide supra). The bridgehead hydrogen, on the other hand, is shifted downfield to δ = 4.03, due to its location in the deshielding zone of the phenyl ring.

The reactivity of **1** and **2** towards tertiary alkyl radicals was studied with **12b** (Scheme 5, Table 3). Deprotonation

Table 3. Products obtained from oxidative cyclization of malonate **12b**

Entry	Base	Oxidant	**14b** [%]	**18b/19b** [%] (ratio)	**20b** [%]	**21b** [%]
1	LiHMDS[a]	**1**	52	32 (4.3:1)	7	−
2	LiHMDS[b]	**1**	36	47 (4.2:1)	5	−
3	LiHMDS[c]	**1**	34	30 (3.3:1)	6	−
4	LDA[d]	**1**	38	34 (4.3:1)	10	−
5	LDA[e]	**1**	36	20 (19:1)	7	12
6	LDA[f]	**1**	30	37 (17.5:1)	10	−
7	LDA[g]	**2**	−	4 (1:1)	−	67

[a] 1.75 equiv. − [b] 2.5 equiv. − [c] 1.5 equiv. and 5 equiv. of 1,4-cyclohexadiene. − [d] 1.5 equiv. − [e] 1.3 equiv. and 2 equiv. of anhydrous $ZnCl_2$. − [f] 1.3 equiv., addition of 10 equiv. of TMEDA prior to addition of **1**. − [g] 1.3 equiv., 4% of **12b** recovered.

with 1.75 equiv. of LiHMDS and oxidative cyclization afforded bicyclic lactone **14b** as the major product, in 52% yield. In addition, an inseparable mixture of a 4.3:1 ratio of cyclopentane-1,1-dicarboxylates **18b** and **19b** was formed in 32% yield, and the cyclized ferrocene adduct **20b** was isolated in 7% yield. The overall cyclization yield was therefore high, but diversification had occurred. When the amount of LiHMDS was increased to 2.5 equiv., decreasing quantities of lactone **14b** and increasing amounts of **18b/19b** were observed (Entry 2). To gain information on the relative rates of oxidation and intermolecular hydrogen abstraction, the oxidative cyclization was performed in the presence of 5 equiv. of 1,4-cyclohexadiene (Entry 3). Significantly, besides a decreased overall cyclization yield, the **18b/19b** ratio decreased to 3.3:1; however, the bicyclic lactone still dominated, with a yield of 34%. Use of the stronger base LDA for deprotonation resulted in a reduction of the yield of **14b** to 38%, with 34% of **18b/19b** and 10% of **20b** being formed (Entry 4). Li−Zn transmetalation complicated the reaction mixture even more (Entry 5). In addition to the products previously obtained, chloride **21b** was formed in 12% yield. Addition of tertiary amine TMEDA to **13b** prior to oxidative cyclization markedly improved the **18/19** ratio, while **14b** was formed in a similar 30% yield (Entry 6). When $CuCl_2$ (**2**) was used as the oxidant, the cyclization result changed dramatically. Chloride **21b** was now by far the major product, while only 4% of a 1:1 mixture of **18b/19b** was formed. The formation of lactone **14b** was inhibited completely under the reaction conditions (Entry 7).

The structure of the lactone **14b** was assigned by NMR. The constitution of the ferrocene adduct **20b** was also established by crystal structure analysis (Figure 2). The structure clearly shows the half-chair cyclopentane ring system, with the ferrocene moiety attached to the exocyclic carbon atom C-6. The bulky ferrocenylisopropyl group is disposed in a pseudoequatorial fashion. The steric crowding around this group is clearly evident in the deviation of the C6−C5−C1 bond angle, which is widened to 121.8(2)°, while the C5−C1−C2 bond angle is compressed to 101.9(2)°. Nonclassical hydrogen bonds are also present in **20b**. Contacts of 270 pm/362.5(3) pm/155.2° were found for O1···H3A−C3, together with values of 250 pm/338.5(3) pm/154.5° for O3···H10−C10, producing a chain arrangement parallel to the *z* axis.

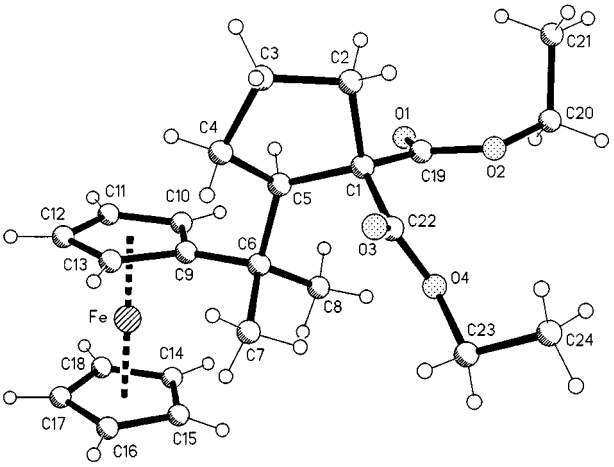
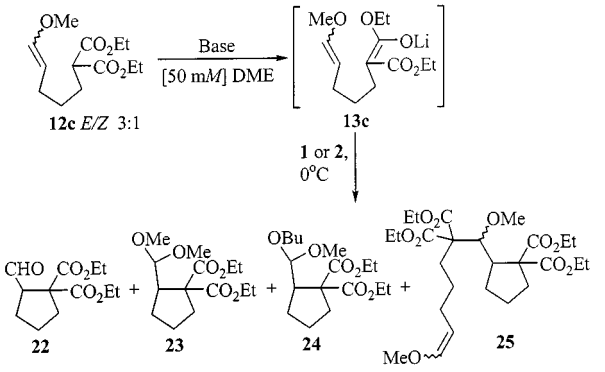


Figure 2. X-ray crystal structure analysis of cyclopentylferrocene **20b**



Scheme 6

Table 4. Product distribution of enolate oxidation/cyclization of **12c**

Entry	Base	Oxidant	**12c** [%]	**22** [%]	**23** [%]	**24** [%]	**25** [%]
1	LDA[a]	**1**	–	14	10	4	35
2	LDA[b]	**1**	–	78	–	–	–
3	LDA[c]	**2**	–	16	24	22	–
4	LDA[d]	**2**	10	43	–	–	–
5	LDA[e]	**2**	25	32	–	–	–

[a] 1.4 equiv. – [b] 1.1 equiv. and 7.7 equiv. of LiBr, 12 min reaction time. – [c] 1.3 equiv. – [d] 1.3 equiv., cyclization at −70 °C. – [e] 1.3 equiv. in [50 mM] THF.

Oxidative Cyclizations of 5-Monosubstituted 4-Pentenylmalonate Enolates

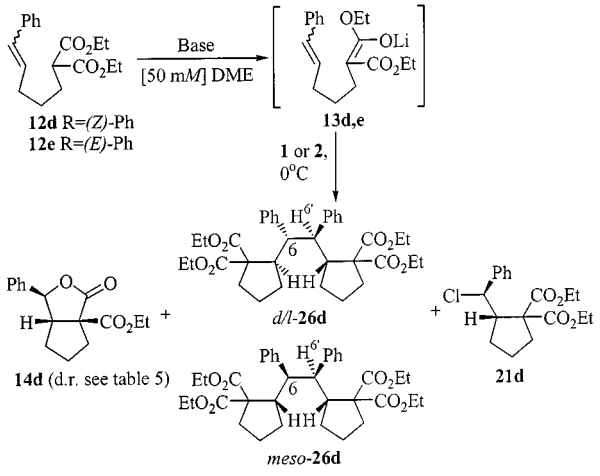
Cyclization of enolate **13c** with an enol ether acceptor (Scheme 6, Table 4) produced after 60 min a partially separable 1.4:1 mixture of cyclized aldehyde **22** and dimethyl acetal **23**, contaminated with a small quantity of *n*-butyl acetal **24**. Surprisingly, mixed dimer **25** was formed in appreciable yield (Entry 1). Shortening of the reaction time to 12 min and use of HMPA as an additive had no significant influence on the cyclization outcome, while application of an excess of 2 equiv. of LDA reduced the overall yield. Addition of 7.7 equiv. of lithium bromide, however, had a dramatic effect, resulting in the exclusive production of the rather unstable aldehyde **22** in good yield (Entry 2). Use of $CuCl_2$ (**2**) as the oxidant induced the formation of **22**, **23**, and **24** in 16%, 24% and 22% yields, respectively (Entry 3). When the same oxidative cyclization was conducted at −70 °C, only **22** was formed in 43% yield, with no formation of **23** and **24** being observed at all (Entry 4). A change in solvent to THF, with oxidative cyclization mediated by $CuCl_2$, gave **22** as the exclusive product in 32% yield even at 0 °C, but significant quantities of **12c** were always recovered (Entry 5). The seemingly not very useful mixtures of **22**−**24**

(Entries 1 and 3) can, however, easily be converted into single products (vide infra).

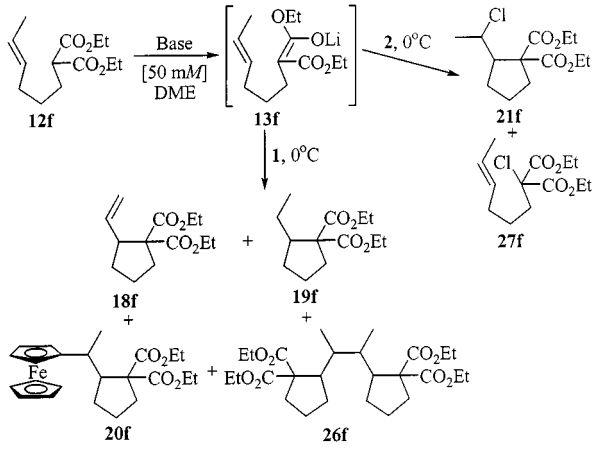
Oxidative cyclization of the 5-phenyl-4-pentenylmalonate enolate (*Z*)-**13d** generated with LDA gave 15% of bicyclic lactone **14d** (*dr* 8:1)[23] and 30% of **26d**, as an inseparable 1:1 mixture of *meso* and *d/l* dimers (Scheme 7, Table 5, Entry 1). A reduction in the concentration and addition of HMPA resulted in a significant increase in the overall yield of both compounds; however, the **14d/26d** ratio remained almost constant (Entry 2). The analogous cyclization of (*E*)-**13e** afforded only 6% of lactone **14d**, but 45% of dimers **26d** (Entry 3). Here, use of LiHMDS as the base was generally not as effective as LDA and resulted in significantly reduced yields of **14d** and **26d** (Entries 4 and 5 vs. Entry 2). Inverse slow addition of the enolate solution to a suspension of **1** did not change the reaction outcome significantly. Use of $CuCl_2$ (**2**) as the oxidant induced the oxidative cyclization of (*Z*)-**12d**, but chlorine transfer occurred to a significant extent, giving (chlorobenzyl)cyclopentanedicarboxylate **21d** in 21% yield and with high diastereoselectivity, in addition to **14d** and **26d** (Entry 6).

The constitution of the dimers **26d** was established by CI mass spectrometry, which showed $[M + H]^+ = 607$ as the base peak. Both dimers must be symmetrical, since only half signal sets were observed in their ^1H and ^{13}C NMR spectra. In both isomers, the H^6 moieties appeared as doublets in the ^1H NMR spectra. More significantly, HMBC spectra revealed a clear two bond cross peak from C6 to $H^{6'}$ for both isomers, strengthening the dimer structure assignment.

As a representative 5-alkyl-substituted 4-pentenylmalonate, the cyclization behavior of (*E*)-4-hexenylmalonate **12f** was studied (Scheme 8, Table 6). Deprotonation of **12f** and oxidation with **1** gave an inseparable mixture of the cyclopentanes **18f** and **19f**, in a 1:1 ratio. In addition, the ferrocene adduct **20f** and a diastereomeric mixture of dimers **26f** were isolated in 18% and 34% yield (Entry 1). When $CuCl_2$ was used as oxidant, the reaction outcome changed com-



Scheme 7



Scheme 8

Table 5. Results of oxidative cyclizations of **12d** and **12e**

Entry	**12**	Base	Oxidant	**14d** [%] (*dr*)	**26d** [%] (*dr*)	**21d** [%] (*dr*)
1	(*Z*)-**12d**	LDA[a]	**1**	15 (8:1)	30 (1:1)	–
2	(*Z*)-**12d**	LDA[b]	**1**	28 (10:1)	48 (1:1)	–
3	(*E*)-**12e**	LDA[c]	**1**	6 (7:1)	45 (1:1)	–
4	(*Z*)-**12d**	LiHMDS[d]	**1**	4 (7:1)	28 (1:1)	–
5	(*E*)-**12e**	LiHMDS[d]	**1**	7 (8:1)	24 (1:1)	–
6	(*Z*)-**12d**	LDA[e]	**2**	15 (9:1)	47 (1:1)	21 (12:1)

[a] 1.5 equiv. – [b] 1.75 equiv. and 7 equiv. of HMPA. – [c] 1.75 equiv. – [d] 2.5 equiv. – [e] 1.3 equiv.

Table 6. Oxidative radical cyclization/radical self-termination of malonate enolate **13f**

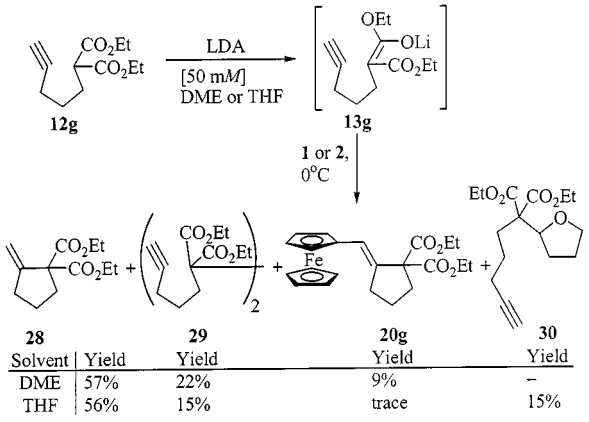
Entry	Base	Oxidant	**18f/19f** [%]	**20f** [%]	**26f** [%]	**21f** [%] (*dr*)	**27f** [%]
1	LiHMDS[a]	**1**	42 (1:1)	18	34[b]	–	–
2	LDA[c]	**2**	–	–	–	71 (3:1)	4

[a] 1.9 equiv. – [b] Diastereomers not assigned. – [c] 1.3 equiv., 12% of **12f** recovered.

pletely. Only the acyclic and cyclic chlorides **27f** and **21f** were formed, in 4% and 71% yields, respectively (Entry 2).

Oxidative Cyclization of 4-Pentynylmalonate Enolate 13g

Cyclizations onto alkynes are valuable reactions as they generate methylenecyclopentanes, which can undergo a variety of further transformations. Oxidative cyclization of malonate **13g** (prepared in 61% yield by alkylation of diethyl malonate with 4-pentynyl tosylate) in DME afforded 2-methylenecyclopentane-1,1-dicarboxylate **28** as the major product in 57% yield (Scheme 9). In addition, 22% of acyclic malonate dimer **29** and 9% of ferrocene adduct **20g** were isolated. To test whether ferrocene **9** or **1** was the actual reagent involved in the formation of **20g**, the reaction was performed in the presence of 2 equiv. of **9**. The **28**/**29**/**20g** ratio was, however, not changed in this experiment. Use of THF as a solvent produced 56% of **28**, while the amounts of **29** and **20g** decreased in favor of the tetrahydrofuran adduct **30**. Use of benzene as the solvent resulted in sharp decreases in the yields of all products, probably because of the lesser solubility of **1** and precipitation of forming $LiPF_6$.



Scheme 9

Oxidative Cyclizations of 4-Pentenylmalonates 12 in the Presence of Free Radical TEMPO (5)

In order to prove that radical intermediates are involved, we studied trapping by stable free radical TEMPO (**5**). This approach produces oxygenated products, and these may be further functionalized to produce valuable synthetic building blocks. This may be especially important as it avoids the unsatisfactory formation of radical-radical reaction products such as dimers and disproportionation products.

Since we knew that the enolate did not react with TEMPO (vide supra), enolates **13** were generated in the usual fashion, followed by sequential addition of a small excess of **5** and the oxidant (Table 7). Oxidative cyclization of enolate **13a** gave 47% of unstable 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)malonate **32a** and 25% of bicyclic lactone **14a** (Entry 1). With LiHMDS as the base, the yield of the acyclic TEMPO trapping product was somewhat lower (33%), while the amount of **14a** remained the same. Surprisingly, malonate **12b** exclusively provided the cyclic trapping product **31b** in 87% yield (Entry 2), with essentially the same result being obtained when **2** was used as the oxidant (Entry 3). The cyclization of **13c** was again characterized by competing pathways. The cyclized mixed piperidinyloxy acetal **31c** was the major product, in 46% yield as a 2:1 diastereomeric mixture, accompanied by 15% of the acyclic trapping product **32c**. In addition, products **22**–**25**, previously obtained in the cyclization experiments in the absence of TEMPO, were isolated in low yields (Entry 4, cf. Table 4). The concentration of TEMPO had only a minor influence on the product ratio (Entry 5). In contrast, the TEMPO trapping of (*E*)-**13d** proved to be highly efficient. The cyclized product **31d** was isolated as a single diastereomer in 72% yield, accompanied by 7% of **32d** (Entry 6).

The configuration of **31d** was established by X-ray crystal structure analysis (Figure 3). The cyclopentane ring adopts an envelope conformation (mean deviation from planarity for C2–O1–C5–C4 = 3.8 pm, with C5 lying 64.6 pm out of the envelope plane). The phenyl ring is located on the same face as the ring hydrogen atom at C-5 and is oriented almost parallel to the *cis*-ester functionality. The distance

Table 7. Oxidative radical cyclization/TEMPO trapping of malonate enolates **13**

Entry	**12**	Base	Oxidant	**31** [%] (*dr*)	**32** [%]	Other products [%]
1	**a**	LDA[a]	**1**	–	47	**14a** (25)
2	**b**	LiHMDS[b]	**1**	87	–	–
3	**b**	LDA[c]	**2**	87	traces	–
4	**c**	LDA[d]	**1**	46 (2:1)[e]	15	**22** (10), **23** (4), **25** (14)
5	**c**	LDA[f]	**1**	37 (1:1)	15	**22** (8), **23** (8), **25** (28)
6	**d**	LiHMDS[g]	**1**	72 (100:0)	7	–
7	**f**	LiHMDS[h]	**1**	50 (1.8:1)	17[i]	–
8	**f**	LiHMDS[k]	**1**	41 (2:1)	42	–
9	**g**	LDA[l]	**1**	–	98	–

[a] 1.75 equiv. – [b] 1.75 equiv. – [c] 1.3 equiv. – [d] 1.4 equiv. – [e] Diastereomers not assigned. – [f] 1.4 equiv. and 2.0 equiv. of **5**. – [g] 1.75 equiv. and 2.0 equiv. of **5**. – [h] 1.0 equiv. and 1.0 equiv. of **5**. – [i] Because of its limited stability, **32f** was characterized as its tartronate derivative **32f′** (Exp. Sect.). – [k] 1.0 equiv. and 2.0 equiv. of **5**, 6% of **12f** recovered. – [l] 1.5 equiv.

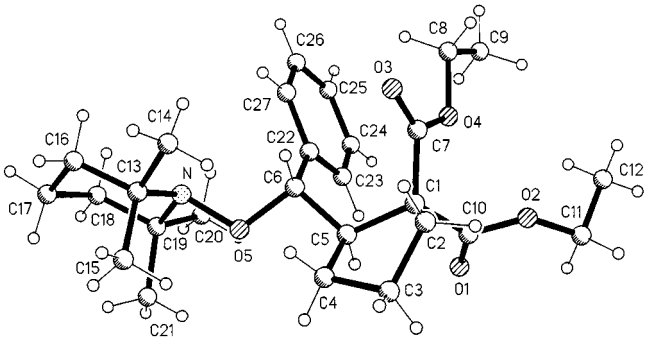
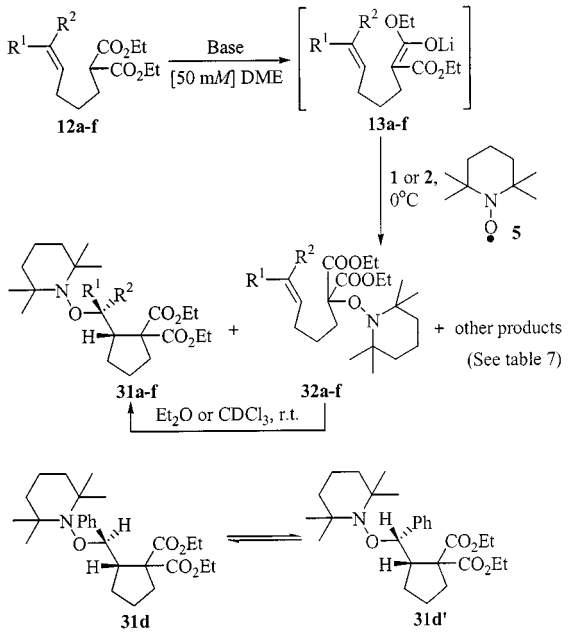


Figure 3. X-ray crystal structure analysis of diethyl 2-[(2,2,6,6-tetramethylpiperidin-1-yloxy)benzyl]cyclopentane-1,1-dicarboxylate (**31d**)

between the ethoxycarbonyl group and the phenyl ring amounts to 363.5 (3) pm for the closest contact between C8···C27. The bulky piperidine ring occupies the free space, directed away from the cyclopentane ring to minimize interactions with the ester groups and the cyclopentane ring. Nonetheless, a remarkably close contact between the C20 methyl group and C22 or C23 of the phenyl ring was still found [320.7(3) pm and 332.6(3) pm, respectively]. Nonclassical hydrogen bonds are also present in **31d**. A contact of 260 pm/354.0(3) pm/159.0° was found for O1···H4B−C4 and one of 246 pm/338.0(3) pm/162.6° for O3···H10−C10. These contacts assemble a chain parallel to [011].

The solution structure of compound **31d** seems to be similar. One of the methyl groups of the piperidine ring is shifted upfield to $\delta = -0.09$ and the *cis*-OCH_2 ester fragment experiences a shift to $\delta = 3.44/3.70$, with double quadruplet multiplicity. This indicates that these groups are located in the shielding zone of the phenyl ring. In the ^1H and ^{13}C NMR spectra at room temperature, the signals of the methyl groups and the carbon atoms of the piperidine ring are broadened considerably. To assign the carbon atoms, we conducted variable temperature measurements. On warming **31d** to 100 °C, in $C_2D_2Cl_4$ solution in an NMR tube, a new set of minor resonances appeared. These were assigned to the diastereomeric TEMPO adduct **31d′**, and represented a final ratio of 2:1 (Scheme 10).[24] This limited configurational stability would need to be taken into account should thermal reactions with these compounds be planned.

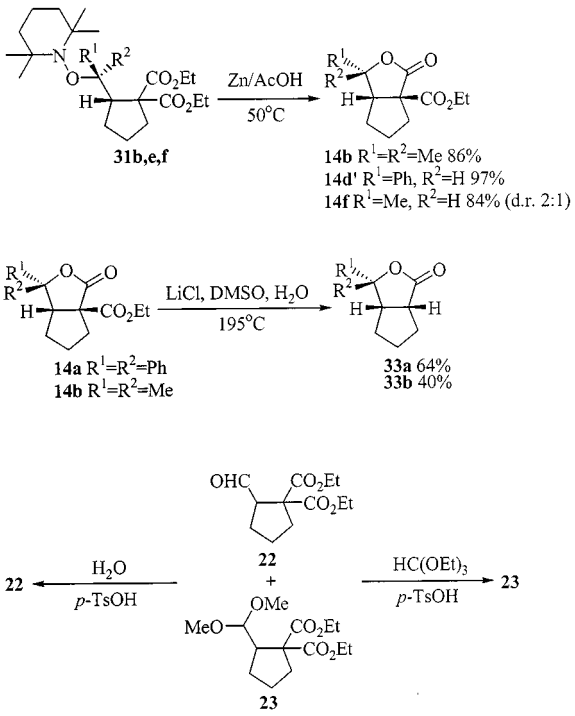
Under these reaction conditions, malonate **12f** provided a mixture of cyclic and unstable acyclic trapping products **31f** and **32f**. The cyclic trapping product **31f** proved to be a 2:1 diastereomeric mixture, the product ratio being dependent on the amount of TEMPO added. With 1 equiv. of **5**, a 3:1 ratio of **31f/32f** was produced in 67% yield (Entry 7). On the other hand, addition of 2 equiv. of **5** prior to oxidative cyclization resulted in 1:1 mixture of **31f/32f** (Entry 8). However, this seemingly not very useful mixture converts completely into the cyclized product after 7 d in $CDCl_3$ or DME/Et_2O, the cyclization stereoselectivity being unchanged in the process. In the freezer in the dark, this reaction did not take place. SET oxidation of the 4-pentynylmalonate enolate **13g** exclusively afforded the acyclic trapping product **32g** in 98% yield (Entry 9).



Scheme 10

Selected Transformations of the Oxidative Cyclization Products

Further investigations were undertaken in order to demonstrate the synthetic value of the cyclization products (Scheme 11). Most importantly, the cyclic TEMPO trapping products **31** represent piperidinyl-protected alcohols.



Scheme 11

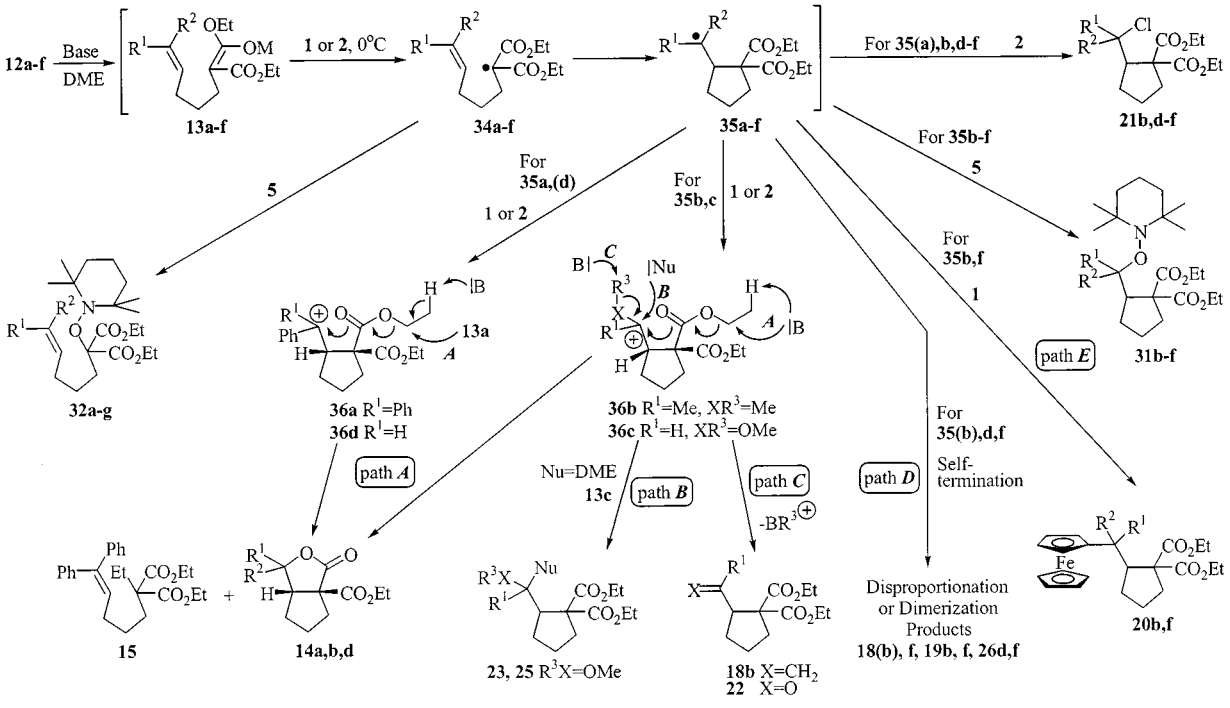
To deprotect the synthetically important alcohol functionality, we cleaved the N−O bond under reductive conditions with Zn/AcOH. Under these conditions, spontaneous lactonization occurred, to give the bicyclic lactones **14b**, **14d′**, and **14f** in good yields. The integrity of the stereocenters was not compromised under the reaction conditions. Thus, oxidative cyclization/TEMPO trapping to give **31**, followed by reductive lactonization to give **14**, represents a complementary pathway to the double oxidative cyclization **12** → **14** for those compounds that do not undergo radical oxidation. Furthermore, the stereochemistry of the lactone is reversed, since direct lactonization and TEMPO trapping occur from opposite faces of prochiral carbenium ion or radical intermediates (vide infra).

Bicyclic lactones **14a**, and **14b** underwent clean Krapcho dealkoxycarbonylation[25] to give bicyclic lactones **33a** and **33b** in 64% and 40% yields. The low yield of **33b** is due to the high volatility of this compound.

Another issue was the product diversity obtained in some runs of the cyclization of enol ether **12c**. The aldehyde/acetal mixture **22**−**24** can be converted either into the aldehyde **22** or into the dimethyl acetal **23**, by acidic hydrolysis or acetalization using trimethyl orthoformate/*p*TsOH.

Mechanistic Interpretation of the Oxidative Cyclizations

All the results can be interpreted according to Scheme 12. Lithium malonate enolates **13** were oxidized efficiently by **1** or **2** regardless of their method of generation. The SET oxidant and its reduced form did not interfere with reactions of the malonyl radicals **34**. In contrast, sodium enolates generated from NaH were not efficiently oxidized either by **1** or by **2** (Table 2, Entries 4 and 7). Radical 5-*exo* cyclizations of malonyl radicals **34a**−**f** occurred as desired to give cyclized radicals **35a**−**f**. At this juncture a diversification point was reached, with the final product distribution largely being determined by radical structure and reagents. Radicals **35a** and **35c** were exclusively oxidized to carbenium ions **36a** and **36c**, which were stabilized by nucleophilic trapping to give **14a**/**15** (path ***A***) or products **23** and **25** (path ***B***). Tertiary alkyl radicals, as exemplified by **35b**, preferentially underwent SET oxidation by **1** to give **36b**, but formation of some disproportionation product **19b** was also detected. For **36b**, nucleophilic lactonization to **14b** was still preferred (path ***A***), but deprotonation to **18b** provided serious competition (path ***C***). A similar situation was found for **36c**, with which dealkylation by base or halides to aldehyde **22** was predominant. Secondary benzyl and alkyl radicals **35d** and **35f** were not oxidized efficiently and provided typical radical disproportionation and/or dimerization products **18f**, **19f**, **26d**, and **26f** (path ***D***). Finally, cyclization of the 4-pentynylmalonyl radical **34g** (not shown) resulted in a vinyl radical **35g**, which was stabilized by hydrogen abstraction from the solvent and addition to **1** to give **28** (Scheme 9). Furthermore, the cyclization to the destabilized vinyl radical **35g** seemed to be reversible, as indicated by the formation of acyclic dimer **29** in this case.[26] The formation of ferrocene adducts **20b**, **20f**, and **20g** occurred as a minor but constant reaction channel (path ***E***). It must be ascribed to a radical coupling, albeit not very efficient, of the ferrocenium ion with the cyclized radical.[27] This is supported by the fact that deliberate addition of excess ferro-



Scheme 12

cene prior to oxidative cyclization of **13g** had no influence on the product distribution.

When **2** was used as the SET oxidant, chlorine transfer occurred. This was found to be less pronounced for benzylic radicals **35a** and **35d** and α-methoxy radical **35c**, for which SET oxidation to carbenium ions **36a**, **36c**, and **36d** and then to **14** or **22**, **23**, and **24** still dominated. For alkyl radicals **35b** and **35f**, chlorine transfer was very efficient, giving **21b** and **21f** almost exclusively and in high yields.

The mechanistic picture is further substantiated by the cyclization experiments in the presence of TEMPO (**5**). Surprisingly, radical coupling with the malonyl radicals **34a−f** was slower or only as fast as radical 5-*exo* cyclization. It was therefore possible to use TEMPO to trap both radical species **34** and **35** involved in the radical cyclization, permitting remote oxygenation after cyclization to give **31b−f** in moderate to high yields. Furthermore, it was also discovered that the malonyl radical-derived TEMPO adducts **32** were prone to homolysis/cyclization in solution under ordinary lab. light, providing **31**. This represents an interesting application of the persistent radical effect.[28]

Factors Influencing the Reaction Course

1.) Enolate Oxidation

It can clearly be seen that the outcome of the reactions is critically dependent on the oxidant. Weak or moderate SET oxidants such as **1** or **2** are best suited for performing malonate enolate SET oxidation. Stronger oxidants do not oxidize malonate enolates **4** to radicals efficiently (Table 1). Even **1** and **2** show subtle differences in their reactivities, however. While **1** oxidizes enolates **4** ($E = +0.03$ V vs. ferrocene in DMSO)[29] or **13a−g** only at temperatures of 0 °C and above, the slightly stronger $CuCl_2$ (**2**) performs well even at −70 °C (Table 4, Entry 4). The rate of enolate oxidation is important, however, since slow enolate oxidation may result in unwanted enolate anion/carbenium ion side reactions in these reaction sequences. This is manifested in the induction by **1** of malonate enolate oxidation/cyclization/radical oxidation of **13a** and **13c** (Table 2, Entries 1 and 2; Table 4, Entries 1 and 3). Compounds **15** or **25** can only arise if oxidation of the enolate is the rate-determining step of the sequence. Apparently 5-*exo* cyclization of **34a** and **34c** − and especially SET oxidation of the cyclized radicals **35a** and **35c** − are very fast, producing carbenium ions **36a** and **36c** while **13a** and **13c** are still present in the reaction mixture. This is further supported by the cyclization experiments in the presence of TEMPO (**5**). While some malonyl radical derived TEMPO adduct **32a** was formed, no cyclized **31a** was detectable. TEMPO trapping of **35a** cannot compete at all with radical oxidation to give carbenium ion **36a** (vide infra), whereas trapping of the α-methoxyalkyl radical **35c** by **5** was competitive with SET oxidation by **1**. However, products **15** and **25** were not formed in oxidative cyclizations of **13a** and **13c** induced by **2** (Table 2 and 4, Entries 5−7 and 3−5). This indicates that SET oxidation of **35a** and **35c** by **2** is faster than the following sequence steps. Thus, if SET oxidation is expected to be slow, the relative rates of enolate oxidation by **1** have to be taken into account. Fortunately, malonates are on the slow end of enolate SET oxidation. Other enolate types are oxidized by **1** appreciably more rapidly, even at lower temperatures.[16]

2.) Radical Oxidation

Radical oxidation is an important issue in these cyclizations, since valuable information on the design of tandem processes can be obtained from these experiments. Radical oxidation by ferrocenium hexafluorophosphate **1** very reliably reflects the known oxidation potentials of radicals.[30] The 1,1-diphenylethyl radical ($E_{1/2} = +0.23$ V vs. SCE)[30a] in **35a** is oxidized very rapidly, exclusively producing carbocation-derived products (Table 2). Radical oxidation of **35a** is much faster even than TEMPO trapping ($k = 4.6\times10^7$ $M^{-1}s^{-1}$),[31] as no cyclized **31a** was detected (Table 7, Entry 1). Thus, **35a** must be oxidized by **1** with a rate constant $k_{ox} > 10^8$ $M^{-1}s^{-1}$. Competitive trapping of radical **35c** by **5** vs. SET oxidation by **1** gave a ratio of **31c**/(**22** + **23** + **25**) of 1.6:1, indicating a rate constant of at least 10^7 $M^{-1}s^{-1}$ for SET oxidation of **35c** to **36c** (Table 7, Entries 4 and 5). Tertiary alkyl radical **35b** was oxidized more slowly, giving rise to some tertiary radical disproportionation (Table 3). The ratio of products **14b** + **18b′** (**18b′** = **18b** − **19b**),[32] derived from carbenium ion **36b**, to radical-derived products (2 × **19b** + **20b**) ranges from 2.5:1 to 7.3:1. Polar additives influence this ratio. TMEDA or $ZnCl_2$ significantly lessened the amount of reduced product **19b** (Table 3, Entries 5 and 6). Some rough information about the rate of tertiary radical oxidation by **1** is provided by the competitive trapping experiments with TEMPO and 1,4-cyclohexadiene. Radical oxidation cannot compete with TEMPO trapping ($k_{t\mathrm{Bu}} = 7\times10^8$ $M^{-1}s^{-1}$),[31] but is significantly faster than hydrogen abstraction from cyclohexadiene ($k = 9.4\times10^3$ $M^{-1}s^{-1}$ for the *tert*-butyl radical at 27 °C)[33] (Table 3, Entry 3). On the basis of these results, the rate for SET oxidation can be roughly estimated as in the range of 10^4-10^5 $M^{-1}s^{-1}$. Thus, radical oxidation may interfere with subsequent intended radical cyclizations, especially if these are slow.

Benzylic radical **35d** ($E_{1/2} = +0.37$ V vs. SCE)[30] undergoes oxidation only very sluggishly, to give lactone **14d**. Dimerization resulting in **26d** is much faster. Secondary alkyl radicals and vinylic radicals are not oxidized at all by **1**. The last three results are significant, since further radical reaction steps can thus be envisaged as following the initial radical cyclization in domino processes without interference of competitive radical oxidation.

$CuCl_2$ (**2**) showed much more highly differentiated behavior towards radicals. The products derived from enolate **13a** indicate that SET oxidation followed by lactonization to **14a** may occur as the major pathway. The formation of 2-(diphenylmethylene)cyclopentane-1,1-dicarboxylate **16** and alcohol **17**, however, can be attributed to chlorine transfer followed by facile β-elimination of HCl or hydrolysis from

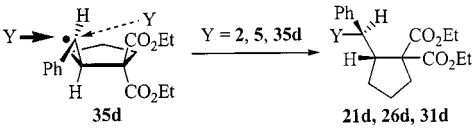
activated diphenylmethyl chloride. Since **16** was never observed in oxidative reactions involving **1**, direct deprotonation of the carbenium ion **36a** seems to be an unlikely pathway to **16**, as the reaction conditions are identical except for the oxidant. Chlorine transfer to **35** becomes more competitive in the case of benzyl radical **35d**, in which the benzylic chloride **21d** was isolated in 21% yield (Table 5, Entry 6). The reaction is not clean, since dimerization, chlorine transfer, and radical oxidation/lactonization occur at the same time. For secondary and tertiary alkyl radicals **35b** and **35f**, on the other hand, chlorine transfer is the dominant pathway, producing chlorides **21b** and **21f** in good yields (Table 3 and 6, Entries 7 and 2). Chlorine transfer from $CuCl_2$ onto alkyl radicals is known to be a very facile process, with rate constants of $k = 1-5\times10^8$ $M^{-1}s^{-1}$.[34] This argument is further substantiated by the oxidative cyclization of **13b** induced by **1** in the presence of $ZnCl_2$. Here, **21b** was formed in only 12% yield under otherwise identical conditions (Table 3, Entry 5). This product should rather result from nucleophilic trapping of the carbenium ion **36b**. Thus, $CuCl_2$ (**2**) is able to induce oxidative radical cyclizations starting from enolates. This reagent oxidizes only the most stabilized radicals to carbenium ions. For most radicals, however, chlorine transfer interferes. For alkyl radicals, this is the dominant pathway, due to its high reaction rates, and may debar subsequent radical reaction steps.

3.) Stereoselectivity of the Cyclizations

High diastereoselectivity was observed in the radical cyclization/trapping sequences involving malonate enolate **13d**. In radical **35d**, the phenyl group is oriented away from the cyclopentane ring, as shown in Scheme . Trapping can occur from one freely exposed face of the radical, while the other face is completely shielded by the two ethyl ester functions in the 1-position. Thus, the TEMPO adduct **31d** and the chlorine transfer product **21d** were formed with high diastereoselectivities. The same preferred conformation may be attributed to the related carbenium ion **36d**, which affords lactone **14d**. However, intramolecular nucleophilic trapping by the *cis*-oriented carbonyl oxygen atom of course occurs from the opposite face. A similar, although much less marked, conformational preference can be derived by analogy for radical **35f**.

4.) Carbenium Ion Stabilization

For phenyl-substituted carbenium ions **36a** and **36d**, intramolecular lactonization is the only pathway observed. A similar situation is found in the *tert*-butyl analogue carbenium ion **36b**, which produces lactone **14b**. However, deprotonation becomes a more serious competitor, due to the unavoidable basic reaction conditions. Attempts to direct the deprotonation/lactonization ratio in one direction or other by application of external bases or higher lithium amide concentration have so far met with only limited success (Table 3). In contrast, no lactonization was observed for **36c** (Scheme 14). This less congested carbenium ion does not

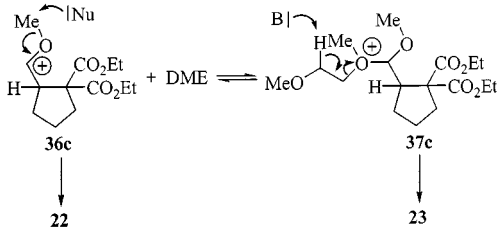


Scheme 13

interact with the neighboring ester functions. Instead, equilibrium with the oxonium ion **37c**, derived from the DME solvent, seems to dominate. This complex most probably fragments to afford dimethyl acetal **23** (Table 4, Entries 1 and 3). This stabilization pathway is further supported by the fact that acetal **23** was not observed when the reaction was performed in THF under otherwise identical conditions. In addition, when a good nucleophile (Br^- or Cl^-) was present, direct demethylation of **36c** to aldehyde **22** was favored over reaction with the solvent (Table 4, Entries 2 and 4). Since compounds **22** and **23** are interconvertible (Scheme 11), conversion into either single product **22** or **23** can be achieved. Future work must clearly be directed to the development of conditions under which more selective carbenium ion stabilization can be achieved.

Comparison with Other Oxidative Cyclization Methods

There are several similar known oxidative cyclization methods starting from carbonyl compounds, with induction by $Mn(OAc)_3$, CAN, $K_3[Fe(CN)_6]$, $Fe(ClO_4)_3$,[23] or $Ti(OiPr)_4$/amine/I_2.[35] The critical question is how the presented method compares. All the previous methods are limited to easily enolizable carbonyl compounds. Most other substrates, such as simple esters, nitriles, or ketones, variously require harshly acidic conditions for oxidation, cyclize sluggishly, or do not react at all. In contrast, the method presented effectively overcomes these limitations, since the carbonyl compound is irreversibly transformed into its enol form under very mild conditions. Although we employed only malonates in this "proof of principle" study, the scope of oxidants **1** or **2** is much broader, as we have observed that all carbonyl structure types[14,16] can be applied successfully in related reactions.



Scheme 14

Another important aspect of oxidative radical cyclizations is their termination. Lactonization to compounds of type **14**, products of radical oxidation, is common for $Mn(OAc)_3$- or CAN-mediated reactions, as also observed with **1**. However, ligand transfer can constitute serious competition, resulting in reduced yields of the desired products. Therefore, in $Mn(OAc)_3$-mediated reactions, $Cu(OAc)_2$ of-

ten needs to be added in order to obtain alkenes by way of copper hydride elimination. In contrast, in our cyclizations employing **1** as SET oxidant, ligand transfer in the form of ferrocene alkylation plays only a minor role, while $CuCl_2$ (**2**) is complementary in its reactivity, giving exclusive ligand transfer for alkyl radicals. This opens up diverse functionalization opportunities for the cyclized radicals. Last but not least, oxidant **1** is efficiently recyclable, while all the other methods, save for a few $Mn(OAc)_3$-mediated electrochemical reactions,[36] do not allow oxidant recycling.

Conclusion

We have shown that radical reactions can conveniently be induced from lithium malonate enolate starting materials. SET oxidation by recyclable ferrocenium hexafluorophosphate (**1**) or $CuCl_2$ (**2**) gave malonyl radicals amenable to typical radical reactions such as dimerization, oxygenation by TEMPO (**5**), or radical 5-*exo* cyclizations. The stabilization of the cyclized radicals depends on the radical structure and the oxidant used, but is now predictable. Tertiary benzyl, alkyl, and α-alkoxy radicals are oxidized by **1** to afford carbenium ions, which is followed by lactonization or deprotonation. Secondary alkyl and benzyl radicals are not oxidized by **1** and give radical self-termination products. However, selective radical trapping by TEMPO (**5**) provided oxygenated cyclopentane derivatives in good yields. The same radical generation is possible with $CuCl_2$ (**2**). However, ligand transfer to the cyclized radicals is a competing or even exclusive stabilization pathway. Kinetic information was derived from the results obtained, and implications for synthetic planning using the accessible intermediates obtainable using oxidants **1** or **2** have been outlined. A major implication of the methodology presented is that radical reactions can in principle be predictably combined with anionic reactions or transformations involving carbocations in sequential processes. Future work must clearly be directed towards verification of these implications and development of more selective carbenium ion stabilization methods to provide higher yields and selectivities. These issues are actively under investigation.

Experimental Section

General Remarks: All reactions were conducted in flame-dried glassware under nitrogen. THF, DME, HMPA, DMSO, diisopropylamine, and hexamethyldisilazane were dried using standard methods. The esters **3** and **11** were distilled prior to use. $CuCl_2$, LiCl, LiBr, and $ZnCl_2$ were dried in vacuum (160 °C, 0.8 mbar) for 3 to 8 h. POLYGRAM SIL G/UV_{254} TLC plates (Macherey−Nagel) were used for monitoring reactions. − Chromatographic separations were performed on silica gel 60 (Fluka, 230−400 mesh) with *n*-hexane/ethyl acetate as eluent in the ratios given. − Melting points are uncorrected. − IR spectra were taken with a Nicolet DX-320 FT-IR spectrometer. − UV/Vis spectra were measured in CH_3CN, with a Hewlett−Packard 8452 diode array spectrometer. − ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, with Bruker DRX 400 or AC 200 spectrometers at 400 or 200, and 100 or 50 MHz, respectively. Connectivity was determined by ^1H-^1H COSY experiments. − ^{13}C NMR assignments were obtained from DEPT experiments. − EI mass spectra were recorded with Finnigan MAT 8430 and MAT 8400 spectrometers at 70 eV. − Combustion analyses were performed at the Microanalytical Laboratories of the Technical University of Braunschweig.

Ferrocenium Hexafluorophosphate (1): Ferrocene (5.58 g, 30.0 mmol) was added to concentrated H_2SO_4 (10 mL) and the mixture was stirred for 45 min. The blue-black reaction mixture was slowly added to a solution of *t*BuOH (5.00 g) in H_2O (170 mL), stirred for 15 min, and filtered. At 0 °C, KPF_6 (11.00 g, 60.0 mmol), dissolved in H_2O (235 mL), was added to the filtrate and the mixture was stirred for 60 min at 0 °C. The blue precipitate was filtered, washed twice with 40 mL ice-cold H_2O, 50 mL EtOH, and ether until the ether remained colorless. Drying for 12 h in vacuum yielded 8.46 g (85%) **1** as a blue powder. Ferrocene (**9**), collected from the oxidative cyclizations, was recrystallized from MeOH or *n*-hexane. Reoxidation as described above gave **1**.

Diethyl 2-Methyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)malonate (6a): Compound **3** (261 mg, 1.50 mmol) was added, at −78 °C under N_2, to a solution of LDA (1.95 mmol, 1.3 equiv.; prepared from 274 μL of *i*Pr_2NH and 1.22 mL of BuLi [1.6 M in hexane]) in 30 mL of dry DME. The solution was stirred between −78 and −60 °C for 30 min. At 0 °C, compound **5** (328 mg, 2.10 mmol) was added, and the red solution was stirred for 5 min. Solid **1** or **2** was added in portions at 0 °C. The mixture was stirred at 0 °C for 2 h, quenched with four drops of a saturated NH_4Cl solution, and allowed to warm to room temperature. The reaction mixture was diluted with 20 mL ether and filtered through a pad of silica gel. The solvent was evaporated and the inhomogeneous residue was preadsorbed on silica gel. Crude flash chromatography (50:1 gradient to 1:1) gave > 90% of **9**, followed by product **6a**, which was further purified by flash chromatography and recrystallization from pentane [R_f (10:1) = 0.39] as a colorless solid, 425 mg (86%) and 435 mg (88%), m.p. 76−77 °C. − IR (KBr): $\tilde{\nu}$ = 2971 cm^{-1} (m), 1760 (s, CO_2), 1737 (s, CO_2), 1267 (s), 1219 (s), 1126 (s), 1110 (s). − ^1H NMR (200 MHz): δ = 0.94 (s, 6 H, NCC*H*$_3$), 1.15−1.48 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.19 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$), 1.34 (s, 6 H, NCC*H*$_3$), 1.64 (s, 3 H, OCC*H*$_3$), 4.14 (q, *J* = 7.1 Hz, 4 H, OC*H*$_2$). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH$_2$*C*H$_3$), 16.9 (t, NCCH$_2$*C*H$_2$), 17.8 (q, OC*C*H$_3$), 20.5 (q, NC*C*H$_3$), 32.9 (q, NC*C*H$_3$), 40.7 (t, NC*C*H$_2$), 60.2 (s, N*C*CH$_3$), 61.4 (t, OCH$_2$), 85.4 (s, NOC), 170.2 (s, CO_2). − MS; *m*/*z* (%) = 314 (10), 156 (100) [TEMPO], 123 (30), 81 (12), 58 (17), 55(15). − $C_{17}H_{31}NO_5$ (329.2): calcd. C 61.96, H 9.49, N 4.25; found C 61.85, H 9.47, N 4.29.

Oxidative Dimerization of Malonate 3 with 1: Compound **3** (261 mg, 1.50 mmol) was added, at −78 °C under N_2, to a solution of LDA (1.95 mmol; prepared from 274 μL of *i*Pr_2NH and 1.22 mL of BuLi [1.6 M in hexane]) in 30 mL of dry DME. The solution was stirred between −78 and −60 °C for 30 min. Solid **1** was added in portions at 0 °C until a blue-green color persisted in the reaction mixture for 30 min. The mixture was stirred at 0 °C for 2 h, quenched with four drops of a saturated NH_4Cl solution, and allowed to warm to room temperature. The reaction mixture was diluted with 30 mL of ether and filtered through a pad of silica gel. The solvent was evaporated and the inhomogeneous residue was preadsorbed on silica gel. Crude flash chromatography (50:1 gradient to 1:1) gave > 90% of **9**, followed by **6b**, **7**, and **8**. The individual compounds were further purified by flash chromatography as indicated in the characterization section.

Diethyl 2-Ferrocenyl-2-methylmalonate (6b): Flash chromatography (50:1) gave 16 mg (3%) of **6b** [R_f (5:1) = 0.48] as an orange oil. − IR (film): $\tilde{\nu}$ = 3463 cm^{-1} (w), 2983 (m), 1733 (s, CO_2), 1268 (s), 1248 (s), 1221 (s), 1204 (m), 1106 (s). − ^1H NMR (200 MHz): δ = 1.22 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.71 (s, 3 H, CCH_3), 4.06 (s, 5 H, *Cp*), 4.12 (d, J = 1.9 Hz, 2 H, C*H*=CH), 4.16 (q, J = 7.1 Hz, 4 H, OCH_2), 4.20 (d, J = 1.7 Hz, 2 H, C*H*=CH). − ^{13}C NMR (50 MHz): δ = 14.1 (q, OCH_2CH_3), 21.5 (q, CCH_3), 54.2 (s, CCH_3), 61.4 (t, OCH_2), 67.5 (d, *Cp*), 68.0 (d, *Cp*), 68.8 (d, *Cp*), 86.2 (s, (*ipso*-Cp)*C*), 170.9 (s, CO_2). − MS; *m*/*z* (%) = 358 (100) [M^+], 286 (49), 285 (44), 257 (24), 219 (18), 213 (18), 91 (45). − HRMS: $C_{18}H_{22}FeO_4$: calcd. 358.0867; found 358.0860 ± 2 ppm.

Tetraethyl Butane-2,2,3,3-tetracarboxylate (7): Flash chromatography (40:1) gave 109 mg (21%) or 384 mg (74%) of **7** [R_f (10:1) = 0.38] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (m), 1767 (m, CO_2), 1748 (s, CO_2), 1459 (m), 1241 (s), 1162 (m), 1058 (m). − ^1H NMR (200 MHz): δ = 1.27 (t, J = 7.1 Hz, 12 H, OCH_2CH_3), 1.89 (s, 6 H, CCH_3), 4.25 (q, J = 7.1 Hz, 8 H, OCH_2). − ^{13}C NMR (50 MHz): δ = 13.7 (q, OCH_2CH_3), 25.5 (q, CCH_3), 62.8 (t, OCH_2), 66.0 (s, CCH_3), 167.1 (s, CO_2). − MS; *m*/*z* (%) = 346 (1) [M^+], 301 (74) [M^+ − OEt], 255 (53) [M^+ − OEt − EtOH], 200 (25) [M^+ − 2 CO_2Et], 181 (21), 174 (100) [$CH_3CH(CO_2Et)_2$], 173 (74) [$CH_3C(CO_2Et)_2$], 171 (25) [M^+ − OEt − 2 CO_2Et], 160 (42), 128 (21), 127 (52) [M^+ − 3 CO_2Et]. − $C_{16}H_{26}O_8$ (346.2): calcd. C 55.48, H 7.57; found C 55.34, H 7.63.

Tetraethyl Butane-1,1,3,3-tetracarboxylate (8): Flash chromatography (40:1) gave 135 mg (26%) of **8** [R_f (10:1) = 0.34] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2985 cm^{-1} (m), 1733 (s, CO_2), 1299 (s), 1250 (m), 1176 (m), 1153 (m), 1111 (m), 1024 (m). − ^1H NMR (200 MHz): δ = 1.21 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.23 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.37 (s, 3 H, CCH_3), 2.50 (d, J = 6.0 Hz, 2 H, $CHCH_2$), 3.49 (t, J = 6.0 Hz, 1H, CH), 4.13 (q, J = 7.0 Hz, 4 H, OCH_2), 4.15 (q, J = 7.1 Hz, 4 H, OCH_2). − ^{13}C NMR (50 MHz): δ = 13.78 (q, OCH_2CH_3), 13.84 (q, OCH_2CH_3), 20.2 (q, CCH_3), 33.8 (t, $CHCH_2$), 48.4 (d, CH_2CH), 52.6 (s, CCH_3), 61.3 (t, OCH_2), 61.5 (t, OCH_2), 169.1 (s, CO_2), 171.3 (s, CO_2). − MS; *m*/*z* (%) = 346 (1) [M^+], 301 (95) [M^+ − OEt], 255 (52) [M^+ − OEt − EtOH], 227 (20) [M^+ − EtOH − CO_2Et], 200 (25) [M^+ − 2 CO_2Et], 174 (100) [$CH_3CH(CO_2Et)_2$], 173 (73) [$CH_3C(CO_2Et)_2$], 171 (25) [M^+ − OEt − 2 CO_2Et], 160 (35), 155 (35) [M^+ − OEt − 2 CO_2Et], 128 (22), 127 (63) [M^+ − 3 CO_2Et]. − $C_{16}H_{26}O_8$ (346.2): calcd. C 55.48, H 7.57; found C 55.48, H 7.72.

Diethyl 2-(4-Pentenyl)malonates 12. − General Procedure: Compound **11** (3.20 g, 20.0 mmol) was added at 0 °C under N_2 to a suspension of NaH (80% in mineral oil, 450 mg, 15.0 mmol) in a dry 100:10 mL THF/DMF mixture and the mixture was stirred for 30 min. The tosylates or bromides **10a**−**g** (10.0 mmol) and anhydrous NaI (600 mg, 4.0 mmol) were added at room temperature. The mixture was heated to reflux until reaction was complete by TLC (12−60 h). The mixture was quenched with a saturated NH_4Cl solution. The aqueous layer was extracted three times with ether. The combined organic layers were dried with Na_2SO_4 and the solvent was evaporated. Excess **11** was distilled off at 50 °C and 0.8 mbar. Purification of the residue by flash chromatography (25:1 gradient to 5:1) yielded malonates **12a**−**g**.

Diethyl 2-(5-Methylhex-4-enyl)malonate (12b): Flash chromatography (25:1 gradient to 10:1) gave 1.72 g (67%) of **12b** [R_f (5:1) = 0.72] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2982 cm^{-1} (m), 1752 (s, CO_2), 1735 (s, CO_2), 1448 (w), 1243 (w), 1146 (m). − ^1H NMR (200 MHz): δ = 1.23 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.35 (m, 2 H, $=CHCH_2CH_2$), 1.55 (s, 3 H, $=CCH_3$), 1.64 (s, 3 H, $=CCH_3$), 1.91 (m, 4 H, $CH_2CH_2CH_2$), 3.28 (t, J = 7.6 Hz, 1 H, $CHCO_2$), 4.15 (q, J = 7.1 Hz, 4 H, OCH_2), 5.05 (t, J = 7.1 Hz, 1 H, =CH). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 17.6 (q, (*Z*)-=CCH_3), 25.6 (q, (*E*)-=CCH_3), 27.4 (t), 27.5 (t), 28.3 (t), 51.9 (d, $CHCO_2$), 61.1 (t, OCH_2), 123.7 (d, =CH), 131.9 (s, =C), 169.4 (s, CO_2). − MS; *m*/*z* (%) = 256 (17) [M^+], 211 (22) [M^+ − OEt], 173 (23), 160 (30) [$EtO_2CCH{=}C(OH)OEt^+$], 137 (25) [M^+ − CO_2Et − EtOH], 136 (60) [M^+ − CO − 2 EtOH], 109 (23) [M^+ − CO − EtOH − CO_2Et], 95 (26), 82 (100), 69 (26), 67 (41), 55 (21). − HRMS: $C_{14}H_{24}O_4$: calcd. 256.1675; found 256.1667 ± 3 ppm. − $C_{14}H_{24}O_4$ (256.2): calcd. C 65.60, H 9.44; found C 65.59, H 9.48.

Diethyl 2-(5-Methoxypent-4-enyl)malonate (12c): Flash chromatography (25:1 gradient to 10:1) gave 1.83 g (71%) of a 6:1 (*E*)/(*Z*) mixture of **12c** [R_f (10:1) = 0.49] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2938 cm^{-1} (m), 1750 (s, CO_2), 1732 (s, CO_2), 1702 (m), 1210 (m), 1151 (m). − **(*E*)-12c:** ^1H NMR (200 MHz): δ = 1.23 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.35 (m, 2 H), 1.88 (m, 4 H), 3.27 (t, J = 7.5 Hz, 1 H, $CHCO_2$), 3.46 (s, 3 H, OCH_3), 4.15 (q, J = 7.1 Hz, 4 H, OCH_2), 4.64 (dt, J = 12.6, 7.3 Hz, 1 H, $=CHCH_2$), 6.25 (d, J = 12.6 Hz, 1 H, =C*H*O). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 27.3 (t), 28.0 (t), 28.4 (t), 51.9 (d, $CHCO_2$), 55.8 (q, OCH_3), 61.2 (t, OCH_2), 102.0 (d, $=CHCH_2$), 147.4 (d, =CHO), 169.5 (s, CO_2). − **(*Z*)-12c:** ^1H NMR (200 MHz): δ = 1.23 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.35 (m, 2 H), 1.88 (m, 4 H), 3.30 (t, J = 7.5 Hz, 1 H, $CHCO_2$), 3.53 (s, 3 H, OCH_3), 4.15 (q, J = 7.1 Hz, 4 H, OCH_2), 4.26 (m, 1 H, $=CHCH_2$), 5.84 (d, J = 6.2 Hz, 1 H, =C*H*O). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 23.2 (t), 27.3 (t), 28.1 (t), 51.8 (d, $CHCO_2$), 55.8 (q, OCH_3), 61.1 (t, OCH_2), 105.7 (d, $=CHCH_2$), 146.6 (d, =CHO), 169.5 (s, CO_2). − MS; *m*/*z* (%) = 258 (2) [M^+], 226 (26), 167 (46) [M^+ − EtOH − OEt], 152 (28), 138 (40), 97 (28), 84 (100), 71 (66). − $C_{13}H_{22}O_5$ (258.3): calcd. C 60.45, H 8.58; found C 60.40, H 8.59.

Diethyl (*Z*)/(*E*)-2-(5-Phenylpent-4-enyl)malonate (12d/12e): Flash chromatography (25:1 gradient to 10:1) gave 2.28 g (75%) of a mixture of **12d** and **12e** (10:1) [R_f (10:1) = 0.48] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2983 cm^{-1} (m), 1750 (s, CO_2), 1733 (s, CO_2), 1236 (m), 1213 (m), 1179 (m), 1147 (m). − UV: λ_{max} (lg ε) = 202 nm (4.38), 216 (3.99), 244 (4.76), 260 (3.89), 268 (3.32), 270 (3.14), 274 (2.91). − **(*Z*)-12d:** ^1H NMR (200 MHz): δ = 1.20 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.44 (tt, J = 7.7, 7.5 Hz, 2 H, $=CHCH_2CH_2$), 1.89 (dt, J = 8.2, 7.5 Hz, 2 H, CH_2CHCO_2), 2.31 (ddt, J = 7.4, 7.3, 1.4 Hz, 2 H, $=CHCH_2$), 3.26 (t, J = 7.5 Hz, 1 H, $CHCO_2$), 4.12 (q, J = 7.1 Hz, 4 H, OCH_2), 5.57 (dt, J = 11.6, 7.2 Hz, 1 H, =C*H*CH_2), 6.38 (d, J = 11.6 Hz, 1 H, C*H*Ph), 7.21 (m, 5 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 27.6 (t), 28.1 (t), 28.3 (t), 51.8 (d, $CHCO_2$), 61.2 (t, OCH_2), 126.5 (d, $=CHCH_2$), 128.1 (d, *Ph*), 128.7 (d, *Ph*), 129.5 (d, *Ph*), 131.8 (d, =CHPh), 137.5 (s, *Ph*), 169.3 (s, CO_2). − **(*E*)-12e:** ^1H NMR (200 MHz): δ = 0.92 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.44 (tt, J = 7.8, 7.6 Hz, 2 H, $=CHCH_2CH_2$), 2.01 (dt, J = 7.6, 7.5 Hz, 2 H, CH_2CHCO_2), 2.03 (dt, J = 7.7, 6.8 Hz, 2 H, $=CHCH_2$), 3.36 (t, J = 7.5 Hz, 1 H, $CHCO_2$), 3.95 (q, J = 7.1 Hz, 4 H, OCH_2), 6.00 (dt, J = 15.8, 6.8 Hz, 1 H, $=CHCH_2$), 6.27 (d, J = 15.8 Hz, 1 H, C*H*Ph), 7.00−7.25 (m, 5 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 27.0 (t), 28.3 (t), 32.5 (t), 51.8 (d, $CHCO_2$), 61.2 (t, OCH_2), 125.9 (d, $=CHCH_2$), 126.9 (d, *Ph*), 128.4 (d, *Ph*), 129.8 (d, *Ph*), 130.5 (d, =CHPh), 137.5 (s, *Ph*), 169.3 (s, CO_2). − MS; *m*/*z* (%) = 304 (53) [M^+], 259 (16) [M^+ − OEt], 185 (40) [M^+ − CO_2Et − EtOH], 184 (70) [M^+ − CO − 2 EtOH], 173 (46), 160 (20) [$EtO_2CCH{=}C(OH)OEt^+$], 130 (100), 129 (71), 128 (33), 117 (53), 115 (62), 91 (41). − HRMS: $C_{18}H_{24}O_4$: calcd. 304.1675; found 304.1667 ± 2 ppm. − $C_{18}H_{24}O_4$ (304.4): calcd. C 71.03, H 7.95; found C 70.80, H 8.17.

Diethyl (*E*)-2-(Hex-4-enyl)malonate (12f): Flash chromatography (25:1 gradient to 10:1) gave 2.08 g (86%) of **12f** [R_f (10:1) = 0.46] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2938 cm^{-1} (m), 1752 (s, CO_2), 1734 (s, CO_2), 1448 (m), 1370 (m), 1264 (m), 1239 (m), 1153 (s). − ^{1}H NMR (200 MHz): δ = 1.23 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.34 (tt, *J* = 7.7, 7.6 Hz, 2 H, $=CHCH_2CH_2$), 1.59 (d, *J* = 4.5 Hz, 3 H, $=CHCH_3$), 1.84 (q, *J* = 7.6 Hz, 2 H, CH_2CHCO_2), 1.97 (q, *J* = 7.0 Hz, 2 H, $=CHCH_2$), 3.27 (t, *J* = 7.5 Hz, 1 H, $CHCO_2$), 4.15 (q, *J* = 7.1 Hz, 4 H, OCH_2), 5.37 (m, 2 H, $CH=CH$). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 17.7 (q, $=CHCH_3$), 27.1 (t), 28.1 (t), 32.0 (t), 51.9 (d, $CHCO_2$), 61.1 (t, OCH_2), 125.3 (d, $=CHCH_2$), 130.4 (d, $=CHCH_3$), 169.4 (s, CO_2). − MS; *m*/*z* (%) = 242 (2) [M^+], 173 (100), 160 (50) [$EtO_2CCH=C(OH)OEt^+$], 150 (66), 122 (96), 95 (32), 68 (60). − $C_{13}H_{22}O_4$ (242.3): calcd. C 64.44, H 9.15; found C 64.43, H 9.19.

Diethyl 2-(Pent-4-ynyl)malonate (12g): Flash chromatography (25:1 gradient to 10:1) gave 1.38 g (61%) of **12g** [R_f (5:1) = 0.44] as a colorless oil. − IR (film): $\tilde{\nu}$ = 3289 (w, ≡C−H), 2940 (w), 2119 (w), 1750 (s), 1732 (s), 1151 (m). − ^{1}H NMR (200 MHz): δ = 1.23 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.57 (m, 2 H), 1.94 (t, *J* = 2.8 Hz, 1 H, ≡CH), 1.99 (m, 2 H), 2.19 (dt, *J* = 7.0, 2.6 Hz, 2 H, $\equiv CCH_2$), 3.31 (t, *J* = 7.5 Hz, 1 H, CH_2CH), 4.16 (q, *J* = 7.1 Hz, 4 H, OCH_2). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH_2CH_3), 18.1 (t, $\equiv CCH_2$), 26.1 (t), 27.7 (t), 51.5 (d, CH_2CH), 61.3 (t, OCH_2), 68.8 (d, ≡CH), 83.4 (s, ≡C), 169.2 (s, CO_2). − MS; *m*/*z* (%) = 226 (< 1) [M^+], 197 (7) [M^+ − Et], 181 (5) [M^+ − OEt], 160 (100) [$EtO_2CCH=C(OH)OEt^+$], 153 (30) [M^+ − CO_2Et], 152 (34) [M^+ − OEt − Et], 134 (18) [M^+ − 2 EtOH], 133 (29), 125 (53), 107 (50) [M^+ − CO_2Et − EtOH], 81 (45), 80 (22), 79 (97), 78 (20), 77 (26), 55 (40). − $C_{12}H_{18}O_4$ (226.3): calcd. C 63.70, H 8.02; found C 63.78, H 8.20.

Oxidative Cyclization of Malonates 12a−g with 1. − General Procedure: Compounds **12a−g** (1.00 mmol) were added at −78 °C under N_2 to a solution of the lithium amide or *n*BuLi in 20 mL dry DME (for the amount of base, see Table 2−6). The solution was stirred between −78 and −60 °C for 30 min. Solid **1** was added in portions at 0 °C until a blue-green color persisted in the reaction mixture for 30 min. The mixture was stirred at 0 °C for 2 h unless otherwise noted. The mixture was quenched with four drops of a saturated NH_4Cl solution and allowed to warm to room temperature. The reaction mixture was diluted with 20 mL of ether and filtered through a pad of silica gel. The solvent was evaporated and the inhomogeneous residue was preadsorbed on silica gel. Crude flash chromatography (50:1 gradient to 1:1) gave > 90% of **9** followed by the products shown in Table 2−6. The individual compounds were further purified by flash chromatography as indicated in the characterization section.

Oxidative Cyclization of Malonates 12a−f with $CuCl_2$ (2). − General Procedure: Compounds **12a−f** (1.00 mmol) were added at −78 °C under N_2 to a solution of the lithium amide in 20 mL of dry DME (for the amount of base, see Table 2−6). The solution was stirred between −78 and −60 °C for 30 min. Solid **2** was added in portions at 0 °C until a brown-green color persisted in the reaction mixture and a brown suspension of excess $CuCl_2$ was observed for 30 min. The mixture was stirred at 0 °C for 2 h unless otherwise noted. The mixture was quenched with four drops of a saturated NH_4Cl solution and allowed to warm to room temperature. The reaction mixture was diluted with 20 mL of ether and filtered through a pad of silica gel, and the solvent was evaporated. Crude flash chromatography of the residue (50:1 gradient to 1:1) gave the products shown in Table 2−6. The individual compounds were further purified by flash chromatography as indicated in the characterization section.

Transmetalation and Oxidative Cyclization of Diethyl 2-(5-Methylhex-4-enyl)malonate (12b): Compound **12b** (256 mg, 1.00 mmol) was added at −78 °C under N_2 to a solution of LDA (1.30 mmol; prepared from 185 μL of iPr_2NH and 810 μL of BuLi [1.6 M in hexane]) in 6 mL of dry DME and the resulting solution was stirred between −78 and 0 °C for 30 min. This solution was transferred by syringe to a suspension of anhydrous $ZnCl_2$ (273 mg, 2.00 mmol) in 14 mL of dry DME and stirred for 40 min at room temperature. Addition of **1** and workup were conducted according to the general procedure.

Ethyl 3-Oxo-1,1-diphenyltetrahydrocyclopenta[*c*]furan-3a-carboxylate (14a): Recrystallization from pentane gave **14a** [R_f (2:1) = 0.71] as colorless blocks; m.p. 88 °C (for yields, see Table 2). − IR (KBr): $\tilde{\nu}$ = 1764 cm^{-1} (s, CO_2), 1725 (s, CO_2), 762 (s, Ph), 702 (s). − UV: λ_{max} (lg ε) = 194 nm (4.67), 204 (4.43), 222 (3.94), 260 (2.12). − ^{1}H NMR (400 MHz): δ = 0.78 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.30 (m, 1 H, $CHCH_2$), 1.73 (m, 3 H, $CHCH_2CH_2$), 2.34 (m, 2 H, CH_2CCO_2), 3.47 (dq, *J* = 10.7, 7.2 Hz, 1 H, OCH_2), 3.76 (dq, *J* = 10.7, 7.2 Hz, 1 H, OCH_2), 4.03 (t, *J* = 8.4 Hz, 1 H, CH_2CH), 7.17−7.32 (m, 6 H, *Ph*), 7.40 (m, 2 H, *Ph*), 7.55 (m, 2 H, *Ph*). − ^{13}C NMR (100 MHz): δ = 13.3 (q, OCH_2CH_3), 26.2 (t), 31.1 (t), 36.5 (t), 55.9 (d, $CHCH_2$), 61.8 (t, OCH_2), 63.2 (s, CCO_2), 89.7 (s, CPh_2), 124.7 (d, *Ph*), 125.5 (d, *Ph*), 127.3 (d, *Ph*), 127.7 (d, *Ph*), 128.3 (d, *Ph*), 128.4 (d, *Ph*), 141.4 (s, *Ph*), 143.4 (s, *Ph*), 170.9 (s, CO_2CH_2), 175.2 (s, CO_2CPh_2). − MS; *m*/*z* (%) = 350 (46) [M^+], 183 (100) [Ph_2COH^+], 140 (42) [M^+ − Ph_2CO − CO], 105 (41). − $C_{22}H_{22}O_4$ (350.4): calcd. C 75.41, H 6.33; found C 75.09, H 6.38.

Diethyl 2-(5,5-Diphenylpent-4-enyl)-2-ethylmalonate (15): Flash chromatography (50:1) gave 42 mg (12%) or 21 mg (6%) of **15** [R_f (5:1) = 0.56] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (m), 1731 (s, CO_2), 1445 (m), 1028 (m), 702 (m). − UV: λ_{max} (lg ε) = 194 nm (4.64), 212 (4.23), 218 (4.08), 226 (3.95), 252 (3.85), 264 (3.69), 274 (3.34), 282 (3.04). − ^{1}H NMR (200 MHz): δ = 0.72 (t, *J* = 7.5 Hz, 3 H, CCH_2CH_3), 1.13 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.22 (m, 2 H, $=CHCH_2CH_2$), 1.78 (m, 2 H, CCH_2CH_2), 1.84 (q, *J* = 7.5 Hz, 2 H, CCH_2CH_3), 2.04 (q, *J* = 7.4 Hz, 2 H, $=CHCH_2$), 4.08 (q, *J* = 7.1 Hz, 4 H, OCH_2), 5.97 (t, *J* = 7.4 Hz, 1 H, =CH), 7.06−7.33 (m, 10 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 8.4 (q, CCH_2CH_3), 14.1 (q, OCH_2CH_3), 24.4 (t, CH_2CH_3), 25.2 (t, CH_2CH_2C), 29.9 (t), 31.3 (t), 57.9 (s, CCH_2), 60.9 (t, OCH_2), 126.8 (d, *Ph*), 126.9 (d, *Ph*), 127.2 (d, *Ph*), 128.0 (d, *Ph*), 128.1 (d, *Ph*), 129.1 (d, =CH), 129.8 (d, *Ph*), 140.1 (s), 142.1 (s), 142.6 (s), 171.7 (s, CO_2). − MS; *m*/*z* (%) = 408 (58) [M^+], 362 (42) [M^+ − EtOH], 289 (30), 288 (80), 206 (100), 205 (23), 191 (24), 188 (24), 178 (20), 115 (27), 91 (27). − HRMS: $C_{26}H_{32}O_4$: calcd. 408.2301; found 408.2292 ± 2 ppm. − $C_{26}H_{32}O_4$ (408.2): calcd. C 76.44, H 7.90; found C 76.27, H 7.90.

Diethyl 2-(Diphenylmethylene)cyclopentane-1,1-dicarboxylate (16): Flash chromatography (50:1) gave 42 mg (11%) of **16** [R_f (5:1) = 0.47] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (m), 1732 (s, CO_2), 1264 (m), 1175 (m), 703 (m). − UV: λ_{max} (lg ε) = 196 nm (4.54), 202 (4.51), 206 (4.46), 220 (4.10), 238 (4.01), 258 (3.82), 272 (3.36). − ^{1}H NMR (200 MHz): δ = 1.09 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.60 (tt, *J* = 7.4, 7.0 Hz, 2 H, CCH_2CH_2), 2.41 (t, *J* = 7.4 Hz, 2 H, CCH_2), 2.43 (t, *J* = 6.9 Hz, 2 H, CCH_2), 3.69 (dq, *J* = 10.7, 7.1 Hz, 2 H, OCH_2), 3.88 (dq, *J* = 10.7, 7.1 Hz, 2 H, OCH_2), 7.09−7.36 (m, 10 H, *Ph*). − ^{13}C NMR (100 MHz): δ = 13.8 (q, OCH_2CH_3), 23.1 (t), 32.7 (t), 40.0 (t), 61.3 (t, OCH_2), 65.0 (s, CCO_2), 126.4 (d, *Ph*), 126.6 (d, *Ph*), 127.5 (d, *Ph*), 128.1 (d, *Ph*), 128.3 (d, *Ph*), 129.2 (d, *Ph*), 138.96 (s), 139.02 (s), 141.0 (s), 144.1 (s), 169.4 (s, CO_2), 171.0 (s, CO_2). − MS; *m*/*z* (%) = 378 (32) [M^+], 260 (33) [M^+ − OEt − CO_2Et], 259 (42) [M^+ − EtOH − CO_2Et],

232 (33) [$M^+ - 2\ CO_2Et$], 231 (100) [$M^+ - EtOH - CO - CO_2Et$], 216 (33), 215 (40), 203 (31), 202 (42), 184 (20), 165 (26). − HRMS: $C_{24}H_{26}O_4$: calcd. 378.1831; found 378.1823 ± 2 ppm.

Diethyl 2-(Diphenylhydroxymethyl)cyclopentane-1,1-dicarboxylate (17): Flash chromatography (50:1) gave 16 mg (4%) of **17** as a colorless oil [R_f (5:1) = 0.52]. − IR (film): $\tilde{\nu}$ = 3459 cm^{-1} (w, OH), 2978 (m), 1730 (s, CO_2), 1242 (s), 1177 (m), 1086 (m), 702 (m). − UV: λ_{max} (lg ε) = 198 nm (4.58), 218 (4.14), 224 (4.06), 230 (3.95), 252 (3.87), 276 (3.23). − ^{1}H NMR (200 MHz): δ = 0.89 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.18 (m, 1 H), 1.24 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.44 (m, 1 H), 1.82 (m, 2 H), 2.24 (dt, *J* = 12.7, 5.7 Hz, 1 H), 2.45 (dd, *J* = 12.2, 5.2 Hz, 1 H), 2.69 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 3.54 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.15 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.47 (t, *J* = 8.0 Hz, 1 H, $CHCH_2$), 4.72 (s, 1 H, OH), 7.00−7.72 (m, 10 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 13.3 (q, OCH_2CH_3), 14.0 (q, OCH_2CH_3), 24.4 (t), 27.8 (t), 39.0 (t), 51.8 (d, CH_2CH), 61.7 (t, OCH_2), 62.0 (t, OCH_2), 64.3 (s, CCH_2), 79.4 (s, COH), 125.2 (d, *Ph*), 125.8 (d, *Ph*), 126.0 (d, *Ph*), 126.4 (d, *Ph*), 127.85 (d, *Ph*), 127.93 (d, *Ph*), 147.0 (s, *Ph*), 147.1 (s, *Ph*), 172.3 (s, CO_2), 174.9 (s, CO_2). − MS; *m*/*z* (%) = 396 (1) [M^+], 379 (8) [$M^+ - OH$], 260 (10) [$M^+ - OH - OEt - CO_2Et$], 232 (9) [$M^+ - OH - CO_2Et - EtOH - CO$], 214 (21), 183 (52) [$Ph_2COH$], 182 (51), 168 (22), 105 (100), 77 (46) [Ph].

Ethyl 1,1-Dimethyl-3-oxo-tetrahydrocyclopenta[*c*]furan-3a-carboxylate (14b): Flash chromatography (30:1) gave **14b** [R_f (2:1) = 0.61] as a colorless oil (for yields, see Table 3). − IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (m), 1769 (s, CO_2), 1735 (s, CO_2), 1272 (s), 1257 (s), 1180 (s), 1162 (s), 1105 (s). − ^{1}H NMR (400 MHz): δ = 1.27 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.36 (s, 3 H, CCH_3), 1.45 (s, 3 H, CCH_3), 1.54 (m, 1 H, $CHCH_2CH_2$), 1.80 (m, 3 H, $CHCH_2CH_2$), 2.25 (m, 2 H, CH_2CCO_2), 2.83 (t, *J* = 5.4 Hz, 1 H, CH), 4.20 (q, *J* = 7.0 Hz, 2 H, OCH_2). − ^{13}C NMR (100 MHz): δ = 13.9 (q, OCH_2CH_3), 24.2 (q, CCH_3), 26.7 (t), 30.0 (t), 30.3 (q, CCH_3), 36.6 (t), 54.5 (d, CH), 62.0 (t, OCH_2), 64.0 (s, CCO_2), 84.8 (s, $C(CH_3)_2$], 171.2 (s, CO_2), 175.4 (s, CO_2). − MS; *m*/*z* (%) = 211 (48) [$M^+ - CH_3$], 182 (74), 140 (48), 137 (68), 135 (40), 109 (100), 95 (43), 67 (59). − $C_{12}H_{18}O_4$ (226.1): calcd. C 63.70, H 8.02; found C 63.84, H 8.00.

Diethyl 2-Isopropenylcyclopentane-1,1-dicarboxylate (18b): Flash chromatography (50:1) gave **18b/19b** [R_f (10:1) = 0.61] as an inseparable mixture (for yields, see Table 3). − IR (film): $\tilde{\nu}$ = 2980 cm^{-1} (m), 1729 (s, CO_2), 1448 (w), 1261 (s), 1211 (m), 1176 (m), 1158 (m), 1031 (w). − ^{1}H NMR (400 MHz): δ = 1.16 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.21 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.52 (m, 1 H, $CHCH_2CH_2$), 1.72 (s, 3 H, $=CCH_3$), 1.74 (m, 1 H, $CHCH_2$), 1.84 (m, 2 H, $CHCH_2CH_2$), 1.98 (ddd, *J* = 14.1, 8.4, 3.1 Hz, 1 H, CH_2CH_2C), 2.58 (ddd, *J* = 13.8, 9.6, 8.1 Hz, 1 H, CH_2CH_2C), 3.30 (dd, *J* = 9.5, 7.9 Hz, 1 H, CH), 4.06 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.12 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.73 (d, *J* = 1.0 Hz, 1 H, $=CH_2$), 4.74 (d, *J* = 1.4 Hz, 1 H, $=CH_2$). − ^{13}C NMR (100 MHz): δ = 13.9 (q, OCH_2CH_3), 14.0 (q, OCH_2CH_3), 23.2 (q, CCH_3), 23.4 (t), 30.8 (t), 35.2 (t), 51.7 (d, CH), 60.9 (t, OCH_2), 61.1 (t, OCH_2), 64.0 (s, CCH_2), 112.2 (t, $=CH_2$), 145.2 (s, =C), 170.9 (s, CO_2), 172.8 (s, CO_2). − MS; *m*/*z* (%) = 254 (22) [M^+], 180 (100) [$M^+ - CO - EtOH$], 163 (26), 135 (55) [$M^+ - CO_2Et - EtOH$], 107 (32) [$M^+ - 2\ CO_2Et$]. − HRMS: $C_{14}H_{22}O_4$: calcd. 254.1518; found 254.1518 ± 2 ppm.

Diethyl 2-Isopropylcyclopentane-1,1-dicarboxylate (19b): − ^{1}H NMR (400 MHz): δ = 0.81 (d, *J* = 6.6 Hz, 3 H, $CHCH_3$), 0.89 (d, *J* = 6.6 Hz, 3 H, $CHCH_3$), 1.16 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.21 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.42 (m, 1 H), 1.71 (m, 1 H, $CHCH_3$), 1.74 (m, 1 H), 1.84 (m, 2 H), 1.98 (m, 1 H), 2.58 (m, 1 H), 3.30 (m, 1 H), 4.08 (q, *J* = 7.1 Hz, 1 H, OCH_2), 4.19 (q, *J* = 7.1 Hz, 1 H, OCH_2). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH_2CH_3), 14.0 (q, OCH_2CH_3), 20.9 (q, $CHCH_3$), 22.8 (t), 22.9 (q, $CHCH_3$), 28.7 (t), 29.5 (d, $CHCH_3$), 36.6 (t), 53.4 (d, $CHCH_2$), 60.9 (t, OCH_2), 61.1 (t, OCH_2), 64.0 (s, CCO_2), 170.9 (s, CO_2), 172.8 (s, CO_2). − HRMS: $C_{14}H_{24}O_4$: calcd. 256.1675; found 256.1674 ± 2 ppm.

Diethyl 2-(2-Ferrocenylprop-2-yl)cyclopentane-1,1-dicarboxylate (20b): Flash chromatography (50:1) and recrystallization from pentane gave **20b** [R_f (10:1) = 0.38] as a yellow solid; m.p. 67−70 °C (for yields, see Table 3). − IR (KBr): $\tilde{\nu}$ = 2979 cm^{-1} (m), 1743 (m, CO_2), 1716 (s, CO_2), 1257 (s), 1182 (m). − UV: λ_{max} (lg ε) = 204 nm (4.63), 232 (3.75), 246 (3.60), 266 (3.37), 284 (2.94), 294 (2.44), 440 (2.12), 458 (2.13). − ^{1}H NMR (200 MHz): δ = 1.13 (s, 3 H, CCH_3), 1.20 (t, *J* = 6.8 Hz, 3 H, OCH_2CH_3), 1.24 (t, *J* = 6.8 Hz, 3 H, OCH_2CH_3), 1.40 (s, 3 H, CCH_3), 1.31−1.88 (m, 5 H), 2.35 (m, 1 H), 2.66 (dd, *J* = 10.0, 7.1 Hz, 1 H, $CHCH_2$), 3.95−4.26 (m, 8 H, OCH_2, *Cp*C), 4.12 (s, 5 H, *Cp*). − ^{13}C NMR (50 MHz): δ = 13.8 (q, OCH_2CH_3), 14.0 (q, OCH_2CH_3), 21.8 (q, CCH_3), 22.6 (t), 27.7 (q, CCH_3), 27.8 (t), 35.6 (s, CCH_3), 38.5 (t), 57.8 (d, $CHCH_2$), 60.8 (t, OCH_2), 60.9 (t, OCH_2), 61.5 (s, CCH_2), 66.4 (d, *Cp*), 66.6 (d, *Cp*), 67.2 (d, *Cp*), 67.5 (d, *Cp*), 68.7 (d, *Cp*), 102.9 (s, (*ipso*-Cp)*C*), 172.0 (s, CO_2), 173.1 (s, CO_2). − MS; *m*/*z* (%) = 440 (100) [M^+], 227 (56) [$M^+ - 2\ CO_2Et - Cp$). − HRMS: $C_{24}H_{32}FeO_4$: calcd. 440.1650; found 440.1650 ± 3 ppm.

Diethyl 2-(2-Chloroprop-2-yl)cyclopentane-1,1-dicarboxylate (21b): Flash chromatography (40:1) gave 35 mg (12%) or 195 mg (67%) of **21b** [R_f (10:1) = 0.45] as a colorless solid; m.p. 32−33 °C. − IR (KBr): $\tilde{\nu}$ = 2984 cm^{-1} (m), 1728 (s, CO_2), 1263 (s), 1181 (m). − ^{1}H NMR (200 MHz): δ = 1.21 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.24 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.57−1.90 (m, 3 H), 1.61 (s, 3 H, CCH_3), 1.70 (s, 3 H, CCH_3), 2.02 (m, 2 H, CH_2CH), 2.55 (m, 1 H), 2.96 (dd, *J* = 10.0, 8.4 Hz, 1 H, $CHCH_2$), 4.05 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.10 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.18 (dq, *J* = 10.8, 7.2 Hz, 2 H, OCH_2). − ^{13}C NMR (50 MHz): δ = 13.6 (q, OCH_2CH_3), 14.0 (q, OCH_2CH_3), 22.0 (t), 28.1 (t), 31.2 (q, CH_3), 35.0 (q, CH_3), 38.3 (t), 57.3 (d, CH), 61.2 (t, OCH_2), 61.3 (t, OCH_2), 72.2 (s, *C*Cl), 170.8 (s, CO_2), 172.8 (s, CO_2). − MS; *m*/*z* (%) = 292/290 (0.2/0.4) [M^+], 254 (20) [$M^+ - HCl$], 213 (34), 181 (57) [$M^+ - HCl - CO_2Et$], 180 (100) [$M^+ - HCl - EtOH - CO$], 163 (23) [$M^+ - HCl - OEt - EtOH$], 135 (65), 134 (45), 107 (36). − $C_{14}H_{23}ClO_4$ (290.8): calcd. C 57.83, H 7.97, Cl 12.19; found C 57.72, H 8.11, Cl 12.15.

Oxidative Cyclization of Malonate 12c with 1: Compound **12c** (258 mg, 1.00 mmol) was added at −78 °C under N_2 to a mixture of anhydrous LiBr (670 mg, 7.70 mmol) and LDA (1.10 mmol; prepared from 155 μL of iPr_2NH and 690 μL of BuLi [1.6 M in hexane]) in 20 mL of dry DME. The mixture was stirred between −78 and −60 °C for 30 min. Solid **1** (1.39 g, 4.20 mmol) was added in four portions at 0 °C. After 5 min, the resulting blue-green color of the reaction mixture changed to brown. The mixture was stirred at 0 °C for 12 min. The mixture was quenched with six drops of a 2 N HCl solution and stirred for 7 min while warming to room temperature. The reaction mixture was diluted with 20 mL of ether and filtered through a pad of silica gel. The solvent was evaporated and the inhomogeneous residue was preadsorbed on silica gel. Flash chromatography (50:1 gradient to 1:1) gave 189 mg (78%) of **22**.

Diethyl 2-Formylcyclopentane-1,1-dicarboxylate (22): Flash chromatography (40:1) gave **22** [R_f (5:1) = 0.35] as a colorless oil (for

yields, see Table 4). − IR (film): $\tilde{\nu}$ = 2983 cm^{-1} (m), 2901 (w, CHO), 2880 (w, CHO), 1735 (s, CHO), 1714 (s, CO_2), 1263 (s), 1213 (m). − ^1H NMR (200 MHz): δ = 1.11 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.15 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.63 (m, 2 H), 1.88 (m, 2 H), 2.17 (m, 2 H), 3.13 (dt, *J* = 8.3, 0.9 Hz, 1 H, CHCHO), 4.06 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.122 (q, *J* = 7.1 Hz, 1 H, OCH_2), 4.125 (q, *J* = 7.1 Hz, 1 H, OCH_2), 9.65 (d, *J* = 0.9 Hz, 1 H, CHO). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH_2CH_3), 14.0 (q, OCH_2CH_3), 22.6 (t), 25.1 (t), 34.6 (t), 57.5 (d, $CHCH_2$), 61.8 (t, OCH_2), 61.9 (t, OCH_2), 62.5 (s, CCO_2), 170.0 (s, CO_2), 171.0 (s, CO_2), 200.0 (d, CHO). − MS; *m*/*z* (%) = 240 (10), 213 (20) [M^+ − CHO], 197 (12) [M^+ − OEt], 169 (35) [M^+ − CO_2Et], 168 (48) [M^+ − EtOH − CO], 141 (40), 140 (100) [M^+ − CO_2Et − CHO], 139 (22) [M^+ − CO − EtOH − CHO], 123 (20) [M^+ − EtOH − CO_2Et], 113 (43), 112 (48), 111 (29), 95 (72) [M^+ − CO_2Et − EtOH − CO], 67 (78).

Diethyl 2-(Dimethoxymethyl)cyclopentane-1,1-dicarboxylate (23): Flash chromatography (10:1) gave 29 mg (10%) or 69 mg (24%) of **23** [R_f (5:1) = 0.35] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2941 cm^{-1} (m), 1731 (s, CO_2), 1729 (s, CO_2), 1447 (m), 1261 (s), 1094 (s), 1073 (s), 1061 (s). − ^1H NMR (200 MHz): δ = 1.19 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.20 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.45 (m, 1 H), 1.73 (m, 3 H), 2.04 (m, 1 H), 2.34 (m, 1 H), 2.98 (m, 1 H, CH_2CH), 3.23 (s, 3 H, OCH_3), 3.25 (s, 3 H, OCH_3), 4.00 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.08 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.19 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 4.35 (d, *J* = 6.7 Hz, 1 H, $CHOCH_3$). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH_2CH_3), 22.9 (t), 25.8 (t), 34.6 (t), 47.7 (d, CH_2CH), 52.9 (q, OCH_3), 54.5 (q, OCH_3), 61.0 (t, OCH_2), 61.2 (t, OCH_2), 62.0 (s, CCO_2), 104.5 (d, $CHOCH_3$), 170.9 (s, CO_2), 172.4 (s, CO_2). − MS; *m*/*z* (%) = 288 (3) [M^+], 257 (20) [M^+ − OMe], 243 (10) [M^+ − OEt], 183 (34) [M^+ − CO − EtOH − OMe], 123 (27) [M^+ − EtOH − CO − 2 OMe − Et], 75 (100). − $C_{14}H_{24}O_6$ (288.2): calcd. C 58.32, H 8.39; found C 58.35, H 8.66.

Diethyl 2-(Butoxymethoxymethyl)cyclopentane-1,1-dicarboxylate (24): Flash chromatography (35:1) gave 13 mg (4%) or 73 mg (22%) of a 1:1 diastereomeric mixture of **24/24′** [R_f (5:1) = 0.43] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2961 cm^{-1} (m), 1732 (s, CO_2), 1261 (m), 1097 (m), 1073 (m), 1046 (m). − **24**: ^1H NMR (400 MHz): δ = 0.84 (t, *J* = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.18 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.19 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.29 (m, 2 H, $CH_2CH_2CH_3$), 1.44 (m, 4 H, CCH_2CH_2, $CH_2CH_2CH_3$), 1.61−1.83 (m, 2 H, $CHCH_2$), 1.95 (m, 1 H, CCH_2CH_2), 2.32 (m, 1 H, CCH_2CH_2), 2.91 (dt, *J* = 8.1, 5.6 Hz, 1 H, CH_2CH), 3.22 (s, 3 H, OCH_3), 3.32 (m, 1 H, OCH_2CH_2), 3.55 (m, 1 H, OCH_2CH_2), 4.00 (m, 2 H, OCH_2CH_3), 4.15 (m, 2 H, OCH_2CH_3), 4.46 (d, *J* = 5.5 Hz, 1 H, $CHOCH_3$). − ^{13}C NMR (100 MHz): δ = 13.8 (q, $CH_2CH_2CH_3$), 13.9 (q, OCH_2CH_3), 19.2 (t, $CH_2CH_2CH_3$), 22.8 (t, $CHCH_2CH_2$), 25.1 (t, $CHCH_2$), 31.8 (t, OCH_2CH_2), 35.3 (t, CCH_2), 48.4 (d, CH_2CH), 54.0 (q, OCH_3), 60.8 (t, OCH_2CH_3), 61.2 (t, OCH_2CH_3), 61.8 (s, CH_2C), 65.3 (t, OCH_2CH_2), 103.6 (d, CHCHO), 170.7 (s, CO_2), 172.4 (s, CO_2). − **24′**: ^1H NMR (400 MHz): δ = 0.84 (t, *J* = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.18 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.20 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.29 (m, 2 H, $CH_2CH_2CH_3$), 1.44 (m, 3 H, CCH_2CH_2, $CH_2CH_2CH_3$), 1.61−1.83 (m, 3 H, $CHCH_2CH_2$), 2.06 (m, 1 H, CCH_2CH_2), 2.32 (m, 1 H, CCH_2CH_2), 3.01 (q, *J* = 7.3 Hz, 1 H, CH_2CH), 3.22 (s, 3 H, OCH_3), 3.41 (m, 1 H, OCH_2CH_2), 3.48 (m, 1 H, OCH_2CH_2), 4.15 (m, 4 H, OCH_2CH_3), 4.39 (d, *J* = 7.2 Hz, 1 H, $CHOCH_3$). − ^{13}C NMR (100 MHz): δ = 13.8 (q, $CH_2CH_2CH_3$), 13.9 (q, OCH_2CH_3), 19.3 (t, $CH_2CH_2CH_3$), 22.7 (t, $CHCH_2CH_2$), 26.2 (t, $CHCH_2$), 31.8 (t, OCH_2CH_2), 35.2 (t, CCH_2), 47.8 (d, CH_2CH), 53.4 (q, OCH_3), 61.1 (t, OCH_2CH_3), 61.2 (t, OCH_2CH_3), 62.2 (s, CH_2C), 67.5 (t, OCH_2CH_2), 103.6 (d, $CHCHO$), 170.8 (s, CO_2), 172.3 (s, CO_2). − MS; *m*/*z* (%) = 299 (20) [M^+ − OMe], 257 (51) [M^+ − OBu], 197 (38) [M^+ − OMe − OBu − Et], 183 (46), 169 (22), 123 (50), 117 (82), 61 (100). − MS (NH_3, CI, pos.): *m*/*z* (%) = 348 (6) [M^+ + NH_4], 299 (100) [M^+ − OMe], 276 (18), 257 (66) [M^+ − OBu].

Diethyl 2-[2,2-Bis(ethoxycarbonyl)-1,7-dimethoxyhept-6-enyl]cyclopentane-1,1-dicarboxylate (25): Flash chromatography (35:1) gave 90 mg (35%) of a 21:5:4:1 diastereomeric mixture of *syn*/*anti*-(*E*)/(*Z*)-**25/25′** [R_f (5:1) = 0.24] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2940 cm^{-1} (w), 1731 (s, CO_2), 1255 (m), 1213 (w). − **25:** ^1H NMR (400 MHz): δ = 1.12 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.14 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.17−1.39 (m, 4 H), 1.42−1.95 (m, 7 H), 2.25 (m, 1 H), 2.72 (dt, *J* = 8.2, 2.9 Hz, 1 H, $CCHCHCH_2$), 3.11 (s, 3 H, $CHOCH_3$), 3.34 (s, 3 H, $=CHOCH_3$), 3.92−4.15 (m, 8 H, OCH_2), 4.18 (m, 1 H, $CCHOCH_3$), 4.55 (m, 1 H, (*Z*)-$=CHCH_2$), 4.62 (dt, *J* = 12.7, 7.3 Hz, 1 H, (*E*)-$=CHCH_2$), 5.72 (d, *J* = 6.2 Hz, 1 H, (*Z*)-$=CHOCH_3$), 6.14 (d, *J* = 12.6 Hz, 1 H, (*E*)-$=CHOCH_3$). − ^{13}C NMR (100 MHz): δ = 13.90 (q, OCH_2CH_3), 13.92 (q, OCH_2CH_3), 13.96 (q, OCH_2CH_3), 13.98 (q, OCH_2CH_3), 23.2 (t), 24.0 (t), 25.8 (t), 28.0 (t), 33.0 (t), 34.7 (t), 47.0 (d, $CCHCHCH_2$), 55.8 (q, OCH_3), 59.2 (q, OCH_3), 60.8 (t, OCH_2), 60.9 (t, OCH_2), 61.1 (t, OCH_2), 61.8 (s, CCH_2), 63.6 (s, CCH_2), 80.9 (d, $CCHOCH_3$), 102.2 (d, (*E*)-$=CHCH_2$), 106.0 (d, (*Z*)-$=CHCH_2$), 147.2 (d, (*Z*)-$=CHOCH_3$), 147.3 (d, (*E*)-$=CHOCH_3$), 170.2 (s, CO_2), 171.15 (s, CO_2), 171.17 (s, CO_2), 172.4 (s, CO_2). − **25′:** ^1H NMR (400 MHz): δ = 1.12 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.14 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.17−1.39 (m, 4 H), 1.42−1.95 (m, 7 H), 2.25 (m, 1 H), 2.72 (m, 1 H, $CCHCHCH_2$), 3.15 (s, 3 H, $CHOCH_3$), 3.41 (s, 3 H, $=CHOCH_3$), 3.92−4.15 (m, 8 H, OCH_2), 4.18 (m, 1 H, $CCHOCH_3$), 4.62 (dt, *J* = 12.7, 7.3 Hz, 1 H, (*E*)-$=CHCH_2$), 4.62 (m, 1 H, (*Z*)-$=CHCH_2$), 5.72 (d, *J* = 6.2 Hz, 1 H, (*Z*)-$=CHOCH_3$), 6.14 (d, *J* = 12.6 Hz, 1 H, (*E*)-$=CHOCH_3$). − ^{13}C NMR (50 MHz): δ = 13.93 (q, OCH_2CH_3), 13.96 (q, OCH_2CH_3), 13.98 (q, OCH_2CH_3), 14.1 (q, OCH_2CH_3), 22.1 (t), 24.0 (t), 26.4 (t), 28.3 (t), 32.7 (t), 35.8 (t), 52.3 (d, $CCHCHCH_2$), 56.7 (q, OCH_3), 59.3 (q, OCH_3), 60.8 (t, OCH_2), 60.9 (t, OCH_2), 61.1 (t, OCH_2), 61.8 (s, CCH_2), 62.9 (s, CCH_2), 85.4 (d, $CCHOCH_3$), 102.4 (d, (*E*)-$=CHCH_2$), 106.0 (d, (*Z*)-$=CHCH_2$), 147.2 (d, (*Z*)-$=CHOCH_3$), 147.3 (d, (*E*)-$=CHOCH_3$), 170.0 (s, CO_2), 171.16 (s, CO_2), 172.0 (s, CO_2). − MS (NH_3, CI, pos.): *m*/*z* (%) = 532 (13) [M^+ + NH_4], 434 (65), 402 (28), 297 (29), 295 (28), 276 (28), 257 (100) [M^+/2]. − $C_{26}H_{42}O_{10}$ (514.6): calcd. C 60.68, H 8.23; found C 60.76, H 8.15.

Ethyl 3-Oxo-1-phenyltetrahydrocyclopenta[*c*]furan-3a-carboxylate (14d): Flash chromatography (35:1) gave a diastereomeric mixture of **14d/14d′** [R_f (5:1) = 0.49] as a colorless oil (for yields, see Table 5). − IR (film): $\tilde{\nu}$ = 2969 cm^{-1} (m), 1779 (s, CO_2), 1741 (s, CO_2), 1453 (w), 1251 (s), 1147 (m), 729 (w), 701 (w). − **14d:** UV: λ_{max} (lg ε) = 192 nm (4.47), 198 (4.24), 206 (4.02), 210 (3.92), 222 (3.54). − ^1H NMR (200 MHz): δ = 1.15 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.55−1.77 (m, 2 H), 1.80−2.04 (m, 2 H), 2.16−2.46 (m, 2 H), 3.08 (m, 1 H, CH_2CH), 4.12 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.00 (d, *J* = 4.6 Hz, 1 H, CHPh), 7.34 (m, 5 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 13.8 (q, OCH_2CH_3), 25.5 (t), 33.8 (t), 35.0 (t), 54.4 (d, CH_2CH), 62.1 (t, OCH_2), 62.3 (s, CCH_2), 85.1 (d, OCHPh), 125.4 (d, *Ph*), 128.4 (d, *Ph*), 128.7 (d, *Ph*), 139.9 (s, *Ph*), 170.6 (s, CO_2), 176.2 (s, CO_2). − **14d′:** ^1H NMR (200 MHz): δ = 1.20 (m, 1 H), 1.28 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.35−1.71 (m, 3 H), 2.35 (m, 3 H), 3.26 (m, 1 H, CH_2CH), 4.24 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.80 (d, *J* = 6.5 Hz, 1 H, CHPh), 7.34 (m, 5 H, *Ph*). −

^{13}C NMR (50 MHz): δ = 14.1 (q, OCH_2CH_3), 25.9 (t), 28.5 (t), 34.5 (t), 51.4 (d, CH_2CH), 62.2 (t, OCH_2), 63.8 (s, CCH_2), 81.4 (d, *C*HPh), 124.9 (d, *Ph*), 127.9 (d, *Ph*), 128.5 (d, *Ph*), 136.5 (s, *Ph*), 169.7 (s, CO_2), 175.9 (s, CO_2). − MS; *m*/*z* (%) = 274 (46) [M^+], 246 (30), 207 (23), 200 (27) [M^+ − OEt − Et], 184 (21) [M^+ − 2 OEt], 167 (28), 165 (26), 161 (22), 141 (67), 140 (100), 129 (22), 115 (38), 112 (42), 111 (30), 105 (38), 77 (36), 67 (46), 57 (30), 55 (29), 43 (69), 41 (58). − $C_{16}H_{18}O_4$ (274.3): calcd. C 70.06, H 6.61; found C 69.92, H 6.54.

α,α′-Bis[2,2-bis(ethoxycarbonyl)cyclopentyl]bibenzyl (26d): Flash chromatography (30:1) and crystallization from pentane gave **26d** [R_f (5:1) = 0.43] as a 1:1 mixture of *meso* and *d*/*l* dimers as colorless crystals; m.p. 82 °C (for yields, see Table 5). − IR (KBr): $\tilde{\nu}$ = 2988 cm^{-1} (m), 1740 (m, CO_2), 1720 (s, CO_2), 1455 (m), 1255 (s), 1103 (m), 703 (m). − UV: λ_{max} (lg ε) = 192 nm (4.75), 208 (4.36), 216 (4.19), 230 (3.39), 232 (3.19), 262 (2.77). − ^{1}H NMR (400 MHz): δ = 0.88 (t, *J* = 6.8 Hz, 6 H, OCH_2CH_3), 0.89 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 0.90 (t, *J* = 6.9 Hz, 6 H, OCH_2CH_3), 0.93 (t, *J* = 7.1 Hz, 6 H, OCH_2CH_3), 1.52 (m, 2 H, $CH_2CH_2CH_2$), 1.63 (m, 2 H, $CH_2CH_2CH_2$*), 1.75 (m, 6 H, $CH_2CH_2CH_2$, $CH_2CH_2CH_2$*, CH_2CH), 1.93 (dt, *J* = 10.5, 9.1 Hz, 2 H, CH_2CH*), 2.16 (m, 2 H, CCH_2*), 2.28 (m, 6 H, CCH_2*, CCH_2), 2.56 (m, 4 H, CH_2CH*, CH_2CH), 3.03 (m, 2 H, $CHCH_2$), 3.16 (m, 2 H, $CHCH_2$*), 3.26 (dq, *J* = 10.7, 7.1 Hz, 2 H, OCH_2), 3.40 (dq, *J* = 10.7, 7.1 Hz, 2 H, OCH_2), 3.47 (dq, *J* = 10.7, 7.0 Hz, 2 H, OCH_2), 3.51 (dq, *J* = 10.9, 7.1 Hz, 2 H, OCH_2), 3.54 (d, *J* = 11.5 Hz, 2 H, C*H*Ph*), 3.60 (d, *J* = 11.4 Hz, 2 H, C*H*Ph), 3.68 (dq, *J* = 10.8, 7.2 Hz, 2 H, OCH_2), 3.74 (dq, *J* = 10.8, 7.2 Hz, 2 H, OCH_2), 3.75 (dq, *J* = 10.8, 7.1 Hz, 2 H, OCH_2), 3.81 (dq, *J* = 10.8, 7.1 Hz, 2 H, OCH_2), 6.55−7.35 (m, 20 H, *Ph*#, *Ph**#). − ^{13}C NMR (50 MHz): δ = 13.5 (q, OCH_2CH_3), 13.6 (q, OCH_2CH_3), 22.8 (t, $CHCH_2CH_2$*), 23.1 (t, $CHCH_2CH_2$), 31.6 (t, $CHCH_2$*), 33.1 (t, $CHCH_2$), 38.1 (t, CH_2C*), 38.8 (t, CH_2C), 47.3 (d, $CHCH_2$), 48.9 (d, $CHCH_2$*), 49.4 (d, *C*HPh), 52.4 (d, *C*HPh*), 60.4 (t, OCH_2), 60.9 (t, OCH_2), 63.0 (s, CCH_2), 63.6 (s, CCH_2*), 126.0 (d, *Ph*#), 126.1 (d, *Ph*#), 126.7 (d, *Ph*#), 131.2 (d, *Ph*#), 138.2 (s, *Ph*), 140.5 (s, *Ph**), 171.1 (s, CO_2), 171.3 (s, CO_2), 172.47 (s, CO_2), 172.53 (s, CO_2). − MS; *m*/*z* (%) = 303 (100) [M^+/2], 229 (43), 155 (20). − MS (NH_3, CI, pos.): *m*/*z* (%) = 624 (3) [$M^+ + NH_4$], 607 (100) [M^+ + H], 535 (7), 322 (22), 305 (34), 303 (42) [M^+/2], 298 (40), 229 (8), 158 (8), 74 (6). − $C_{36}H_{46}O_8$ (606.8): calcd. C 71.26, H 7.64; found C 71.08, H 7.69. − Resonances marked with an asterisk * can be assigned to one diastereomer on the basis of C,H correlation and HMBC spectra; #: broadened signals.

Diethyl 2-(Chlorophenylmethyl)cyclopentane-1,1-dicarboxylate (21d): Flash chromatography (50:1) gave 71 mg (21%) of **21d** [R_f (5:1) = 0.50] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (m), 1779 (m), 1727 (s, CO_2), 1263 (s), 1209 (m), 1179 (m), 1151 (m), 1096 (m), 700 (m). − UV: λ_{max} (lg ε) = 194 nm (4.59), 210 (3.98), 216 (3.90), 220 (3.85), 230 (3.51), 236 (3.26), 248 (2.90), 268 (2.77), 282 (2.62). − ^{1}H NMR (400 MHz): δ = 1.13 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.22 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.53 (m, 1 H), 1.82 (m, 1 H), 1.97 (m, 3 H), 2.50 (m, 1 H), 3.14 (dt, *J* = 9.1, 5.0 Hz, 1 H, C*H*CHPh), 3.95 (m, 2 H, OCH_2), 4.06 (m, 1 H, OCH_2), 4.19 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH_2), 5.56 (d, *J* = 4.9 Hz, 1 H, C*H*Ph), 7.20−7.43 (m, 5 H, *Ph*). − ^{13}C NMR (100 MHz): δ = 13.8 (q, 2 OCH_2CH_3), 22.1 (t), 26.8 (t), 35.8 (t), 53.8 (d, *C*HCHPh), 61.4 (t, OCH_2), 61.6 (t, OCH_2), 62.3 (s, CH_2C), 64.3 (d, *C*HPh), 127.5 (d, *Ph*), 127.8 (d, *Ph*), 128.1 (d, *Ph*), 141.5 (s, *Ph*), 170.4 (s, CO_2), 172.1 (s, CO_2). − MS; *m*/*z* (%) = 340/338 (25/74) [M^+], 303 (19) [M^+ − Cl], 294/292 (29/82) [M^+ − EtOH], 257 (11) [M^+ − Cl − OEt], 229 (35) [M^+ − Cl − CO_2Et], 220/218 (36/100) [M^+ − 2 EtOH − CO], 183 (70) [M^+ − Cl − 2 EtOH − CO], 173 (45), 155 [M^+ − Cl − 2 EtOH − 2 CO], 129 (49), 128 (25), 127 (42), 125 (45), 115 (25), 91 (35). − HRMS: $C_{18}H_{23}ClO_4$: calcd. 338.1285; found 338.1280 ± 2 ppm.

Diethyl 2-Vinylcyclopentane-1,1-dicarboxylate (18f): Flash chromatography (50:1) gave 101 mg (42%) of **18f/19f** [R_f (10:1) = 0.42] as an inseparable mixture. − IR (film): $\tilde{\nu}$ = 2982 cm^{-1} (m), 1729 (s, CO_2), 1263 (m), 1223 (w), 1183 (m), 1098 (w). − ^{1}H NMR (200 MHz): δ = 1.22 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.25 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.65 (m, 2 H), 1.70−2.15 (m, 3 H), 2.46 (m, 1 H), 3.50 (m, 1 H, =CHC*H*), 4.08 (dq, *J* = 10.7, 7.1 Hz, 1 H, OCH_2), 4.16 (dq, *J* = 10.8, 7.1 Hz, 2 H, OCH_2), 4.24 (dq, *J* = 10.7, 7.1 Hz, 1 H, OCH_2), 4.98 (dd, *J* = 10.3, 1.9 Hz, 1 H, $=CH_2$), 5.13 (dd, *J* = 17.2, 1.9 Hz, 1 H, $=CH_2$), 5.81 (ddd, *J* = 17.2, 10.2, 7.9 Hz, 1 H, =CH). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH_2CH_3), 22.8 (t), 30.7 (t), 34.4 (t), 47.9 (d, =CH*C*H), 60.7 (t, OCH_2), 61.0 (t, OCH_2), 64.0 (s, CCO_2), 115.6 (t, $=CH_2$), 137.7 (d, =CH), 171.5 (s, CO_2), 172.6 (s, CO_2). − MS; *m*/*z* (%) = 240 (11) [M^+], 195 (10) [M^+ − OEt], 167 (20) [M^+ − CO_2Et], 166 (100) [M^+ − EtOH − CO], 138 (25), 149 (17) [M^+ − OEt − EtOH], 138 (22) [M^+ − CO_2Et − Et], 120 (18), 93 (28). − HRMS: $C_{13}H_{20}O_4$: calcd. 240.1362; found 240.1356 ± 3 ppm.

Diethyl 2-Ethylcyclopentane-1,1-dicarboxylate (19f): − ^{1}H NMR (200 MHz): δ = 0.89 (t, *J* = 6.9 Hz, 3 H, $CHCH_2CH_3$), 1.00 (m, 1 H), 1.21 (t, *J* = 7.0 Hz, 6 H, OCH_2CH_3), 1.58 (m, 2 H), 1.72−2.11 (m, 3 H), 2.39 (m, 2 H), 3.19 (quint, *J* = 7.8 Hz, 1 H, CH), 4.12 (m, 4 H, OCH_2). − ^{13}C NMR (50 MHz): δ = 13.0 (q, $CHCH_2CH_3$), 14.0 (q, OCH_2CH_3), 22.9 (t), 24.2 (t), 30.3 (t), 33.8 (t), 49.7 (d, CH), 60.8 (t, OCH_2), 63.4 (s, CCH_2), 170.6 (s, CO_2), 172.0 (s, CO_2). − MS; *m*/*z* (%) = 197 (25) [M^+ − OEt], 173 (100), 127 (43), 95 (71).

Diethyl 2-(1-Ferrocenylethyl)cyclopentane-1,1-dicarboxylate (20f): Flash chromatography (50:1) gave 77 mg (18%) of **20f** as a 1.8:1 diastereomeric mixture [R_f (10:1) = 0.39] as a yellow solid; m.p. 71−75 °C. − IR (KBr): $\tilde{\nu}$ = 2971 cm^{-1} (m), 1724 (s, CO_2), 1182 (m). − UV: λ_{max} (lg ε) = 204 nm (4.59), 232 (3.70), 242 (3.58), 256 (3.46), 268 (3.29), 412 (2.13), 440 (2.11). − ^{1}H NMR (400 MHz): δ = 1.07 (d, *J* = 7.0 Hz, 3 H, $CHCH_3$), 1.17 (t, *J* = 6.9 Hz, 3 H, OCH_2CH_3*), 1.18 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.29 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3*), 1.30 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.39 (d, *J* = 6.8 Hz, 3 H, $CHCH_3$*), 1.47 (m, 4 H), 1.67 (m, 3 H), 1.90 (m, 2 H), 2.31 (m, 5 H), 2.69 (ddd, *J* = 9.8, 7.4, 3.7 Hz, 1 H, C*H*CH_2), 2.98 (dq, *J* = 7.0, 3.4 Hz, 1 H, C*H*CH_3), 3.99−4.28 (m, 16 H, OCH_2, OCH_2*, *Cp*C, *Cp*C*), 4.06 (s, 5 H, *Cp**), 4.07 (s, 5 H, *Cp*). − ^{13}C NMR (100 MHz): δ = 13.9 (q, OCH_2CH_3*), 14.1 (q, OCH_2CH_3), 15.8 (q, $CHCH_3$), 20.4 (q, $CHCH_3$*), 22.1 (t*), 22.3 (t), 25.7 (t), 31.1 (t*), 32.4 (d, *C*HCH_3), 35.22 (t), 35.24 (d, *C*HCH_3*), 37.1 (t*), 53.1 (d, *C*HCH_2), 54.9 (d, *C*HCH_2*), 60.8 (t, OCH_2*), 60.99 (t, OCH_2), 61.05 (t, OCH_2), 62.8 (s, CCH_2*), 63.0 (s, CCH_2), 65.5 (d, *Cp**), 66.07 (d, *Cp*), 66.14 (d, *Cp**), 66.6 (d, *Cp*), 66.9 (d, *Cp*), 67.0 (d, *Cp**), 67.94 (d, *Cp*), 68.35 (d, *Cp**), 68.41 (d, *Cp*), 69.14 (d, *Cp**), 95.2 (s, (*ipso*-Cp)*C**), 96.1 (s, (*ipso*-Cp)*C*), 171.3 (s, CO_2*), 171.5 (s, CO_2), 172.5 (s, CO_2), 173.2 (s, CO_2*). − MS; *m*/*z* (%) = 426 (20) [M^+], 213 (44), 121 (20). − HRMS: $C_{23}H_{30}FeO_4$: calcd. 426.1494; found 426.1490 ± 3 ppm. − Resonances marked with an asterisk * correspond to the minor diastereomer.

2,3-Bis[2,2-bis(ethoxycarbonyl)cyclopentyl]butane (26f): Flash chromatography (40:1) gave 82 mg (34%) of **26f** [R_f (5:1) = 0.51] as a 6.7:6.5:4.7:3:1.7 diastereomeric mixture. − IR (film): $\tilde{\nu}$ = 2979 cm^{-1} (m), 1728 (s, CO_2), 1257 (s), 1218 (m), 1178 (m), 1163 (m),

1038 (m). − ^{1}H NMR (400 MHz): δ = 0.60 (d, *J* = 6.5 Hz, 3 H, CHC*H*$_3$*), 0.64 (d, *J* = 7.0 Hz, 3 H, CHC*H*$_3$#), 0.67 (d, *J* = 7.1 Hz, 3 H, CHC*H*$_3$#), 0.71 (d, *J* = 6.4 Hz, 6 H, CHC*H*$_3$+), 0.77 (d, *J* = 6.7 Hz, 3 H, CHC*H*$_3$*), 0.80 (d, *J* = 6.4 Hz, 3 H, CHC*H*$_3$$), 0.82 (d, *J* = 6.4 Hz, 3 H, CHC*H*$_3$$), 0.90 (d, *J* = 6.9 Hz, 6 H, CHC*H*$_3$§), 1.22 (m, 62 H, C*H*$_2$, OCH$_2$C*H*$_3$), 1.30−2.10 (m, 64 H), 2.37 (m, 9 H, CH$_2$, C*H*CH$_2$), 2.54 (m, 2 H, C*H*CH$_2$), 2.74 (m, 1 H, C*H*CH$_2$), 2.81 (m, 1 H, C*H*CH$_2$), 2.91 (m, 1 H, C*H*CH$_2$), 4.00−4.21 (m, 32 H, OCH$_2$). − ^{13}C NMR (100 MHz): δ = 10.5 (q, CH*C*H$_3$#), 11.6 (q, CH*C*H$_3$*), 12.8 (q, CH*C*H$_3$*), 12.9 (q, CH*C*H$_3$$), 13.6 (q, CH*C*H$_3$+), 13.87 (q, OCH$_2$*C*H$_3$), 13.94 (q, OCH$_2$*C*H$_3$), 13.99 (q, OCH$_2$*C*H$_3$), 14.03 (q, OCH$_2$*C*H$_3$), 14.1 (q, OCH$_2$*C*H$_3$), 14.3 (q, CH*C*H$_3$$), 15.3 (q, CH*C*H$_3$#), 16.9 (q, CH*C*H$_3$§), 22.3 (t), 22.6 (t), 22.7 (t), 22.9 (t), 23.0 (t), 23.2 (t), 23.8 (t), 25.5 (t), 25.6 (t), 27.5 (t), 29.3 (t), 29.8 (t), 30.2 (t, 2 CH$_2$), 30.8 (t), 33.6 (d, *C*HCH$_3$#), 34.8 (d, *C*HCH$_3$#), 34.9 (t), 35.2 (t), 36.1 (t), 36.6 (d, *C*HCH$_3$*), 37.1 (d, *C*HCH$_3$*), 37.2 (d, *C*HCH$_3$+), 37.3 (t), 37.66 (t), 37.73 (t), 37.8 (t), 39.2 (d, *C*HCH$_3$$), 40.1 (d, *C*HCH$_3$§), 42.7 (d, *C*HCH$_3$$), 44.0 (d), 47.0 (d), 48.0 (d), 51.0 (d), 51.3 (d), 51.47 (d), 51.49 (d), 51.6 (d), 60.6 (t, OCH$_2$), 60.7 (t, OCH$_2$), 60.78 (t, OCH$_2$), 60.81 (t, OCH$_2$), 60.86 (t, OCH$_2$), 60.94 (t, OCH$_2$), 61.0 (t, OCH$_2$), 62.6 (s, *C*CH$_2$), 62.67 (s, *C*CH$_2$), 62.72 (s, *C*CH$_2$), 63.15 (s, *C*CH$_2$), 63.18 (s, *C*CH$_2$), 63.5 (s, *C*CH$_2$), 64.2 (s, *C*CH$_2$), 171.5 (s, CO$_2$), 171.6 (s, CO$_2$), 171.8 (s, CO$_2$), 171.9 (s, CO$_2$), 172.0 (s, CO$_2$), 172.66 (s, CO$_2$), 172.71 (s, CO$_2$), 172.75 (s, CO$_2$), 172.81 (s, CO$_2$), 173.3 (s, CO$_2$), 173.4 (s, CO$_2$), 173.5 (s, CO$_2$). − MS; *m*/*z* (%) = 482 (3) [M$^+$], 241 (100), 167 (52). − HRMS: $C_{26}H_{42}O_8$: calcd. 482.2880; found 482.2870 ± 3 ppm. − Resonances marked with $, #, §, *, + correspond to different diastereomers.

Diethyl 2-(1-Chloroethyl)cyclopentane-1,1-dicarboxylate (21f): Flash chromatography (50:1) gave 196 mg (71%) of **21f** as a 3:1 diastereomeric mixture [R_f (10:1) = 0.40] and as a colorless oil. − IR (film): ṽ = 2983 (w), 1730 (s, CO$_2$), 1263 (m), 1211 (w). − ^{1}H NMR (200 MHz): δ = 1.20 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$*), 1.21 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.24 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.41 (d, *J* = 6.6 Hz, 3 H, CHC*H*$_3$*), 1.51 (d, *J* = 6.7 Hz, 3 H, CHC*H*$_3$), 1.60 (m, 1 H, 1H*), 1.76−2.04 (m, 4 H, 4 H*), 2.35 (m, 1 H*), 2.47 (m, 1 H), 2.90 (ddd, *J* = 9.7, 7.8, 3.9 Hz, 1 H, C*H*CHCl), 2.93 (m, 1 H, C*H*CHCl*), 4.08 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH$_2$), 4.08 (m, 1 H, OCH$_2$), 4.11 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH$_2$), 4.13 (q, *J* = 7.1 Hz, 2 H, OCH$_2$*), 4.21 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH$_2$), 4.24 (m, 2 H, OCH$_2$*), 4.44 (dq, *J* = 6.7, 6.6 Hz, 1 H, CHCl*), 4.48 (dq, *J* = 6.7, 3.9 Hz, 1 H, CHCl). − ^{13}C NMR (50 MHz): δ = 13.83 (q, OCH$_2$CH$_3$*), 13.86 (q, OCH$_2$*C*H$_3$), 13.93 (q, OCH$_2$*C*H$_3$), 13.98 (q, OCH$_2$*C*H$_3$*), 22.60 (t*), 22.62 (t), 23.5 (q, CH*C*H$_3$*), 25.3 (q, CH*C*H$_3$), 26.6 (t), 28.3 (t*), 35.6 (t), 36.6 (t*), 52.4 (d, *C*HCH$_2$), 55.1 (d, *C*HCH$_2$*), 57.8 (d, CHCl*), 59.4 (d, CHCl), 61.2 (t, OCH$_2$*), 61.37 (t, OCH$_2$*), 61.45 (t, OCH$_2$), 61.5 (t, OCH$_2$), 62.3 (s, *C*CO$_2$), 62.4 (s, *C*CO$_2$*), 170.2 (s, CO$_2$), 170.7 (s, CO$_2$*), 172.1 (s, CO$_2$*), 172.4 (s, CO$_2$). − MS; *m*/*z* (%) = 278/276 (1/3) [M$^+$], 241 (33) [M$^+$ − Cl], 235 (37), 231 (29), 230 (29), 195 (26) [M$^+$ − Cl − OEt], 184 (21), 173 (75), 167 (100) [M$^+$ − Cl − EtOH − CO], 166 (66), 149 (23), 139 (34), 127 (42), 121 (27), 95 (58), 93 (60), 67 (36). − $C_{13}H_{21}ClO_4$ (276.8): calcd. C 56.42, H 7.65; found 56.14, H 7.91. − Resonances marked with an asterisk * correspond to the minor diastereomer.

Diethyl 2-Chloro-2-(hex-4-enyl)malonate (27f): Flash chromatography (50:1) gave 11 mg (4%) of **27f** [R_f (10:1) = 0.38] as a colorless oil. − ^{1}H NMR (200 MHz): δ = 1.26 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$), 1.60 (d, *J* = 4.8 Hz, 3 H, =CHC*H*$_3$), 1.50 (m, 2 H), 1.95 (m, 2 H), 2.19 (m, 2 H), 4.23 (q, *J* = 7.1 Hz, 4 H, OCH$_2$), 5.36 (m, 2 H). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH$_2$*C*H$_3$), 17.8 (q, CH*C*H$_3$), 23.8 (t), 31.9 (t), 36.9 (t), 62.8 (t, OCH$_2$), 71.0 (s, CCl), 125.8 (d, =*C*HCH$_3$) 130.1 (d, =*C*HCH$_2$), 166.8 (s, CO$_2$).

Diethyl 2-Methylenecyclopentane-1,1-dicarboxylate (28): Flash chromatography (50:1) gave 129 mg (57%) or 127 mg (56%) of **28** [R_f (10:1) = 0.50] as a colorless oil. − IR (film): ṽ = 2983 cm^{-1} (m), 1731 (s, CO$_2$), 1267 (s), 1247 (s), 1214 (m), 1146 (m). − ^{1}H NMR (200 MHz): δ = 1.18 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$), 1.66 (quint, *J* = 7.0 Hz, 2 H, CCH$_2$C*H*$_2$), 2.27 (t, *J* = 6.9 Hz, 2 H, CH$_2$CCO$_2$), 2.38 (dt, *J* = 7.2, 2.1 Hz, 2 H, =CCH$_2$), 4.12 (q, *J* = 7.1 Hz, 4 H, OCH$_2$), 5.18 (t, *J* = 1.9 Hz, 1 H, =C*H*$_2$), 5.24 (t, *J* = 2.2 Hz, 1 H, =C*H*$_2$). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH$_2$*C*H$_3$), 24.0 (t), 33.7 (t), 36.1 (t), 61.3 (t, OCH$_2$), 63.5 (s, *C*CO$_2$), 111.7 (t, =CH$_2$), 148.2 (s, =C), 170.5 (s, CO$_2$). − MS; *m*/*z* (%) = 226 (28) [M$^+$], 181 (18) [M$^+$ − OEt], 180 (24) [M$^+$ − EtOH], 154 (20), 153 (92) [M$^+$ − CO$_2$Et], 152 (100) [M$^+$ − EtOH − CO], 126 (20), 125 (76), 108 (30) [M$^+$ − CO$_2$Et − OEt], 107 (22) [M$^+$ − CO$_2$Et − EtOH], 81 (38), 79 (44). − HRMS: $C_{12}H_{18}O_4$: calcd. 226.1205; found 226.1199 ± 2 ppm. − $C_{12}H_{18}O_4$ (226.1): calcd. C 63.70, H 8.02; found C 63.64, H 8.34.

Diethyl 2-(Ferrocenylmethylene)cyclopentane-1,1-dicarboxylate (20g): Flash chromatography (50:1) gave 37 mg (9%) of **20g** [R_f (10:1) = 0.45] as a yellow oil. − IR (film): ṽ = 2981 cm^{-1} (m), 1729 (s), 1301 (m), 1260 (s), 1245 (s), 1219 (m), 1150 (m), 1105 (m), 1097 (m), 1029 (m). − UV: λ$_{max}$ (lg ε) = 194 nm (4.42), 202 (4.39), 230 (4.25), 284 (4.03), 304 (3.31), 312 (3.00), 452 (2.58). − ^{1}H NMR (200 MHz): δ = 1.25 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$), 1.80 (tt, *J* = 7.0, 6.9 Hz, 2 H, =CCH$_2$C*H*$_2$), 2.30 (t, *J* = 6.9 Hz, 2 H, CCH$_2$), 2.51 (dt, *J* = 7.2, 2.5 Hz, 2 H, CCH$_2$), 4.09 (s, 5 H, *Cp*), 4.20 (m, 8 H, OCH$_2$, *Cp*C), 4.32 (t, *J* = 1.8 Hz, 1 H, =CH). − ^{13}C NMR (50 MHz): δ = 14.1 (q, OCH$_2$*C*H$_3$), 24.6 (t), 31.8 (t), 36.0 (t), 61.4 (t, OCH$_2$), 65.1 (s, =C*C*), 68.7 (d, *Cp*), 69.0 (d, *Cp*), 82.2 (s, (*ipso*-Cp)*C*), 124.7 (d, =CH), 136.7 (s, =C), 171.0 (s, CO$_2$). − MS; *m*/*z* (%) = 410 (16) [M$^+$], 337 (2) [M$^+$ − CO$_2$Et], 240 (12), 167 (21), 166 (100), 149 (16), 138 (21), 121 (17), 120 (19), 93 (27). − HRMS: $C_{22}H_{26}FeO_4$: calcd. 410.1180; found 410.1172 ± 3 ppm. − $C_{22}H_{26}FeO_4$ (410.1): calcd. C 64.40, H 6.39; found C 64.18, H 6.46.

Tetraethyl Dodeca-1,11-diyne-6,6,7,7-tetracarboxylate (29): Flash chromatography (15:1) gave 50 mg (22%) or 34 mg (15%) of **29** [R_f (1:1) = 0.59] as a colorless oil. − IR (film): ṽ = 3282 cm^{-1} (w, ≡CH), 2984 (w), 2118 (w, C≡C), 1731 (s, CO$_2$), 1258 (s), 1218 (s), 1182 (m). − ^{1}H NMR (200 MHz): δ = 1.24 (t, *J* = 7.1 Hz, 12 H, OCH$_2$C*H*$_3$), 1.58 (m, 4 H), 1.92 (t, *J* = 2.6 Hz, 2 H, ≡CH), 2.13 (m, 4 H, CH$_2$CCO$_2$) 2.17 (dt, *J* = 7.1, 2.6 Hz, 4 H, ≡CCH$_2$), 4.15 (q, *J* = 7.1 Hz, 4 H, OCH$_2$), 4.17 (q, *J* = 7.1 Hz, 4 H, OCH$_2$). − ^{13}C NMR (50 MHz): δ = 13.8 (q, OCH$_2$*C*H$_3$), 18.9 (t), 24.7 (t), 30.5 (t), 61.4 (t, OCH$_2$), 62.7 (s, *C*CO$_2$), 68.5 (d, C≡*C*H), 83.7 (s, ≡C), 169.4 (s, CO$_2$). − MS; *m*/*z* (%) = 405 (49) [M$^+$ − OEt], 311 (20), 265 (20), 225 (100) [M$^+$/2], 179 (56) [M$^+$/2 − EtOH], 178 (26), 153 (28), 152 (58) [M$^+$/2 − CO$_2$Et], 125 (20), 93 (22), 91 (28), 79 (24), 77 (20), 59 (37), 43 (24). − $C_{24}H_{34}O_8$ (450.2): calcd. C 63.98, H 7.61; found C 63.78, H 7.81.

Diethyl 2-Pent-4-ynyl-2-(tetrahydrofuran-2-yl)malonate (30): Flash chromatography (30:1) gave 44 mg (15%) of **30** [R_f (5:1) = 0.32] as a colorless oil. − IR (film): ṽ = 3282 cm^{-1} (m, ≡CH), 2981 (m), 2118 (w, C≡C), 1729 (s, CO$_2$), 1260 (s), 1180 (m), 1069 (m). − ^{1}H NMR (200 MHz): δ = 1.23 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.26 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.40−1.59 (m, 2 H), 1.76 (m, 2 H), 1.88 (t, *J* = 2.6 Hz, 1 H, ≡CH), 2.00 (m, 4 H), 2.14 (dt, *J* = 7.4, 2.4 Hz, 2 H, ≡CCH$_2$), 3.70 (m, 2 H, OC*H*$_2$CH$_2$), 4.14 (q, *J* = 7.1 Hz, 4 H, OC*H*$_2$CH$_3$), 4.29 (t, *J* = 7.4 Hz, 1 H, OC*H*CH$_2$). − ^{13}C NMR (100 MHz): δ = 14.0 (q, OCH$_2$*C*H$_3$), 18.9 (t), 24.0 (t),

25.8 (t), 27.8 (t), 32.0 (t), 61.06 (t, O*C*H$_2$), 61.09 (t, O*C*H$_2$), 61.15 (s, *C*CH), 68.53 (t, O*C*H$_2$CH$_2$), 68.54 (s, ≡*C*), 80.3 (d, O*C*HCH$_2$), 83.8 (d, ≡*C*H), 169.9 (s, *C*O$_2$), 170.2 (s, *C*O$_2$). − MS; *m*/*z* (%) = 251 (5) [M$^+$ − OEt], 229 (8) [M$^+$ − CH$_2$CH$_2$CH$_2$C≡CH], 223 (35) [M$^+$ − CO$_2$Et], 222 (42) [M$^+$ − EtOH − CO], 183 (24) [M$^+$ − CH$_2$CH$_2$CH$_2$C≡CH − EtOH], 169 (100), 149 (22), 141 (22), 123 (47), 95 (41), 71 (42).

Treatment of Malonates 12a−g with TEMPO (5). − General Procedure: Compounds **12a−g** (1.00 mmol) were added at −78 °C under N$_2$ to a solution of the lithium amide in 20 mL of dry DME (for the amount of base, see Table 7). The solution was stirred between −78 and −60 °C for 30 min. At 0 °C, compound **5** (172 mg, 1.10 mmol) was added and the red solution was stirred for 5 min. Solid **1** or **2** was added in portions at 0 °C. The mixture was stirred at 0 °C for 2 h, quenched with four drops of a saturated NH_4Cl solution, and allowed to warm to room temperature. The reaction mixture was diluted with 20 mL of ether and filtered through a pad of silica gel. The solvent was evaporated and the inhomogeneous residue was preadsorbed on silica gel. Flash chromatography (50:1 gradient to 1:1) gave the products shown in Table 7, followed by unchanged **5**.

Diethyl 2-(5,5-Diphenylpent-4-enyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)malonate (32a): Flash chromatography (50:1) gave 252 mg (47%) of **32a** [R_f (5:1) = 0.64] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2978 cm^{-1} (m), 1738 (s, *C*O$_2$), 1446 (m), 1364 (m), 1259 (m), 1179 (m). − UV: λ_{max} (lg ε) = 194 nm (4.62), 218 (4.17), 250 (4.06), 276 (3.45), 284 (3.14). − ^{1}H NMR (200 MHz): δ = 1.06 (s, 6 H, NCC*H*$_3$), 1.16 (s, 6 H, NCC*H*$_3$), 1.24 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$), 1.40 (m, 8 H), 2.12 (m, 4 H), 4.17 (q, *J* = 7.2 Hz, 4 H, OCH$_2$), 6.06 (t, *J* = 7.4 Hz, 1 H, =CH), 7.12−7.79 (m, 10 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 14.1 (q, OCH$_2$*C*H$_3$), 17.0 (t, NCCH$_2$*C*H$_2$), 20.9 (q, NC*C*H$_3$), 24.7 (t, =CHCH$_2$*C*H$_2$), 30.0 (t, =CH*C*H$_2$), 33.4 (q, NC*C*H$_3$), 34.0 (t, *C*H$_2$CO$_2$), 41.2 (t, NC*C*H$_2$CH$_2$), 60.9 (s, N*C*CH$_3$), 61.1 (t, OCH$_2$), 88.9 (s, *C*CO$_2$), 126.78 (d, *Ph*), 126.85 (d, *Ph*), 127.2 (d, *Ph*), 128.0 (d, *Ph*), 128.2 (d, *Ph*), 129.5 (d, =CH), 129.9 (d, *Ph*), 140.3 (s), 142.1 (s), 142.7 (s), 169.4 (s, *C*O$_2$). − MS; *m*/*z* (%) = 379 (76) [M$^+$ − TEMPO], 302 (85), 289 (48), 273 (100), 260 (91), 232 (41), 193 (27), 183 (54), 167 (45), 142 (52), 105 (98), 77 (37), 69 (46), 55 (36).

Diethyl 2-[2-(2,2,6,6-Tetramethylpiperidin-1-yloxy)prop-2-yl]cyclopentane-1,1-dicarboxylate (31b): Flash chromatography (50:1) gave 358 mg (87%) of **31b** [R_f (10:1) = 0.48] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2977 cm^{-1} (m), 2935 (m), 1728 (s, *C*O$_2$), 1255 (s). − ^{1}H NMR (200 MHz): δ = 1.00 (s, 3 H, NCC*H*$_3$), 1.06 (s, 3 H, NCC*H*$_3$), 1.10 (s, 3 H, NCC*H*$_3$), 1.13 (s, 3 H, NCCH$_3$), 1.17 (t, *J* = 7.3 Hz, 3 H, OCH$_2$C*H*$_3$), 1.18 (t, *J* = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$), 1.27 (m, 6 H, CC*H*$_2$C*H*$_2$C*H*$_2$C), 1.27 (s, 3 H, CHCC*H*$_3$), 1.40 (s, 3 H, CHCC*H*$_3$), 1.73 (m, 3 H), 2.05 (m, 2 H), 2.40 (m, 1 H), 3.42 (dd, *J* = 8.4, 8.0 Hz, 1 H, CH), 3.96 (dq, *J* = 10.8, 7.1 Hz, 1 H, OCH$_2$), 4.10 (m, 2 H, OCH$_2$), 4.22 (dq, *J* = 10.8, 7.2 Hz, 1 H, OCH$_2$). − ^{13}C NMR (50 MHz): δ = 13.7 (q, OCH$_2$*C*H$_3$), 14.0 (q, OCH$_2$*C*H$_3$), 17.1 (t, NCCH$_2$*C*H$_2$), 20.6 (q, NC*C*H$_3$), 21.1 (q, NC*C*H$_3$), 22.4 (t, CHCH$_2$*C*H$_2$), 23.2 (q, CHC*C*H$_3$), 25.2 (q, CHC*C*H$_3$), 27.4 (t, CH*C*H$_2$), 34.9 (q, NC*C*H$_3$), 35.4 (q, NC*C*H$_3$), 37.3 (t, *C*H$_2$CO$_2$), 41.1 (t, NC*C*H$_2$CH$_2$*C*H$_2$C), 55.9 (d, CH), 59.3 (s, N*C*CH$_3$), 60.84 (s, N*C*CH$_3$), 60.86 (t, OCH$_2$), 61.0 (t, OCH$_2$), 62.7 (s, *C*CO$_2$), 80.9 (s, CON), 171.7 (s, *C*O$_2$), 173.0 (s, *C*O$_2$). − MS; *m*/*z* (%) = 255 (83) [M$^+$ − TEMPO], 181 (100) [M$^+$ − TEMPO − EtOH − CO], 163 (38), 142 (61), 135 (65) [M$^+$ − TEMPO − 2 EtOH − CO], 134 (30), 107 (28). − $C_{23}H_{41}NO_5$ (411.6): calcd. C 67.12, H 10.04, N 3.40; found C 66.81, H 10.09, N 3.31.

Diethyl 2-[Methoxy(2,2,6,6-tetramethylpiperidin-1-yloxy)methyl]-cyclopentane-1,1-dicarboxylate (31c): Flash chromatography (50:1) gave 190 mg (46%) or 153 mg (37%) of **31c** as a 2:1 diastereomeric mixture [R_f (10:1) = 0.38] as colorless crystals; m.p. 41−42 °C. − IR (KBr): $\tilde{\nu}$ = 2982 cm^{-1} (m), 1745 (m, *C*O$_2$), 1727 (s, *C*O$_2$), 1363 (m), 1270 (m), 1259 (m). − ^{1}H NMR (200 MHz): δ = 1.01 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.05 (s, 3 H, NCCH$_3$*), 1.07 (s, 3 H, NCCH$_3$), 1.171 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.174 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.21 (t, *J* = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$), 1.22 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H*$_3$, OCH$_2$C*H*$_3$*), 1.24 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$*), 1.35−1.70 (m, 8 H, 8 H*), 1.75−2.20 (m, 3 H, 3 H*), 2.38 (m, 1 H, 1 H*), 2.68 (m, 1 H, CH$_2$C*H**), 2.89 (dt, *J* = 8.2, 2.1 Hz, 1 H, CH$_2$C*H*), 3.47 (s, 3 H, OCH$_3$), 3.50 (s, 3 H, OCH$_3$*), 4.14 (q, *J* = 7.1 Hz, 2 H, OCH$_2$*), 4.16 (q, *J* = 7.2 Hz, 6 H, OCH$_2$, OCH$_2$*), 4.95 (d, *J* = 2.2 Hz, 1 H, OCH), 5.08 (d, *J* = 8.0 Hz, OCH*). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH$_2$*C*H$_3$, OCH$_2$*C*H$_3$*), 14.0 (q, OCH$_2$*C*H$_3$, OCH$_2$*C*H$_3$*), 17.3 (t, CCH$_2$*C*H$_2$, CCH$_2$*C*H$_2$*), 19.9 (q, NC*C*H$_3$), 20.0 (q, NC*C*H$_3$*), 20.5 (q, NC*C*H$_3$, NC*C*H$_3$*), 22.0 (t*), 22.5 (t), 24.2 (t), 26.8 (t*), 32.3 (q, NC*C*H$_3$), 32.5 (q, NC*C*H$_3$*), 33.9 (q, NC*C*H$_3$), 34.2 (q, NC*C*H$_3$*), 34.7 (t), 35.8 (t*), 40.2 (t, C*C*H$_2$CH$_2$CH$_2$C), 40.3 (t, C*C*H$_2$CH$_2$CH$_2$C), 40.5 (t, C*C*H$_2$CH$_2$*C*H$_2$C*), 49.2 (d, CH$_2$*C*H), 52.6 (d, CH$_2$*C*H*), 59.1 (s, N*C*CH$_3$*), 59.4 (s, N*C*CH$_3$), 60.2 (q, OCH$_3$), 60.3 (q, OCH$_3$*), 60.6 (s, N*C*CH$_3$), 60.8 (t, OCH$_2$, OCH$_2$*), 61.0 (t, OCH$_2$), 61.1 (t, OCH$_2$*), 62.1 (s, *C*CO$_2$*), 62.4 (s, *C*CO$_2$), 106.5 (d, CHO*), 107.6 (d, CHO), 171.0 (s, *C*O$_2$*), 171.1 (s, *C*O$_2$), 172.3 (s, *C*O$_2$), 172.5 (s, *C*O$_2$*). − MS; *m*/*z* (%) = 257 (100) [M$^+$ − TEMPO], 197 (41), 183 (96) [M$^+$ − TEMPO − EtOH − CO], 142 (44), 140 (27), 123 (38). − $C_{22}H_{39}NO_6$ (413.5): calcd. C 63.90, H 9.51, N 3.39; found C 63.91, H 9.85, N 3.16. − Resonances marked with an asterisk * correspond to the minor diastereomer.

Diethyl 2-[Phenyl(2,2,6,6-tetramethylpiperidin-1-yloxy)methyl]-cyclopentane-1,1-dicarboxylate (31d): Flash chromatography (50:1) gave 331 mg (72%) of **31d** [R_f (5:1) = 0.66] as colorless crystals; m.p. 85−87 °C. − IR (KBr): $\tilde{\nu}$ = 2974 cm^{-1} (m), 1731 (s, *C*O$_2$), 1456 (m), 1259 (s), 1196 (s), 703 (m). − UV: λ_{max} (lg ε) = 192 nm (4.60), 200 (4.18), 204 (4.04), 210 (3.98), 214 (3.92), 216 (3.88), 224 (3.49), 228 (3.27), 236 (3.09). − ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$): δ = −0.09 (br. s, 3 H, NCCH$_3$), 0.88 (s, 3 H, NCCH$_3$), 0.95 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.02 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.11 (s, 3 H, NCCH$_3$), 1.35 (s, 3 H, NCCH$_3$), 1.28−1.55 (m, 8 H), 1.80 (m, 1 H), 2.10 (m, 1 H), 2.19−2.36 (m, 2 H), 3.37 (m, 2 H, C*H*CHPh, OCH$_2$), 3.69 (m, 1 H, OCH$_2$), 3.76 (m, 2 H, OCH$_2$), 4.94 (d, *J* = 10.4 Hz, 1 H, CHC*H*Ph), 7.16−7.33 (m, 5 H, *Ph*). − ^{13}C NMR (100 MHz, C$_2$D$_2$Cl$_4$): δ = 13.6 (q, OCH$_2$*C*H$_3$), 13.9 (q, OCH$_2$*C*H$_3$), 17.0 (t, NCCH$_2$*C*H$_2$), 20.3 (q, NC*C*H$_3$$^{\#}$), 22.7 (t, CHCH$_2$*C*H$_2$), 29.8 (t, CH*C*H$_2$), 32.6 (q, NC*C*H$_3$$^{\#}$), 34.0 (q, NC*C*H$_3$$^{\#}$), 37.0 (t, *C*H$_2CO_2$), 40.6 (t, NC*C*H$_2CH_2$*C*H$_2C^{\#}$), 49.7 (d, *C*HCH$_2$), 58.7 (s, N*C*CH$_3$$^{\#}$), 60.7 (t, OCH$_2$), 61.0 (t, OCH$_2$), 62.9 (s, *C*CO$_2$), 83.5 (d, *C*HPh), 126.4 (d, *Ph*), 127.4 (d, *Ph*), 129.6 (d, *Ph*), 139.3 (s, *Ph*), 170.6 (s, *C*O$_2$), 172.2 (s, *C*O$_2$). − MS; *m*/*z* (%) = 303 (100), 229 (97), 155 (51). − $C_{27}H_{41}NO_5$ (459.6): calcd. C 70.54, H 9.00, N 3.05; found C 71.03, H 9.25, N 2.94. − Resonances marked with # are broad and of very low intensity at room temperature.

Isomerization of 31d to 31d′: During a high-temperature NMR experiment (25−100 °C) to assign the broad resonances at room temperature, we observed the formation of diastereomer **31d′**. The final **31d/31d′** ratio was 2:1. A diastereomeric mixture of **31d/31d′** (*dr* = 9:1) in C$_2$D$_2$Cl$_4$ isomerized to a 1:1 diastereomeric mixture on exposure to daylight in an NMR tube for 9 d and temporary heating to 100 °C. Isomerization was monitored by NMR spectroscopy.

Compound 31d′: ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 0.48 (br. s, 3 H, NCCH$_3$), 0.88 (s, 3 H, NCCH$_3$), 1.11 (s, 3 H, NCCH$_3$), 1.15 (t, *J* = 7.0 Hz, 3 H, OCH$_2$C*H$_3$*), 1.23 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H$_3$*), 1.28−1.55 (m, 8 H), 1.35 (s, 3 H, NCCH$_3$), 1.80 (m, 1 H), 1.82 (m, 1 H), 2.19−2.36 (m, 2 H), 3.37 (m, 1 H, C*H*CHPh), 3.69−3.83 (m, 2 H, OCH$_2$), 3.84 (m, 1 H, OCH$_2$), 4.14 (m, 1 H, OCH$_2$), 5.11 (d, *J* = 5.9 Hz, 1 H, CHC*H*Ph), 7.16−7.33 (m, 5 H, *Ph*). − ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ = 13.5 (q, OCH$_2$*C*H$_3$), 13.8 (q, OCH$_2$*C*H$_3$), 17.0 (t, NCCH$_2$*C*H$_2$), 20.3 (q, NC*C*H$_3$#), 21.3 (t, CHCH$_2$*C*H$_2$), 25.7 (t, CH*C*H$_2$), 32.6 (q, NC*C*H$_3$#), 34.0 (q, NC*C*H$_3$#), 35.0 (t, *C*H$_2$CCO$_2$), 40.6 (t, NC*C*H$_2$CH$_2$*C*H$_2$C#), 48.4 (d, *C*HCH$_2$), 58.7 (s, N*C*CH$_3$#), 60.8 (t, OCH$_2$), 61.1 (t, OCH$_2$), 62.3 (s, *C*CO$_2$), 84.6 (d, *C*HPh), 126.9 (d, *Ph*), 127.0 (d, *Ph*), 131.4 (d, *Ph*), 140.0 (s, *Ph*), 170.6 (s, CO$_2$), 172.0 (s, CO$_2$). − Resonances marked with # are broad and of very low intensity at room temperature.

Cyclization of the Mixture 31f/32f. − a) A solution of a 2.2:1 mixture of **32f/31f** (130 mg, 0.33 mmol) in 1 mL of $CDCl_3$ was stored at room temperature in daylight in an NMR tube for 7 d, monitoring by NMR spectroscopy. The solvent was removed in vacuum. Flash chromatography (50:1 gradient to 30:1) of the crude product gave 120 mg (92%) of **31f**. − **b)** The crude orange reaction solution of **31f/32f** in 20 mL of DME/ether (1:1), obtained from cyclization according to the general procedure after filtration through a pad of silica gel, was stirred at room temperature under ordinary lab light for 7 d. The solvent was removed in vacuum and the residue was preadsorbed on silica gel. Flash chromatography 50:1 gradient to 15:1) gave 92% ferrocene and a total yield of 231 mg (58%) of **31f**, based on **12f**.

Diethyl 2-[1-(2,2,6,6-Tetramethylpiperidin-1-yloxy)ethyl]-cyclopentane-1,1-dicarboxylate (31f): Flash chromatography (50:1) gave 199 mg (50%) or 163 mg (41%) of **31f** as a 2:1 diastereomeric mixture and **32f** [R_f (10:1) = 0.39] as a colorless oil. − IR (film): $\tilde{\nu}$ = 2938 cm^{-1} (m), 2935 (m), 1739 (s, CO$_2$), 1219 (s). − ^{1}H NMR (400 MHz): δ = 1.00 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.04 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.05 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.08 (s, 6 H, NCCH$_3$, NCCH$_3$*), 1.11 (m, 3 H, CHC*H$_3$*), 1.20 (t, *J* = 7.0 Hz, 6 H, OCH$_2$C*H$_3$*), 1.21 (t, *J* = 7.0 Hz, 6 H, OCH$_2$C*H$_3$**), 1.24 (d, *J* = 5.7 Hz, 3 H, CHC*H$_3$*), 1.32 (m, 12 H, NCC*H$_2$*C*H$_2$*C*H$_2$*, NCC*H$_2$*C*H$_2$*C*H$_2$**), 1.52 (m, 2 H, CHCH$_2$C*H$_2$*, CHCH$_2$C*H$_2$**), 1.80 (m, 4 H, CHC*H$_2$*C*H$_2$*, CHC*H$_2$*C*H$_2$**), 2.07 (m, 4 H, CHC*H$_2$*CH$_2$C*H$_2$*, CHC*H$_2$*CH$_2$C*H$_2$**), 2.38 (dt, *J* = 13.7, 7.6 Hz, 1 H, CH$_2$C*H$_2$*CCH*), 2.51 (dt, *J* = 13.1, 8.3 Hz, 1 H, CH$_2$C*H$_2$*CCH), 2.63 (dt, *J* = 8.0, 5.7 Hz, 1 H, C*H*CH$_2$), 2.84 (dt, *J* = 7.7, 7.0 Hz, 1 H, C*H*CH$_2$*), 4.08 (dq, *J* = 7.4, 6.1 Hz, 1 H, C*H*CH$_3$), 4.12 (q, *J* = 7.2 Hz, 4 H, OCH$_2$, OCH$_2$*), 4.14 (q, *J* = 7.2 Hz, 4 H, OCH$_2$, OCH$_2$*), 4.17 (m, 1 H, C*H*CH$_3$*). − ^{13}C NMR (100 MHz): δ = 13.92 (q, OCH$_2$*C*H$_3$, OCH$_2$*C*H$_3$*), 13.94 (q, OCH$_2$*C*H$_3$, OCH$_2$*C*H$_3$*), 16.9 (t, CCH$_2$*C*H$_2$CH$_2$C*), 17.3 (t, CCH$_2$*C*H$_2$CH$_2$C), 17.4 (q, CH*C*H$_3$*), 18.4 (q, CH*C*H$_3$), 20.6 (q, NC*C*H$_3$, NC*C*H$_3$*), 20.7 (q, NC*C*H$_3$, NC*C*H$_3$*), 22.4 (t, CHCH$_2$*C*H$_2$), 22.6 (t, CHCH$_2$*C*H$_2$*), 26.8 (t, CH*C*H$_2$), 26.9 (t, CH*C*H$_2$*), 33.97 (q, NC*C*H$_3$, NC*C*H$_3$*), 34.03 (q, NC*C*H$_3$, NC*C*H$_3$*), 35.6 (t, *C*H$_2$CCO$_2$), 36.7 (t, *C*H$_2$CCO$_2$*), 40.3 (t, NC*C*H$_2$CH$_2$CH$_2$, NC*C*H$_2$CH$_2$CH$_2$*), 40.7 (t, NC*C*H$_2$CH$_2$CH$_2$, NC*C*H$_2$CH$_2$CH$_2$*), 51.7 (d, *C*HCH$_2$*), 51.9 (d, *C*HCH$_2$), 58.7 (s, N*C*CH$_3$, N*C*CH$_3$*), 60.5 (s, N*C*CH$_3$, N*C*CH$_3$*), 60.9 (t, OCH$_2$, OCH$_2$*), 61.1 (t, OCH$_2$, OCH$_2$*), 62.1 (s, *C*CO$_2$*), 63.4 (s, *C*CO$_2$), 77.6 (d, *C*HCH$_3$*), 77.8 (d, *C*HCH$_3$), 170.8 (s, CO$_2$), 171.0 (s, CO$_2$*), 172.5 (s, CO$_2$*), 172.8 (s, CO$_2$). − MS (NH$_3$, CI, pos.): *m*/*z* (%) = 398 (100) [M$^+$ + H], 241 (10) [M$^+$ − TEMPO], 167 (4). − $C_{22}H_{39}NO_5$ (397.6): calcd. C 66.47, H 9.89, N 3.52; found C 66.25, H 9.99, N 3.40. − Resonances marked with an asterisk * correspond to minor diastereomer.

Diethyl 2-(Hex-4-enyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-malonate (32f): − ^{1}H NMR (200 MHz): δ = 1.08 (s, 6 H, NCCH$_3$), 1.16 (s, 6 H, NCCH$_3$), 1.25 (t, *J* = 6.9 Hz, 6 H, OCH$_2$C*H$_3$*), 1.34−1.42 (m, 8 H), 1.59 (d, *J* = 3.2 Hz, 3 H, CHC*H$_3$*), 1.95 (m, 2 H), 2.14 (m, 2 H), 4.17 (q, *J* = 7.2 Hz, 4 H, OCH$_2$), 5.36 (m, 2 H, C*H*=C*H*). − ^{13}C NMR (50 MHz): δ = 14.2 (q, OCH$_2$*C*H$_3$), 17.1 (t, NCCH$_2$*C*H$_2$), 18.0 (q, CH*C*H$_3$), 21.0 (q, NC*C*H$_3$), 24.2 (t, CHCH$_2$*C*H$_2$), 32.8 (t, CH*C*H$_2$), 33.4 (q, NC*C*H$_3$), 34.1 (t, *C*H$_2$CCO$_2$), 41.3 (t, NC*C*H$_2$CH$_2$*C*H$_2$C), 60.9 (s, N*C*CH$_3$), 61.1 (t, OCH$_2$), 89.0 (s, *C*CO$_2$), 125.3 (d, =CH), 131.0 (d, =CH), 169.5 (s, CO$_2$).

Diethyl 2-(Pent-4-ynyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-malonate (32g): Flash chromatography (50:1) gave 374 mg (98%) of **32g** [R_f (10:1) = 0.37] as a colorless oil. − IR (film): $\tilde{\nu}$ = 3289 cm^{-1} (w, ≡CH), 2936 (m), 2119 (w, C≡C), 1740 (s, CO$_2$), 1366 (m), 1302 (w), 1263 (s), 1217 (m), 1180 (m), 1086 (m). − ^{1}H NMR (200 MHz): δ = 0.88 (s, 6 H, NCCH$_3$), 0.95 (s, 6 H, NCCH$_3$), 1.05 (t, *J* = 7.1 Hz, 6 H, OCH$_2$C*H$_3$*), 1.15−1.43 (m, 8 H), 1.71 (t, *J* = 2.5 Hz, 1 H, ≡CH), 1.97 (dt, *J* = 6.9, 2.4 Hz, 2 H, ≡CCH$_2$), 2.07 (m, 2 H), 3.97 (q, *J* = 7.1 Hz, 4 H, OCH$_2$). − ^{13}C NMR (50 MHz): δ = 14.0 (q, OCH$_2$*C*H$_3$), 16.9 (t, NCCH$_2$*C*H$_2$), 18.7 (t), 20.8 (q, NC*C*H$_3$), 23.5 (t), 33.3 (q, NC*C*H$_3$), 33.6 (t), 41.1 (t, NC*C*H$_2$), 60.8 (s, N*C*CH$_2$), 61.0 (t, OCH$_2$), 68.6 (d, ≡*C*H), 83.8 (s, ≡C), 88.6 (s, CH$_2$*C*O), 169.1 (s, CO$_2$). − MS; *m*/*z* (%) = 381 (<1) [M$^+$], 156 (100) [TEMPO], 140 (16), 123 (19) [M$^+$ − TEMPO − CO$_2$Et − Et], 79 (18), 69 (18), 55 (21). − $C_{21}H_{35}NO_5$ (381.5): calcd. C 66.11, H 9.25, N 3.67; found C 65.91, H 9.50, N 3.29.

Deprotection of 31b, 31d, 31f, and 32f. − General Procedure: Zn dust (850 mg, 13.00 mmol) was added at 50 °C to solutions of **31b**, **31d**, **31f**, and **32f** (1.00 mmol) in 2 mL/1 mL/1 mL of AcOH/H$_2$O/THF. The mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the mixture was diluted with ether and filtered through a pad of silica gel. The filtrate was neutralized with saturated NaHCO$_3$ solution and washed twice with water. The solvent was removed in vacuum, and the crude products **14b**, **14d′**, **14f**, and **32f′** were purified by flash chromatography (50:1 gradient to 15:1).

Ethyl 1-Methyl-3-oxotetrahydrocyclopenta[*c*]furan-3a-carboxylate (14f): Flash chromatography (20:1) gave 178 mg (84%) of **14f** [R_f (5:1) = 0.37] as a 2:1 diastereomeric mixture and as a colorless oil. − IR (film): $\tilde{\nu}$ = 2981 cm^{-1} (m), 1771 (s, CO$_2$), 1739 (s, CO$_2$), 1255 (s). − ^{1}H NMR (200 MHz): δ = 1.21 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H$_3$*), 1.22 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H$_3$**), 1.32 (d, *J* = 6.6 Hz, 3 H, CHC*H$_3$*), 1.39 (d, *J* = 6.4 Hz, 3 H, CHC*H$_3$**), 1.47−2.01 (m, 4 H, 4 H*), 2.06−2.24 (m, 1 H, 1 H*), 2.25−2.41 (m, 1 H, 1 H*), 2.68 (m, 1 H, C*H*CH$_2$*), 2.87 (dt, *J* = 7.3, 6.3 Hz, 1 H, C*H*CH$_2$), 4.15 (q, *J* = 7.3 Hz, 2 H, OCH$_2$), 4.16 (q, *J* = 7.2 Hz, 2 H, OCH$_2$*), 4.22 (m, 1 H, C*H*CH$_3$*), 4.81 (dq, *J* = 6.5, 6.4 Hz, 1 H, C*H*CH$_3$). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH$_2$*C*H$_3$*), 14.0 (q, OCH$_2$*C*H$_3$), 16.0 (q, CH*C*H$_3$), 21.9 (q, CH*C*H$_3$*), 25.6 (t*), 26.3 (t), 27.1 (t), 33.9 (t*), 34.1 (t), 35.1 (t*), 50.8 (d, *C*HCH$_2$), 52.3 (d, *C*HCH$_2$*), 61.9 (t, OCH$_2$, OCH$_2$*), 62.7 (s, *C*CH$_2$*), 63.8 (s, *C*CH$_2$), 77.0 (d, *C*HCH$_3$), 82.4 (d, *C*HCH$_3$*), 170.0 (s, CO$_2$), 170.4 (s, CO$_2$*), 176.0 (s, CO$_2$*), 176.1 (s, CO$_2$). − MS; *m*/*z* (%) = 211 (10), 168 (63), 140 (58), 139 (40) [M$^+$ − CO$_2$Et], 123 (28), 122 (34), 111 (21), 95 (100), 94 (26), 93 (33), 67 (55), 43 (26). − $C_{11}H_{16}O_4$ (212.2): calcd. C 62.25, H 7.60; found C 62.30, H 7.95. − Resonances marked with an asterisk * correspond to minor diastereomer.

Diethyl 2-Hex-4-enyltartronate (32f′): Flash chromatography (50:1 gradient to 15:1) gave 209 mg (81%) of **32f′** [R_f (3:1) = 0.42] as a

Table 8. Crystal data, data collection, and refinement parameters for **14a**, **20b**, and **31d**

Compound	**14a**	**20b**	**31d**
Empirical formula	$C_{22}H_{22}O_4$	$C_{24}H_{32}FeO_4$	$C_{27}H_{41}NO_5$
M_r	350.40	440.35	459.61
Crystal habit	colorless tablet	colorless prism	orange prism
Crystal size [mm]	0.84×0.46×0.15	0.60×0.60×0.30	0.60×0.45×0.27
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Cell constants:			
a [pm]	1424.5(3)	1491.8(3)	1077.6(4)
b [pm]	1026.9(2)	1784.3(4)	1098.7(5)
c [pm]	1209.4(3)	814.6(3)	1125.3(5)
α [°]	90	90	99.85(3)
β [°]	99.29(2)	96.87(2)	98.33(3)
γ [°]	90	90	99.53(3)
V [nm^3]	1.7459	2.1528	1.2738
Z	4	4	2
D_x [Mg m^{-3}]	1.333	1.359	1.198
μ [mm^{-1}]	0.091	0.728	0.081
Transmissions		0.751−0.768	
F(000)	744	936	500
T [°C]	−130	−130	−130
$2\theta_{max}$	50	5	50
No. of reflections:			
measured	6278	6855	4730
unique	3083	3866	4484
R_{int}	0.034	0.026	0.015
Parameters	236	266	304
$wR(F^2$, all refl.)	0.112	0.074	0.108
R [F, > 4σ(F)]	0.044	0.030	0.043
S	1.03	1.03	1.05
max. Δρ [e Å^3]	0.30	0.26	0.23

colorless oil. − IR (film): $\tilde{\nu}$ = 3499 cm^{-1} (w, OH), 2977 (m), 2935 (m), 1731 (s, CO_2), 1259 (s), 1188 (m), 1145 (w). − ^{1}H NMR (200 MHz): δ = 1.20 (t, J = 7.1 Hz, 6 H, OCH_2CH_3), 1.34 (tt, J = 7.4, 7.0 Hz, 2 H, $=CHCH_2CH_2$), 1.59 (d, J = 4.3 Hz, 3 H, $=CHCH_3$), 1.93 (m, 4 H, $CH_2CH_2CH_2$), 3.70 (s, 1 H, OH), 4.18 (q, J = 7.1 Hz, 4 H, OCH_2), 5.34 (m, 2 H, $CH=CH$). − ^{13}C NMR (50 MHz): δ = 13.9 (q, OCH_2CH_3), 17.8 (q, $=CHCH_3$), 23.0 (t), 26.5 (t*), 32.1 (t), 34.0 (t), 34.1 (t*), 62.3 (t, OCH_2), 78.9 (s, COH), 124.4 (d, $=CHCH_2$*), 125.3 (d, $=CHCH_2$), 129.7 (d, $=CHCH_3$*), 130.5 (d, $=CHCH_3$), 169.4 (s, CO_2). − MS; m/z (%) = 258 (10) [M$^+$], 212 (22) [M$^+$ − EtOH], 194 (43) [M$^+$ − EtOH − CO], 185 (21) [M$^+$ − CO_2Et], 184 (46) [M$^+$ − EtOH − CO], 176 (100), 166 (44), 165 (37), 139 (52), 128 (23), 111 (37), 93 (24), 83 (31), 69 (20), 68 (88), 55 (47). − $C_{13}H_{22}O_5$ (258.3): calcd. C 60.45, H 8.58; found C 60.32, H 8.95. − Resonances marked with an asterisk * correspond to minor (*Z*)isomer.

Deethoxycarbonylation of Lactones 14a and 14b: Mixtures of **14a** or **14b** (0.25 mmol) and anhydrous LiCl (21 mg, 0.50 mmol) in H_2O (4 μL, 0.22 mmol) and dry DMSO (0.8 mL) were heated to 195 °C under N_2 for 3 h. The brown mixtures were diluted with 10 mL of ether and filtered through pads of silica gel. The filtrates were washed twice with saturated Na_2CO_3 solution and dried with Na_2SO_4. After evaporation of the solvent in vacuum, purification by flash chromatography (18:1) gave 10 mg (11%) of **14a** and 45 mg (64%) of **33a**, or 16 mg (40%) of **33b**.

3,3-Diphenylhexahydrocyclopenta[*c*]furan-1-one (33a): Flash chromatography (18:1) gave 45 mg (64%) of **33a** [R_f (5:1) = 0.39] as a colorless solid; m.p. 96−98 °C. − IR (KBr): $\tilde{\nu}$ = 1770 cm^{-1} (s, CO_2), 1447 (m), 1202 (m), 1159 (m), 964 (m), 758 (m), 699 (m). − UV: λ_{max} (lg ε) = 192 nm (4.67), 202 (4.47), 204 (4.40), 216 (4.00), 220 (3.96), 234 (3.36), 240 (2.76), 260 (2.67). − ^{1}H NMR (200 MHz): δ= 1.17 (m, 1 H), 1.61 (m, 3 H), 2.03 (m, 2 H), 3.00 (ddd, J = 8.3, 8.0, 3.5 Hz, 1 H, CHCPh), 3.58 (m, 1 H, $CHCO_2$), 7.13−7.52 (m, 10 H, *Ph*). − ^{13}C NMR (50 MHz): δ = 25.6 (t), 28.5 (t), 29.6 (t), 46.6 (d), 50.5 (d), 89.8 (s, *C*Ph), 125.1 (d, *Ph*), 125.5 (d, *Ph*), 127.2 (d, *Ph*), 127.8 (d, *Ph*), 128.2 (d, *Ph*), 128.6 (d, *Ph*), 142.1 (s, *Ph*), 144.1 (s, *Ph*), 179.7 (s, CO_2). − MS; m/z (%) = 278 (20) [M$^+$], 183 (100), 105 (58). − HRMS: $C_{19}H_{18}O_2$: calcd. 278.1307; found 278.1300 ± 3 ppm.

3,3-Dimethylhexahydrocyclopenta[*c*]furan-1-one (33b): Flash chromatography (18:1) gave 16 mg (40%) of **33b** [R_f (5:1) = 0.36] as a volatile liquid. − ^{1}H NMR (200 MHz): δ = 1.33 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.60 (m, 4 H), 1.94 (m, 2 H), 2.46 (m, 1 H), 3.15 (m, 1 H). − ^{13}C NMR (50 MHz): δ = 23.7 (q, CH_3), 26.4 (t), 28.5 (t), 29.2 (t), 30.0 (q, CH_3), 46.5 (d), 50.2 (d), 84.3 (s, CCH_3), 180.2 (s, CO_2). − MS; m/z (%) = 155 (2) [M$^+$ + H], 154 (0.4) [M$^+$], 139 (98), 110 (38), 95 (66), 67 (100), 59 (58), 43 (82).

Acetalization of Diethyl 2-Formylcyclopentane-1,1-dicarboxylate (22): A solution of aldehyde **22** (140 mg, 0.58 mmol) and *p*TsOH (25 mg, 0.15 mmol) in $HC(OMe)_3$ (2 mL) and methanol (5 mL) was stirred at room temperature for 24 h. After neutralization with 79 mg solid Na_2CO_3 and stirring for 30 min, the solvent was removed in vacuum. The residue was dissolved in 15 mL ether and filtered through a pad of silica gel. Removal of the ether in vacuum gave 117 mg (70%) of pure acetal **23**.

X-ray Crystallographic Studies of 14a, 20b, and 31d:[37] A summary of the crystal data, data collection, and refinement parameters is

given in Table 8. A cut tablet (**14a**) or a cut prism (**20b** and **31d**) was mounted on a glass fiber in inert oil and transferred to the cold gas stream of a Stoe STADI-4 diffractometer fitted with a Siemens LT-2 low temperature attachment. The data were measured by ω/θ scans using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). An absorption correction using a semiempirical method (ψ scans) was applied for **20b**. All unique data were used for calculations.[38] Each structure was solved by direct methods and refined anisotropically by full-matrix least squares on F^2. Hydrogen atoms (except rigid methyl groups) were refined with a riding model.

Acknowledgments

We thank the Fonds der Chemischen Industrie, the DFG, and the Dr. Otto Röhm Gedächtnisstiftung for generous financial support of this work. Prof. Dr. H. Hopf's encouragement and generous support is gratefully acknowledged.

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Received September 21, 2000
[O00489]