Difluoroboroxymolybdenum Fischer Carbene Complexes as Precursors of Acyl Radicals: Dimerization and Trapping with Electron-Deficient Alkenes

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Abstract: Pentacarbonyl acyl molybdates **1** react with boron trifluoride to give difluoroboroxy Fischer carbene complexes **2**, which undergo loss of the metal fragment at room temperature to form 1,2-diketones **3**, 1,2-hydroxy ketones **4**, or dimers **5** through a dimerization or decarbonylation–dimerization process of acyl radicals. Decomposition of **2** in the presence of electron-deficient alkenes **11** and **18** furnishes the two-, three-, and four-component coupling products **12, 13, 19, 20**, and **21**.

Keywords: acyl radicals · carbene complexes · coupling reactions · molybdenum · radical reactions

Introduction

Fischer carbene complexes have found a number of highly interesting applications as building blocks for organic synthesis.[1] While the majority of work in this field has been focused on alkoxy and aminocarbene complexes, few studies have been devoted to the preparation and reactivity of modified complexes with a second electron-deficient metal attached to the carbene heteroatom.[2] Up to now only examples of titanoxy,[3] zirconoxy,[4] sililoxy,[5] phosphite,[6] and boroxy[7] carbene complexes have been reported. Recently, we have described the preparation of boroxycarbene complexes and their transformation into oxaborolane or oxazaborolidine derivatives by an intramolecular C–H insertion process.[8] Söderberg et al. have found that lithium and tetramethylammonium acyl metalates are formally acetyl anion equivalents, adding to electron-deficient olefins in a Michael fashion.[9] Moreover, it is possible to generate acyl iodides by oxidation of tetramethylammonium and lithium acyl metalate complexes with iodine.[10] Finally, generation of acyl radicals from chromium carbene complexes by using Mn^{III}[11] and Cu^{II}[12] salts as oxidants has been reported. In this context, we have recently described a simple method of forming acyl radicals from difluoroboroxy Fischer carbene complexes under very mild reaction conditions and in the absence of an oxidant.[13] We further investigated the generation of acyl radicals from this type of carbene complex and their trapping with a selection of electron-deficient olefins. The formation of two-, three-, and four-component coupling products are described herein in detail.

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Results and Discussion

The treatment of pentacarbonyl acyl molybdate intermediates **1**, obtained by reaction of molybdenum hexacarbonyl and the corresponding organolithium compound,[14] with boron trifluoride diethyl ether complex in diethyl ether at $-60\,^{\circ}C$ readily led to difluoroboroxycarbene complexes **2**. Although complexes **2** are unstable, compound **2b** could be characterized by ^{13}C NMR spectroscopy. Upon warming to room temperature, compounds **2a–c** underwent loss of the metal fragment affording, after hydrolysis, mixtures of 1,2-diketones **3** and 1,2-hydroxy ketones **4** (entries 1–3, Table 1). In the case of **2c**, small amounts of dimer **5c** (7%) and bis(2-naphthyl) ketone (9%) were also obtained (entry 3, Table 1). However, dimers **5** were the only products observed when starting from carbene complexes **2d**, **e** (entries 4, 5, Table 1) (Scheme 1). Moreover, when the decomposition of **2a–c** was carried out in the presence of benzaldehyde, formation of hydroxy ketones **4** was not observed but a mixture of diketones **3** and 1,2-diphenyl-1,2-ethanediol was obtained.

Table 1. 1,2-Diketones **3**, 1,2-hydroxy ketones **4**, and dimers **5** from pentacarbonyl acyl molybdates **1** and boron trifluoride etherate.

Entry	Starting molybdate	R	Product (yield (%)[a])		
1	**1a**	Bu	**3a** (35)	**4a** (30)	
2	**1b**	Ph	**3b** (38)	**4b** (25)	
3	**1c**	2-Naph[b]	**3c** (24)	**4c** (22)	**5c** (7)[c]
4	**1d**	(*E*)-PhCH=CH			**5d** (42)
5	**1e**	PhC≡C			**5e** (33)

[a] Yield of isolated product based on $[Mo(CO)_6]$. [b] 2-Naph = 2-naphthyl. [c] Bis(2-naphthyl) ketone (9%) was also obtained.

A plausible pathway explaining the formation of the products described above is shown in Scheme 2. Keeping in mind that theoretical calculations carried out on boroxy Fischer carbene complexes have shown a strong interaction

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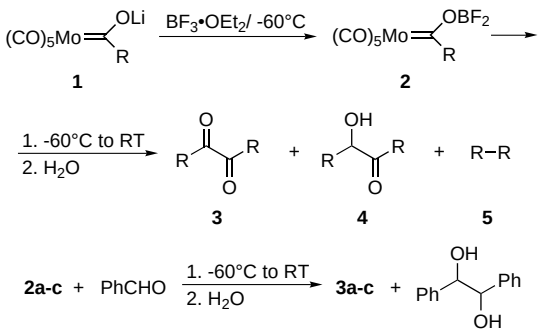
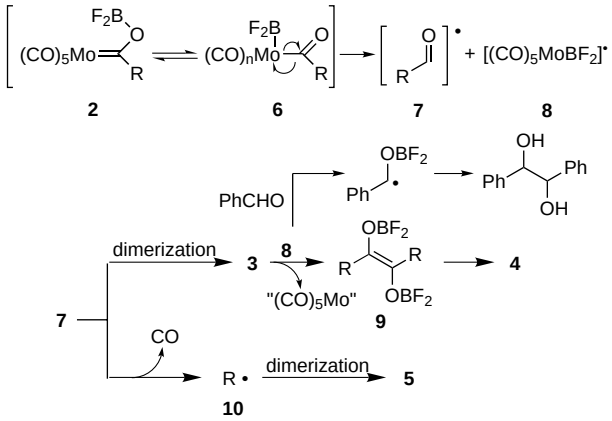


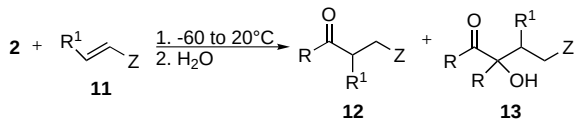
Scheme 1. Preparation of difluoroboroxymolybdenum carbene complexes **2** and their evolution to dimerization products **3**, **4**, or **5**.



Scheme 2. Mechanism for the formation of dimerization products **3**, **4**, and **5**.

between the molybdenum and the boron atom,[8] which could be responsible for the cleavage of the otherwise strong boron–oxygen bond, we can consider an equilibrium between the difluoroboroxy Fischer carbene complexes **2** and the acylmolybdenum complexes **6**. Homolytic scission of the carbon–molybdenum bond in **6** leads to the acyl radicals **7** and the radical species **8**.[15] The acyl radical **7** can subsequently undergo a dimerization process to afford the 1,2-diketones **3**. The formation of 1,2-hydroxyketones **4** can be understood by considering the reaction of **3** and the radical species **8** by a double electron transfer with release of "$Mo(CO)_5$", giving the endiol derivatives **9**. Hydrolysis of **9** would then afford the 1,2-hydroxy ketones **4**. This electron transfer process is avoided in the presence of benzaldehyde, which acts as a trapping agent for the unpaired electron of the radical species **8**, generating the corresponding radical anion, which dimerizes to give rise to 1,2-diphenyl-1,2-ethanediol after protonation. Formation of dimers **5** can be understood as the result of decarbonylation[16] of **7** and dimerization of the radical species **10** thus obtained.

To explore the synthetic utility of this new reaction, we have tried to trap the acyl radicals generated in this process with electron-poor olefins. Thus, upon warming carbene complexes **2** in the presence of an excess of alkenes **11** (2–10 equiv) from $-60\,^{\circ}C$ to room temperature, the expected formal Michael addition products **12** were isolated (Scheme 3, and Table 2).[17]



Scheme 3. Coupling reactions of difluoroboroxymolybdenum carbene complexes **2** and electron-poor olefins **11**.

Table 2. Reaction of difluoroboroxymolybdenum carbene complexes **2** and alkenes **11** to give 1,4-difunctionalized compounds **12** and hydroxy ketone derivatives **13**.

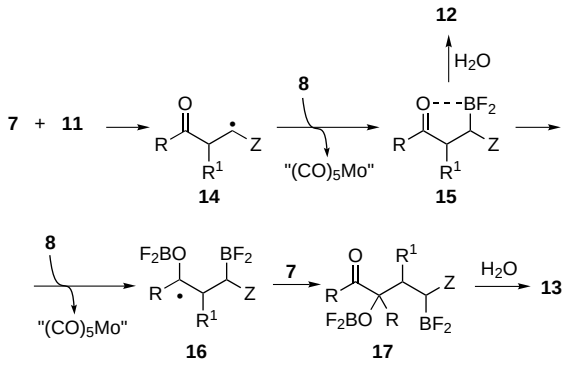
Entry	Starting carbene	R	Alkene	R^1	Z	Product	Yield [%][a]
1	**2a**	Bu	**11a**	H	COMe	**12a**	56
2	**2b**	Ph	**11a**	H	COMe	**12b**	42
3	**2c**	2-Naph	**11a**	H	COMe	**12c**	41
4	**2d**	(*E*)-PhCH=CH	**11a**	H	COMe	**12d**	37
5	**2f**	c-C_5H_9	**11a**	H	COMe	**12e**	52
6	**2a**	Bu	**11b**	H	CO_2Me	**12f/13a**	31/29
7	**2b**	Ph	**11b**	H	CO_2Me	**12g**	33
8	**2d**	(*E*)-PhCH=CH	**11b**	H	CO_2Me	**12h**	34
9	**2a**	Bu	**11c**	Me	CO_2Me	**12i**	40
10	**2a**	Bu	**11d**	Ph	CO_2Et	**12j**	37
11	**2a**	Bu	**11e**	H	CN	**12k/13b**	32/32
12	**2b**	Ph	**11e**	H	CN	**12l**	38

[a] Yield of isolated product based on $[Mo(CO)_6]$.

In addition, starting from carbene complex **2a** and olefins **11b** or **11e**, hydroxy ketone derivatives **13a, b** were respectively isolated together with the corresponding Michael adducts **12f** or **12k** (Scheme 3 and Table 2, entries 6 and 11). It is noteworthy that these hydroxy ketone derivatives **13** are the result of a three-component coupling reaction into which two fragments coming from the carbene complex and one derived from the alkene have been incorporated. In contrast with the observations of Söderberg et al.[9] in related systems, we have never observed the formation of products with more than one molecule of alkene in their structure, although a large excess of olefin is used.

A plausible mechanism accounting for the formation of products **12** as well as hydroxy ketone derivatives **13** is outlined in Scheme 4. Firstly, direct addition of acyl radicals **7**, generated following the pathway shown in Scheme 2, to the alkene **11** leads to radical intermediates **14**.[18] Further electron transfer from **8** to intermediates **14** induces loss of "$Mo(CO)_5$" and formation of boron enolates **15**. Hydrolysis of **15** leads to the formal 1:1 Michael addition products **12**. The lack of formation of adducts with more than one alkene in their structure, when a large excess of electron-deficient

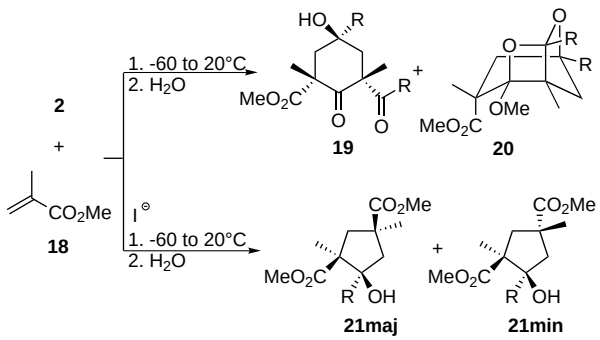
Abstract in Spanish: *Los pentacarbonil acil molibdatos **1** reaccionan con trifluoruro de boro para dar lugar a los complejos difluoroboroxicarbeno de Fischer **2**, que, a temperatura ambiente, experimentan una pérdida del fragmento metálico, originando 1,2-dicetonas **3**, 1,2-hidroxicetonas **4** o dímeros **5** a través de un proceso de dimerización o descarbonilación-dimerización de radicales acilo. La descomposición de **2** en presencia de los alquenos electrónicamente deficientes **11** y **18** conduce a los productos de acoplamiento de dos, tres y cuatro componentes **12**, **13**, **19**, **20** y **21**.*



Scheme 4. Mechanism explaining the formation of products **12** and **13**.

olefins is used, can be attributed to the stabilizing interaction between the boron atom and the oxygen atom of the carbonyl group in **15**, which prevents reaction with a second molecule of the alkene. Otherwise, formation of **13** can be understood by considering a second electron transfer from the radical species **8** to the boron enolates **15**, which affords the radical intermediates **16**.[19] These intermediates **16** can react with another molecule of acyl radical **7** to generate products **17**, which, after hydrolysis, lead to the hydroxy ketone derivatives **13**. The fact that products **13** were only observed when alkenes **11b** and **11e** were used can be attributed to their lower reactivity compared with 3-buten-2-one **11a**. Thus we considered that the concentration of acyl radicals **7** and species **8** would be higher when olefins **11b** or **11e** were used as trapping agents, allowing **8** to interact with the boron enolates **15**. In addition, the reluctance to form **13** when alkenes with $R^1 \neq H$ (**11c, d**) are used (Table 2, entries 9, 10), as well as when the R group of the carbene complex **2** is alkenyl or a bulky group (Table 2, entries 7, 8, 12) could be due either to steric hindrance or to electronic effects, which prevent the electron transfer from **8** to the ketone carbonyl group of **15**.

A completely different outcome was observed when methyl methacrylate **18** was used as trapping agent in the decomposition of difluoroboroxymolybdenun carbene complexes **2**. In these cases only small amounts (< 10%) of the Michael adducts analogous to **12** were obtained and the main reaction products were a mixture of the cyclohexanone derivatives **19** and the tricyclic compounds **20** (Scheme 5 and Table 3). Surprisingly, if the reaction described above is performed in the presence of iodide anions, the cyclopentanedicarboxylate



Scheme 5. Three- and four-component coupling reaction of difluoroboroxymolybdenum carbene complexes **2** and methyl methacrylate **18**.

Table 3. Reaction of difluoroboroxymolybdenum carbene complexes **2** and methyl methacrylate **18** to give compounds **19**, **20**, and **21**.

Entry	Starting carbene	R	Iodide	Product	Yield [%][a]
1	**2a**	Bu		**19a/20a**	36/30
2	**2g**	Pr		**19b/20b**	40/25
3	**2h**	n-C_8H_{17}		**19c**	52
4	**2a**	Bu	NaI[b]	**21a-maj/min**	36/13
5	**2g**	Pr	NaI	**21b-maj/min**	35/12
6	**2h**	n-C_8H_{17}	NaI	**21c-maj/min**	34/10
7	**2i**	n-C_7H_{15}	NaI	**21d-maj/min**	37/12

[a] Yield of isolated product based on $[Mo(CO)_6]$. [b] The reaction has also been carried out with LiI and KI and yields and diastereoisomeric ratio were very similar.

derivatives **21** were isolated as a mixture of diastereoisomers (Scheme 5 and Table 3). To determine the influence on other anions in the outcome of the reaction, a set of experiments were carried out using F^-, Cl^-, and Br^-. In all of these cases, **19** and **20** were the only products obtained and no trace of **21** was detected. Also, the formation of compounds **19**, **20**, or **21** is only observed when the R groups in difluroboroxymolybdenum carbene complexes **2** are primary alkyl groups. In contrast, if the reaction is carried out with **2f** ($R = c\text{-}C_5H_9$) we have only observed the formation of the Michael adduct methyl 4-cyclopentyl-2-methyl-4-oxo-butanoate (54%), analogous to **12**. The structure and relative configuration of the generated stereocenters of **19**, **20**, **21maj**, and **21min** were unequivocally determined by two-dimensional (COSY, HMQC, HMBC, and NOESY) NMR spectral analysis. Importantly, compounds **19** and **20** are the products of a four-component coupling reaction, two fragments coming from the carbene complex **2** and the other two coming from methyl methacrylate **18**. On the other hand, cyclopentanedicarboxylate derivatives **21** are the products of a three-component coupling reaction, two fragments coming from methyl methacrylate **18** and the other one coming from the carbene complex **2**. Also remarkable is the stereoselectivity found in the formation of **19** and **21**, where only two of the four possible diastereoisomers are obtained (**20** can be considered as a diastereoisomer of **19**).

Although we have no firm evidence regarding the course of the reaction leading to **19**, **20**, and **21**, a tentative, plausible mechanism is outlined in Scheme 6. All of the steps involved in this mechanism have been reported in the literature for related reactions. An initial addition of acyl radicals **7** to methyl methacrylate **18** results in the formation of the tertiary radicals **22**.[18] These radicals **22**, which are more stable than secondary radicals such as **14** (Scheme 4), collapse with a second molecule of acyl radical **7** to form the tricarbonyl compounds **23**. Further electron transfer from **8** to the most accessible carbonyl group of **23** produces ketyl radicals **24**,[19] which can add to another molecule of methyl methacrylate **18**, giving rise to new radical intermediates **25**.[20] A ring-closing reaction[21] leads to cyclohexane derivatives **26**, which form **27** after electron transfer from **8**. Final hydrolysis of these intermediates furnishes **19** and **20** (Scheme 6, pathway a). Formation of **19** or **20** seems to depend on the relative stereochemistry of the new chiral centers generated in the reaction.

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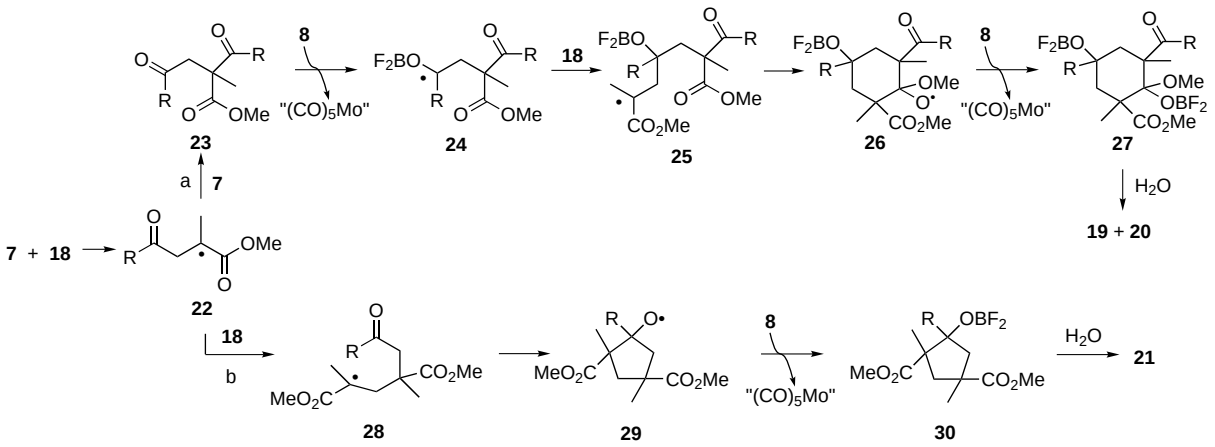

Scheme 6. Proposed mechanism for the generation of coupling products **19**, **20**, and **21**.

For the formation of 1,3-cyclopentanedicarboxylate derivatives **21**, we propose the mechanism outlined in Scheme 6, pathway b. We first consider the formation of tertiary radicals **22** as described above, but now these intermediates **22** are added to an additional molecule of methyl methacrylate **18** to form new tertiary radicals **28**. A ring-closing reaction[21] leads to **29**, which produces **30** after electron transfer from **8**. Final hydrolysis of **30** generates the cyclopentanedicarboxylate derivatives **21**. It is reasonable to assume a tight-radical structure for species **8** which would explain the long lifetime that allows it to participate in the different steps of the process.

As has been described above, the outcome of the reaction between difluoroboroxymolybdenum carbene complexes **2** and methyl methacrylate **18** is strongly dependent on the presence of iodide anions. The role of the iodide in these reactions is not clear, but it is reasonable to think that it is involved in the formation of acyl radicals **7**, especially in controlling their concentration in the reaction media. Thus, if the concentration of **7** is high enough, the radical intermediates **22** can interact with it to produce compounds **19** and **20** (Scheme 6, pathway a). In contrast, if the concentration of acyl radicals **7** is lower, presumably in the presence of iodide, intermediates **22** can be added to methyl methacrylate **18**, ultimately affording the cyclopentanedicarboxylate derivatives **21** (Scheme 6, pathway b). Finally, the reluctance to form the three- and four-component coupling products when R are secondary alkyl groups could be understood, on the basis of the proposed mechanism, as the result of the steric hindrance of the R group in the reaction of **22** with either **7** or **18**. Instead, electron transfer from **8**, followed by hydrolysis, is preferred and the Michael adduct is generated.

Conclusion

We have described a simple method of generating acyl radicals from difluoroboroxy Fischer carbene complexes under very mild reaction conditions and in the absence of an oxidant. These acyl radicals undergo dimerization to give 1,2-diketones or dimerization followed by reduction to afford 1,2-hydroxy ketones. Additionally, the acyl radicals can be trapped with electron-poor olefins, leading to 1,4-addition products or in some cases hydroxy ketones, which incorporate two fragments from the carbene complex and one from the alkene. Furthermore, the reaction of difluoroboroxymolybdenum carbene complexes with methyl methacrylate results in the formation of three- or four-component coupling products, depending on the reaction conditions, with a high degree of diastereoselectivity. All of these products are highly functionalized and are easily obtained starting from simple and easily available reagents.

Experimental Section

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2, using oven-dried glassware and syringes. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Merck). Flash column chromatography was carried out on silica gel 60, 230–240 mesh (Sds). Melting points were obtained on a Büchi–Tottoli apparatus with open capillary tubes and are uncorrected. ^1H (^{13}C) NMR spectra were recorded at 200 (50), 300 (75), or 400 (100) MHz with tetramethylsilane ($\delta = 0.0$, ^1H NMR) and $CDCl_3$ ($\delta = 77.0$, ^{13}C NMR) as internal standards. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on an HP 5987A instrument, and the intensities are reported as a percentage relative to the base peak after the corresponding *m/z* value. High-resolution mass spectra (HRMS) were determined on a Finnigan MAT95 spectrometer. Elemental analyses were performed with a Perkin Elmer elemental analyzer. All commercially available reagents were used without further purification unless otherwise indicated. Solvents were distilled under positive pressure of dry N_2 before use: Et_2O from sodium benzophenone ketyl.

Pentacarbonyl [difluroboroxy(phenyl)methylene]molybdenum (2b): To a well-stirred suspension of molybdenum hexacarbonyl (0.80 g, 3 mmol) in dry diethyl ether (30 mL), an ethereal solution of phenyllithium (3 mmol) was added at 0 °C and the solution was stirred for 1 h at room temperature. The solution was cooled to −60 °C and $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) was added. The resulting mixture was stirred under nitrogen at −60 °C for 15 min and then at −30 °C for 1 h. The solvent was removed under vacuum (0.1 mmHg) at low temperature (−30 °C), yielding the carbene complex **2b**, as a diethyl ether complex. It was rapidly characterized without any further purification. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 347.9$, 215.2, 206.3, 157.4, 130.8, 127.4, 124.8, 65.6, 14.5.

General procedure for the synthesis of diketones 3 and hydroxy ketones 4 or dimers 5: A solution of the pentacarbonyl acyl molybdate **1** in diethyl ether (30 mL) was obtained by reaction of molybdenum hexacarbonyl (0.80 g, 3 mmol) and the organolithium reagent (3 mmol) at −60 °C. $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) was slowly added and the resulting mixture was allowed to warm up to room temperature overnight. The mixture was

hydrolyzed with water and extracted with diethyl ether (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography (hexane:ethyl acetate) to afford products **3** and **4** or **5**. Spectral data for **3b**, **4b**, **5d**, and **5e** were in complete accordance with those of samples of commercially available products and spectral data for **3a**,[22] **3c**,[23] **4a**,[24] **4c**,[25] and **5c**[26] were in agreement with literature values.

General procedure for the synthesis of compounds 12 and 13: A solution of the pentacarbonyl acyl molybdate **1** in diethyl ether (30 mL) was obtained by reaction of molybdenum hexacarbonyl (0.80 g, 3 mmol) and the organolithium reagent (3 mmol) at $-60\,^{\circ}C$. $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) was slowly added. The solution was stirred at $-60\,^{\circ}C$ for 15 min and then an excess of the corresponding alkene **11** (2–10 equiv) was added. The resulting mixture was allowed to warm up to room temperature overnight. The mixture was hydrolyzed with water and extracted with diethyl ether (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography (hexane:ethyl acetate) to afford products **12** and **13**. Spectral data for **12a** and **12b** were in complete accordance with literature values.[27,28]

1-(2-Naphthyl)-1,4-pentanedione (12c): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with naphthyllithium (6 mL of a 0.5 M solution in diethyl ether, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and 3-buten-2-one **11a** (0.48 mL, 6 mmol). Work-up as described in the general procedure above produced **12c** (0.28 g) as a colorless oil. $R_f = 0.12$ (hexane/ethyl acetate 5:1); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.22$ (s, 3H; Me), 2.88 (t, $J = 6.2$ Hz, 2H; CH_2CO), 3.32 (t, $J = 6.2$ Hz, 2H; CH_2CO), 7.25–8.5 (m, 7H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 207.3$, 198.2, 135.2, 133.5, 132.1, 129.5, 129.2, 128.1, 127.4, 126.4, 123.4, 36.7, 32.1, 29.7; HRMS (70 eV, EI): calcd for $C_{15}H_{14}O_2$ [M^+] 226.1004, found 226.0994; elemental analysis (%) calcd for $C_{15}H_{14}O_2$: C 79.62, H 6.24; found: C 79.93, H 6.10.

(*E*)-7-Phenyl-6-hepten-2,5-dione (12d): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with (*E*)-2-phenylethenyllithium (10 mL of a 0.3 M solution in diethyl ether, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and 3-buten-2-one **11a** (0.48 mL, 6 mmol). Work-up as described above yielded **12d** (0.22 g) as a colorless oil. $R_f = 0.22$ (hexane/ethyl acetate 3:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.22$ (s, 3H; Me), 2.81 (t, $J = 6.4$ Hz, 2H; CH_2CO), 2.97 (t, $J = 6.4$ Hz, 2H; CH_2CO), 6.75 (d, $J = 16.3$ Hz, 1H; =CHCO), 7.35–7.5 (m, 5H; ArH), 7.58 (d, $J = 16.3$ Hz, 1H; =C*H*Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 207.2$, 198.3, 142.6, 134.2, 130.3, 128.7, 128.1, 125.7, 36.8, 34.0, 29.8; HRMS (70 eV, EI): calcd for $C_{13}H_{14}O_2$ [M^+] 202.0999, found 202.0993; elemental analysis (%) calcd for $C_{13}H_{14}O_2$: C 77.20, H 6.98; found: C 77.33, H 6.81.

1-Cyclopentyl-1,4-pentanedione (12e): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with cyclopentyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and 3-buten-2-one **11a** (0.48 mL, 6 mmol). Work-up as above yielded **12e** (0.26 g) as a colorless oil. $R_f = 0.30$ (hexane/ethyl acetate 5:1); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.45–1.90$ (m, 8H; $4 \times CH_2$ aliphatic ring), 2.17 (s, 3H; Me), 2.68–2.70 (m, 4H; $2 \times CH_2CO$), 2.88 (quintuplet, $J = 7.9$ Hz, 1H; CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 211.7$, 207.3, 51.1, 36.7, 35.0, 29.8, 28.7, 25.8; HRMS (70 eV, EI): calcd for $C_{10}H_{16}O_2$ [M^+] 168.1150, found 168.1149; elemental analysis (%) calcd for $C_{10}H_{16}O_2$: C 71.39, H 9.59; found: C 71.35, H 9.66.

Methyl 4-oxooctanoate (12f) and methyl 4-butyl-4-hydroxy-5-oxononanoate (13a): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with butyllithium (1.87 mL of a 1.6 M solution in hexanes, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl acrylate **11b** (2.7 mL, 30 mmol). Work-up as above yielded **12f** (0.16 g) and **13a** (0.22 g) as colorless oils.

12f: $R_f = 0.42$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.89 (t, $J = 7.1$ Hz, 3H; MeC), 1.22–1.41 (m, 2H; CH_2CH_3), 1.51–1.62 (m, 2H; CH_2CH_2Me), 2.43 (t, $J = 7.3$ Hz, 2H; CH_2CO), 2.56 (t, $J = 6.4$ Hz, 2H; CH_2CO), 2.71 (t, $J = 6.4$ Hz, 2H; CH_2CO), 3.66 (s, 3H; MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 209.0$, 173.3, 51.6, 42.3, 36.8, 27.6, 25.7, 22.2, 13.7. LRMS (70 eV, EI): *m/z* (%): 141 (50) [$M^+ - 31$], 130 (77), 115 (100), 98 (82), 85 (90), 57 (98); HRMS (70 eV, EI): calcd for $C_8H_{13}O_2$ [$M^+ - 31$] 141.0922, found 141.0915.

13a: $R_f = 0.36$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.89 (t, $J = 6.8$ Hz, 3H; MeC), 0.92 (t, $J = 6.8$ Hz, 3H; MeC), 1.19–148 (m, 4H; $2 \times CH_2$), 1.50–1.78 (m, 4H; $2 \times CH_2$), 1.97–2.17 (m, 4H; $2 \times CH_2$), 2.30–2.55 (m, 4H; $2 \times CH_2$), 3.68 (s, 3H; MeO), 3.97 (brs, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 213.9$, 173.7, 80.5, 51.6, 38.3, 35.6, 33.4, 28.2, 25.4, 25.2, 22.8, 22.2, 13.8; HRMS (70 eV, EI): calcd for $C_{14}H_{26}O_4$ [M^+] 258.1831, found 258.1831; elemental analysis (%) calcd for $C_{14}H_{26}O_4$: C 65.09, H 10.14; found: C 65.14, H 10.11.

Methyl 4-oxo-4-phenylbutanoate (12g): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with phenyllithium (6 mL of a 0.5 M solution in diethyl ether, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl acrylate **11b** (2.7 mL, 30 mmol). Work-up as above yielded **12g** (0.19 g) as a colorless oil. $R_f = 0.20$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.75$ (t, $J = 6.5$ Hz, 2H; CH_2), 3.31 (t, $J = 6.5$ Hz, 2H;, CH_2), 4.70 (s, 3H; Me), 7.20–8.10 (m, 5H; ArH); HRMS (70 eV, EI): calcd for $C_{11}H_{12}O_3$ [M^+] 192.0786, found 192.0788; elemental analysis (%) calcd for $C_{11}H_{12}O_3$: C 68.74, H 6.29; found: C 68.79, H 6.21.

Methyl (*E*)-6-phenyl-5-hexenoate (12h): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with (*E*)-2-phenylethenyllithium (10 mL of a 0.3 M solution in diethyl ether, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl acrylate **11b** (2.7 mL, 30 mmol). Work-up as above led to **12h** (0.22 g) as a colorless oil. $R_f = 0.20$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.70$ (t, $J = 6.4$ Hz, 2H; CH_2), 3.02 (t, $J = 6.4$ Hz, 2H; CH_2), 3.70 (s, 3H; Me), 6.75 (d, $J = 16.4$ Hz, 1H; =CHCO), 7.20–7.55 (m, 5H; ArH), 7.60 (d, $J = 16.4$ Hz, 1H; =C*H*Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 197.8$, 173.2, 142.8, 134.2, 130.4, 128.8, 128.2, 125.6, 51.6, 35.1, 27.7; LRMS (70 eV, EI): *m/z* (%): 218 (8) [M^+], 187 (15), 131 (100), 103 (50); HRMS (70 eV, EI): calcd for $C_{13}H_{14}O_3$ [M^+] 218.0951, found 218.0943.

Methyl 3-methyl-4-oxooctanoate (12i): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with butyllithium (1.87 mL of a 1.6 M solution in hexanes, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl crotonate **11c** (3 mL, 30 mmol). Work-up as above yielded **12i** (0.22 g) as a colorless oil. $R_f = 0.50$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.3$ Hz, 3H; *Me*CH_2), 1.10 (d, $J = 6.9$ Hz, 3H; *Me*CH), 1.18–1.32 (m, 2H; MeCH_2), 1.44–1.60 (m, 2H; MeCH_2CH_2), 2.23 (dd, $J = 16.8$, 5.1 Hz, 1H; CHHCO$_2$), 2.37–2.45 (m, 2H; CH_2CO), 2.72 (dd, $J = 16.8$, 9.0 Hz, 1H; CHHCO$_2$), 2.89–3.01 (m, 1H; CH), 3.59 (s, 3H; MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 212.8$, 172.6, 51.4, 41.8, 40.6, 36.5, 25.4, 22.1, 16.5, 13.6; LRMS (70 eV, EI): *m/z* (%): 186 (2) [M^+], 155 (35), 144 (45), 85 (100), 57 (98); HRMS (70 eV, EI): calcd for $C_{10}H_{18}O_3$ [M^+] 186.1257, found 186.1256.

Ethyl 4-oxo-3-phenyloctanoate (12j): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with butyllithium (1.87 mL of a 1.6 M solution in hexanes, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and ethyl cynnamate **11d** (2.5 mL, 15 mmol). Work-up as above yielded **12j** (0.29 g) as a colorless oil. $R_f = 0.60$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.80$ (t, $J = 7.3$ Hz, 3H; Me), 1.21 (t, $J = 7.3$ Hz, 3H; Me), 1.41–1.58 (m, 4H; $2 \times CH_2C$), 2.38–2.50 (m, 2H; CH_2CO), 2.52 (dd, $J = 16.8$, 4.7 Hz, 1H; CHHCO$_2$), 3.21 (dd, $J = 16.8$, 10.1 Hz, 1H; CHHCO$_2$), 4.09 (q, $J = 7.3$ Hz, 2H; CH_2O), 4.17 (dd, $J = 10.1$, 4.7, 1H; CH), 7.16–7.36 (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 209.0, 172.0, 137.5, 128.9, 128.1, 127.5, 60,5, 54.0, 41.1, 37.0, 25.6, 21.9, 145.0, 13.6; HRMS (70 eV, EI): calcd for $C_{16}H_{22}O_3$ [M^+] 262.1569, found 262.1573; elemental analysis (%) calcd for $C_{16}H_{22}O_3$: C 73.25, H 8.45; found: C 73.31, H 8.39.

4-Oxooctanenitrile (12k) and 4-butyl-4-hydroxy-5-oxononanenitrile (13b): Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with butyllithium (1.87 mL of a 1.6 M solution in hexanes, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and acrylonitrile **11e** (1.96 mL, 30 mmol). Work-up as above yielded **12k** (0.13 g) and **13b** (0.21 g) as colorless oils.

12k: $R_f = 0.22$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.90 (t, $J = 7.3$ Hz, 3H; Me), 1.28 (sextuplet, $J = 7.3$ Hz, 2H; CH_2Me), 1.57 (quintuplet, $J = 7.3$ Hz, 2H; CH_2CH_2Me), 2.44 (t, $J = 7.3$ Hz, 2H; CH_2CO), 2.57 (t, $J = 7.3$ Hz, 2H; CH_2CO), 2.78 (t, $J = 7.3$ Hz, 2H; CH_2CN); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 206.3$, 119.0, 42.0, 37.5, 25.6, 22.1, 13.6, 11.2; HRMS (70 eV, EI): calcd for $C_8H_{13}NO$ (M^+) 139.1000, found 139.0990.

13b: $R_f = 0.25$ (hexane/ethyl acetate 5:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.89 (t, $J = 6.8$ Hz, 3H; Me), 0.92 (t, $J = 6.8$ Hz, 3H; Me), 1.19–1.78 (m,

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10H; 5 × CH_2), 2.02–2.22 (m, 4H; 2 × CH_2), 2.50 (t, J = 7.4 Hz, 2H; CH_2CO), 4.00 (br s, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.8, 119.2, 79.9, 37.9, 35.7, 33.9, 25.3, 25.0, 22.8, 22.1, 13.7, 11.4; LRMS (70 eV, EI): *m/z* (%): 224 (4) [$M^+ - 1$], 140 (100), 85 (40), 57 (52), 41 (60); HRMS (70 eV, EI): calcd for $C_{13}H_{22}NO_2$ [$M^+ - 1$] 224.1650, found 224.1648.

4-Oxo-4-phenylbutanenitrile (12l): Reaction of [Mo(CO)$_6$] (0.80 g, 3 mmol) in diethyl ether (30 mL) with phenyllithium (6 mL of a 0.5 M solution in diethyl ether, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and acrylonitrile **11e** (1.96 mL, 30 mmol). Work-up as above yielded **12l** (0.18 g) as a colorless oil. R_f = 0.20 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.77 (t, J = 7.4 Hz, 2H; CH_2CO), 3.38 (t, J = 7.4 Hz, 2H; CH_2CN), 7.00–8.20 (m, 5H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.3, 135.5, 133.8, 128.8, 127.9, 119.1, 34.2, 11.7; LRMS (70 eV, EI): *m/z* (%): 159 (12) [M^+], 105 (100), 77 (83); HRMS (70 eV, EI): calcd for $C_{10}H_9NO$ [M^+] 159.0676, found 159.0684.

Synthesis of methyl 4-cyclopentyl-2-methyl-4-oxo-butanoate: A solution of the pentacarbonyl acyl molybdate **1** in diethyl ether (30 mL) was obtained by reaction of molybdenum hexacarbonyl (0.80 g, 3 mmol) and cyclopentyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) at −60 °C. $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) was slowly added, the solution was stirred at −60 °C for 15 min, and then an excess of methyl methacrylate **18** (3 g, 30 mmol) was added. The resulting mixture was allowed to warm up to room temperature overnight. The mixture was hydrolyzed with water and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography (hexane:ethyl acetate) to afford methyl 4-cyclopentyl-2-methyl-4-oxo-butanoate (0.32 g, 54%) as a colorless oil. R_f = 0.35 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, J = 7.0 Hz, 3H; MeC), 1.40–1.85 (m, 8H; 4 × CH_2 aliphatic ring), 2.46 (dd, J = 20.6, 8.4 Hz, 1H; CH*H*CO), 2.71–2.95 (m, 3H; C*H*HCO and 2 × CHCO), 3.60 (s, 3H; MeO); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.7, 176.1, 51.5, 51.0, 44.6, 34.3, 28.4, 25.7, 16.8; HRMS (70 eV, EI): calcd for $C_{11}H_{18}O_3$ [M^+] 198.1256, found 198.1260; elemental analysis (%) calcd for $C_{11}H_{18}O_3$: calcd C 66.64, H 9.15; found C 66.69, H 9.11.

General procedure for the synthesis of compounds 19 and 20: A solution of the pentacarbonyl acyl molybdate **1** in diethyl ether (30 mL) was obtained by reaction of molybdenum hexacarbonyl (0.80 g, 3 mmol) and the organolithium reagent (3 mmol) at −60 °C. $BF_3 \cdot OEt_2$ was slowly added (0.36 mL, 3 mmol), the solution was stirred at −60 °C for 15 min, and then an excess of methyl methacrylate **18** (3 g, 30 mmol) was added. The resulting mixture was allowed to warm up to room temperature overnight. The mixture was hydrolyzed with water and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography (hexane:ethyl acetate) to afford products **19** and **20**.

Methyl (1*R, 3*R**, 5*S**)-5-butyl-5-hydroxy-1,3-dimethyl-2-oxo-3-(1-oxopentyl)cyclohexanecarboxylate (19a) and methyl (1*S**, 3*R**, 5*R**, 6*R**, 9*R**)-1,3-dibutyl-5-methoxy-6,9-dimethyl-2,4-dioxa-9-tricyclo[3.2.2.0^{3,6}]nonanecarboxylate (20a)**: Reaction of [Mo(CO)$_6$] (0.80 g, 3 mmol) in diethyl ether (30 mL) with butyllithium (1.87 mL of a 1.6 M solution in hexanes, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl methacrylate **18** (3 g, 30 mmol). Work-up as above yielded **19a** (0.37 g) and **20a** (0.32 g) as colorless oils.

19a: R_f = 0.25 (hexane/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, J = 5.6 Hz, 3H; *Me*CH_2), 0.90 (t, J = 5.6 Hz, 3H; *Me*CH_2), 1.02–1.70 (m with 2s at 1.12 and 1.38, 16H; 5 × CH_2 and 2 × MeC), 2.20 (d, J = 14.2 Hz, 1H; C*H*HCO$_2$), 2.38–2.50 (m, 2H; CH_2CO), 2.61 (d, J = 14.2 Hz, 1H; CH*H*CO$_2$), 2.62 (d, J = 19.0 Hz, 1H; C*H*HCO), 3.01 (d, J = 19.0 Hz, 1H; CH*H*CO), 3.71 (s, 3H; MeO), 4.08 (br s, 1H; OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.8, 211.9, 173.1, 76.9, 56.4, 55.4, 52.8, 47.7, 43.0, 41.3, 37.8, 25.7, 25.2, 23.0, 22.0, 19.0, 13.9, 13.6; HRMS (70 eV, EI): calcd for $C_{19}H_{32}O_5$ [M^+] 340.2250, found 340.2250; elemental analysis (%) calcd for $C_{19}H_{32}O_5$: C 67.03, H 9.47; found C 67.14, H 9.39.

20a: R_f = 0.55 (hexane/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 5.8 Hz, 3H; *Me*CH_2), 0.90 (t, J = 5.8 Hz, 3H; *Me*CH_2), 1.12 (s, 3H; *Me*CBu), 1.20–1.40 (m with s at 1.32, 13H; 5 × CH_2 and MeCCO$_2$), 1.42 (d, J = 14.6 Hz, 1H; C*H*HCCO$_2$Me), 1.58 (d, J = 9.9 Hz, 1H; C*H*HCCBu), 1.71 (d, J = 9.9 Hz, 1H; CH*H*CCBu), 1.72–1.76 (m, 2H; CH_2COO), 3.02 (d, J = 14.6 Hz, 1H; CH*H*CCO$_2$Me), 3.44 (s, 3H; CO_2Me), 3.68 (s, 3H; MeO); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.0, 111.3, 106.9, 87.9, 58.1, 54.3, 51.7, 50.8, 42.8, 41.8, 34.5, 30.9, 26.5, 25.3, 23.7, 23.3, 22.7, 13.9, 13.8, 10.9; HRMS (70 eV, EI): calcd for $C_{20}H_{34}O_5$ [M^+] 354.2406, found 354.2411; elemental analysis (%) calcd for $C_{20}H_{34}O_5$: C 67.77, H 9.67; found: C 67.90, H 9.59.

Methyl (1*R, 3*R**, 5*S**)-5-hydroxy-1,3-dimethyl-2-oxo-3-(1-oxobutyl)-5-propyl cyclohexanecarboxylate (19b) and methyl (1*S**, 3*R**, 5*R**, 6*R**, 9*R**)-5-methoxy-6,9-dimethyl-1,3-dipropyl-2,4-dioxa-9-tricycle[3.2.2.0^{3,6}]-nonanecarboxylate (20b)**: Reaction of [Mo(CO)$_6$] (0.80 g, 3 mmol) in diethyl ether (30 mL) with propyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl methacrylate **18** (3 g, 30 mmol). Work-up as above yielded **19b** (0.37 g) and **20b** (0.24 g) as colorless oils.

19b: R_f = 0.25 (hexane/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, J = 5.6 Hz, 3H; *Me*CH_2), 0.90 (t, J = 5.6 Hz, 3H; *Me*CH_2), 1.02–1.70 (m with 2s at 1.15 and 1.38, 12H; 3 × CH_2 and 2 × MeC), 2.17 (d, J = 14.2 Hz, 1H; C*H*HCCO$_2$), 2.35–2.42 (m, 2H; CH_2CO), 2.59 (d, J = 14.2 Hz, 1H; CH*H*CCO$_2$), 2.60 (d, J = 19.0 Hz, 1H; C*H*HCCO), 2.97 (d, J = 19.0 Hz, 1H; CH*H*CCO), 3.68 (s, 3H; MeO), 4.08 (br s, 1H; OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.8, 211.7, 173.0, 76.5, 56.3, 55.3, 52.8, 47.6, 45.1, 41.2, 40.4, 21.9, 18.9, 17.1, 16.3, 14.4, 13.4; LRMS (70 eV, EI): *m/z* (%): 312 (2) [M^+], 294 (17), 241 (38), 235 (68), 223 (52), 165 (88), 129 (80), 69 (100); HRMS (70 eV, EI): calcd for $C_{17}H_{28}O_5$ [M^+] 312.1936, found 312.1938.

20b: R_f = 0.55 (hexane/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 5.8 Hz, 3H; *Me*CH_2), 0.90 (t, J = 5.8 Hz, 3H; *Me*CH_2), 1.13 (s, 3H; *Me*CPr), 1.31 (s, 3H; MeCCO$_2$), 1.32–1.55 (m with d at 1.42, J = 14.6 Hz, 7H; 3 × CH_2 and C*H*HCCO$_2$Me), 1.58 (d, J = 9.9 Hz, 1H; C*H*HCCPr), 1.67–1.74 (m with d at 1.70, J = 9.9 Hz, 3H; CH_2COO and CH*H*CCPr), 3.02 (d, J = 14.6 Hz, 1H; CH*H*CCO$_2$Me), 3.44 (s, 3H; CO_2Me), 3.69 (s, 3H; MeO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.0, 111.3, 106.8, 87.9, 58.1, 54.3, 51.7, 50.8, 42.8, 41.8, 37.1, 33.3, 23.7, 17.8, 16.5, 14.7, 14.2, 10.9; HRMS (70 eV, EI): calcd for $C_{18}H_{30}O_5$ (M^+) 326.2093, found 326.2094; elemental analysis (%) calcd for $C_{18}H_{30}O_5$: C 66.23, H 9.26; found: C 66.29, H 9.19.

Methyl (1*R, 3*R**, 5*S**)-5-hydroxy-1,3-dimethyl-5-octyl-2-oxo-3-(1-oxobutyl)cyclohexanecarboxylate (19c)**: Reaction of [Mo(CO)$_6$] (0.80 g, 3 mmol) in diethyl ether (30 mL) with octyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) and methyl methacrylate **18** (3 g, 30 mmol). Work-up as above led to **19c** (0.70 g) as a colorless oil. R_f = 0.27 (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 5.6 Hz, 3H; *Me*CH_2), 0.87 (t, J = 5.6 Hz, 3H; *Me*CH_2), 1.02–1.75 (m with 2s at 1.13 and 1.41, 32H; 13 × CH_2 and 2 × MeC), 2.20 (d, J = 14.2 Hz, 1H; C*H*HCCO$_2$), 2.38–2.48 (m, 2H; CH_2CO), 2.62 (d, J = 14.2 Hz, 1H; CH*H*CCO$_2$), 2.63 (d, J = 19.0 Hz, 1H; C*H*HCCO), 3.00 (d, J = 19.0 Hz, 1H; CH*H*CCO), 3.70 (s, 3H; MeO), 4.10 (br s, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 215.8, 212.0, 173.1, 76.5, 56.5, 55.4, 52.9, 47.7, 43.3, 41.3, 38.2, 31.7, 31.6, 30.0, 29.4, 29.2, 29.1, 29.0, 23.8, 23.0, 22.5, 22.0, 19.0, 13.9; HRMS (70 eV, EI): calcd for $C_{27}H_{48}O_5$ [M^+] 452.3502, found 452.2505; elemental analysis (%) calcd for $C_{27}H_{48}O_5$: C 71.64, H 10.69; found: C 71.74, H 10.57.

General procedure for the synthesis of compounds 21: A solution of the pentacarbonyl acyl molybdate **1** in diethyl ether (30 mL) was obtained by reaction of [Mo(CO)$_6$] (0.80 g, 3 mmol) and the organolithium reagent (3 mmol) at −60 °C. $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol) was slowly added, the solution was stirred at −60 °C for 15 min, and then an excess of methyl methacrylate **18** (3 g, 30 mmol) and sodium iodide[29] (0.9 g, 6 mmol) was added. The resulting mixture was allowed to warm up to room temperature overnight. The mixture was hydrolyzed with water and extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by flash column chromatography (hexane:ethyl acetate) to afford products **21**.

Dimethyl (1*S, 2*R**, 4*R**)-4-butyl-4-hydroxy-1,3-dimethyl-1,3-cyclopentanedicarboxylate (21a-maj) and dimethyl (1*S**, 2*R**, 4*S**)-4-butyl-4-hydroxy-1,3-dimethyl-1,3-cyclopentanedicarboxylate (21a-min)**: Reaction of [Mo(CO)$_6$] (0.80 g, 3 mmol) in diethyl ether (30 mL) with butyllithium (1.87 mL of a 1.6 M solution in hexanes, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol), methyl methacrylate **18** (3 g, 30 mmol), and

sodium iodide (0.9 g, 6 mmol). Work-up as above yielded **21a-maj** (0.30 g) and **21a-min** (0.11 g) as colorless oils.

21a-maj: $R_f = 0.22$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.22 (s, 3H; MeCCO), 1.32 (s, 3H; *Me*CCH_2CO), 1.18–1.90 (m, 6H; $3 \times CH_2$), 1.56 (d, $J = 14.4$ Hz, 1H; CC*H*HC), 1.70 (d, $J = 14.3$ Hz, 1H; C*H*HCO), 2.52 (d, $J = 14.3$ Hz, 1H; CH*H*CO), 3.23 (d, $J = 14.4$ Hz, 1H; CCH*H*C), 3.59 (br s, 1H; OH), 3.68 and 3.71 (2s, 6H; $2 \times$ MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 179.8$, 176.2, 85.3, 56.9, 52.4, 51.8, 47.6, 47.0, 45.8, 34.7, 27.7, 26.3, 23.2, 23.0, 14.0; HRMS (70 eV, EI): calcd for $C_{15}H_{26}O_5$ [M^+] 286.1780, found 286.1784; elemental analysis (%) calcd for $C_{15}H_{26}O_5$: C 62.91, H 9.15; found: C 62.99, H 9.08.

21a-min: $R_f = 0.37$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.10 (s, 3H; MeCCO), 1.41 (s, 3H; *Me*CCH_2CO), 1.20–1.70 (m, 6H; $3 \times CH_2$), 1.78 (d, $J = 14.6$ Hz, 1H; C*H*HCO), 2.32 (d, $J = 14.5$ Hz, 1H; CC*H*HC), 2.41 (d, $J = 14.5$ Hz, 1H; CCH*H*C), 2.43 (d, $J = 14.6$ Hz, 1H; CH*H*CO), 3.37 (br s, 1H; OH), 3.67 (s, 3H; MeO), 3.69 (s, 3H; MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 179.2$, 177.3, 85.3, 56.1, 52.1, 51.8, 47.3, 46.4, 45.9, 35.7, 28.6, 26.2, 23.2, 20.8, 14.0; HRMS (70 eV, EI): calcd for $C_{15}H_{26}O_5$ (M^+) 286.1780, found 286.1784; elemental analysis (%) calcd for $C_{15}H_{26}O_5$: C 62.91, H 9.15; found: C 63.02, H 9.06.

Dimethyl (1*S, 2*R**, 4*R**)-4-hydroxy-1,3-dimethyl-4-propyl-1,3-cyclopentanedicarboxylate (21b-maj) and dimethyl (1*S**, 2*R**, 4*S**)-4-hydroxy-1,3-dimethyl-4-propyl-1,3-cyclopentanedicarboxylate (21b-min)**: Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with propyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol), methyl methacrylate **18** (3 g, 30 mmol), and sodium iodide (0.9 g, 6 mmol). Work-up as above yielded **21b-maj** (0.28 g) and **21b-min** (0.10 g) as colorless oils.

21b-maj: *$R_f = 0.25$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 6.7$ Hz, 3H; MeCH_2), 1.22 (s, 3H; MeCCO), 1.33 (s, 3H; MeCCH_2CO), 1.18–1.90 (m, 4H; $2 \times CH_2$), 1.58 (d, $J = 14.4$ Hz, 1H; CC*H*HC), 1.71 (d, $J = 14.3$ Hz, 1H; C*H*HCO), 2.51 (d, $J = 14.3$ Hz, 1H; CH*H*CO), 3.24 (d, $J = 14.4$ Hz, 1H; CCH*H*C), 3.68 (s, 3H, MeO), 3.70 (s, 3H, MeO), 3.79 (br s, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 179.9$, 176.2, 85.3, 56.9, 52.4, 51.8, 47.6, 47.1, 45.8, 37.3, 27.7, 23.0, 17.4, 14.6; HRMS (70 eV, EI): calcd for $C_{14}H_{24}O_5$ [M^+] 272.1624, found 272.1622; elemental analysis (%) calcd for $C_{14}H_{24}O_5$: C 61.74, H 8.88; found: C 61.67, H 8.81.

21b-min: $R_f = 0.35$ (hexane/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.11 (s, 3H; MeCCO), 1.42 (s, 3H; *Me*CCH_2CO), 1.20–1.72 (m, 4H; $2 \times CH_2$), 1.77 (d, $J = 14.6$ Hz, 1H; C*H*HCO), 2.32 (d, $J = 14.5$ Hz, 1H; CC*H*HC), 2.42 (d, $J = 14.5$ Hz, 1H; CCH*H*C), 2.43 (d, $J = 14.6$ Hz, 1H; CH*H*CO), 3.39 (br s, 1H; OH), 3.67 (s, 3H; MeO), 3.69 (s, 3H, MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 179.2, 177.3, 85.3, 56.1, 52.1, 51.8, 47.3, 46.4, 45.9, 38.4, 28.6, 20.8, 17.3, 14.6; HRMS (70 eV, EI): calcd for $C_{14}H_{24}O_5$ [M^+] 272.1624, found 272.1623; $C_{14}H_{24}O_5$: C 61.74, H 8.88; found: C 61.78, H 8.80.

Dimethyl (1*S, 2*R**, 4*R**)-4-hydroxy-1,3-dimethyl-4-octyl-1,3-cyclopentanedicarboxylate (21c-maj) and dimethyl (1*S**, 2*R**, 4*S**)-4-hydroxy-1,3-dimethyl-4-octyl-1,3-cyclopentanedicarboxylate (21c-min)**: Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with octyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol), methyl methacrylate **18** (3 g, 30 mmol), and sodium iodide (0.9 g, 6 mmol). Work-up as above yielded **21c-maj** (0.35 g) and **21c-min** (0.10 g) as colorless oils.

21c-maj: $R_f = 0.25$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.21 (s, 3H; MeCCO), 1.32 (s, 3H; *Me*CCH_2CO), 1.15–1.92 (m, 14H; $7 \times CH_2$), 1.58 (d, $J = 14.4$ Hz, 1H; CC*H*HC), 1.70 (d, $J = 14.3$ Hz, 1H; C*H*HCO), 2.52 (d, $J = 14.3$ Hz, 1H; CH*H*CO), 3.26 (d, $J = 14.4$ Hz, 1H; CCH*H*C), 3.69 (s, 3H; MeO), 3.71 2s, 3H; MeO), 3.79 (br s, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 179.9$, 176.2, 85.3, 56.9, 52.4, 51.8, 47.6, 47.0, 45.8, 35.0, 31.7, 30.2, 29.5, 29.1, 27.7, 24.1, 23.0, 22.5, 13.9; HRMS (70 eV, EI): calcd for $C_{19}H_{34}O_5$ [M^+] 342.2406, found 342.2411; elemental analysis (%) calcd for $C_{19}H_{34}O_5$: C 66.64, H 10.01; found C 66.71, H 9.91.

21c-min: $R_f = 0.40$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.11 (s, 3H; MeCCO), 1.41 (s, 3H; *Me*CCH_2CO), 1.15–1.70 (m, 14H; $7 \times CH_2$), 1.78 (d, $J = 14.6$ Hz, 1H; C*H*HCO), 2.31 (d, $J = 14.5$ Hz, 1H; CC*H*HC), 2.41 (d, $J = 14.5$ Hz, 1H; CCH*H*C), 2.43 (d, $J = 14.6$ Hz, 1H; CH*H*CO), 3.37 (br s, 1H; OH), 3.67 (s, 3H, MeO), 3.69 (s, 3H, MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 179.2$, 177.3, 85.3, 56.1, 52.1, 51.8, 47.3, 46.3, 45.9, 36.1, 31.7, 30.1, 29.5, 29.1, 28.6, 24.0, 22.5, 20.8, 13.9; HRMS (70 eV, EI): calcd for $C_{19}H_{34}O_5$ [M^+] 342.2406, found 342.2409; elemental analysis (%) calcd for $C_{19}H_{34}O_5$: C 66.64, H 10.01; found: C 66.69, H 9.94.

Dimethyl (1*S, 2*R**, 4*R**)-4-heptyl-4-hydroxy-1,3-dimethyl-1,3-cyclopentanedicarboxylate (21d-maj) and dimethyl (1*S**, 2*R**, 4*S**)-4-heptyl-4-hydroxy-1,3-dimethyl-1,3-cyclopentanedicarboxylate (21d-min)**: Reaction of $[Mo(CO)_6]$ (0.80 g, 3 mmol) in diethyl ether (30 mL) with heptyllithium (10 mL of a 0.3 M solution in hexane, 3 mmol) was followed by addition of $BF_3 \cdot OEt_2$ (0.36 mL, 3 mmol), methyl methacrylate **18** (3 g, 30 mmol), and sodium iodide (0.9 g, 6 mmol). Work-up as above yielded **21d-maj** (0.36 g) and **21d-min** (0.12 g) as colorless oils.

21d-maj: $R_f = 0.25$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.21 (s, 3H; MeCCO), 1.32 (s, 3H; *Me*CCH_2CO), 1.15–1.92 (m, 12H; $6 \times CH_2$), 1.55 (d, $J = 14.2$ Hz, 1H; CC*H*HC), 1.68 (d, $J = 14.6$ Hz, 1H; C*H*HCO), 2.50 (d, $J = 14.6$ Hz, 1H; CH*H*CO), 3.22 (d, $J = 14.2$ Hz, 1H; CCH*H*C), 3.66 (s, 3H; MeO), 3.68 (s, 3H; MeO), 3.76 (br s, 1H; OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 179.9$, 176.2, 85.3, 56.9, 52.4, 51.8, 47.6, 47.0, 45.8, 35.0, 31.7, 30.1, 29.2, 27.7, 24.1, 23.0, 22.5, 13.9; HRMS (70 eV, EI): calcd for $C_{18}H_{32}O_5$ [M^+] 328.2249, found 328.2239.

21d-min: $R_f = 0.40$ (hexane/ethyl acetate 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 6.7$ Hz, 3H; *Me*CH_2), 1.12 (s, 3H; MeCCO), 1.41 (s, 3H; *Me*CCH_2CO), 1.08–1.70 (m, 12H; $6 \times CH_2$), 1.78 (d, $J = 14.6$ Hz, 1H; C*H*HCO), 2.31 (d, $J = 14.5$ Hz, 1H; CC*H*HC), 2.40 (d, $J = 14.5$ Hz, 1H; CCH*H*C), 2.43 (d, $J = 14.6$ Hz, 1H; CH*H*CO), 3.37 (br s, 1H; OH), 3.67 (s, 3H, MeO); 3.69 (s, 3H, MeO); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 179.2, 177.3, 85.3, 56.1, 52.1, 51.9, 47.3, 46.4, 46.0, 36.1, 31.7, 30.1, 29.2, 28.7, 24.0, 22.5, 20.9, 14.0; HRMS (70 eV, EI): calcd for $C_{18}H_{32}O_5$ [M^+] 328.2249, found 328.2239.

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