Synthesis and Radical Polymerization of Various 2-Cyclopropylacrylates[‡]

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Fourteen new alkyl 2-cyclopropylacrylates **1a–n** with various substituents R^1–R^5 were synthesized from readily available precursors by applying standard transformations such as cyanohydrin formation from an aldehyde, alcoholysis to an α-hydroxycarboxylic ester, oxidation and Wittig methylenation of an α-oxocarboxylic ester. Overall yields ranged from 33 to 54%. A new method for the hydrolysis of dimethyl cyclopropanedicarboxylates to the corresponding half-esters was developed. The α-oxocarboxylates **7g–n** were prepared by dirhodium tetraacetate catalyzed cyclopropanation of alkenes **8g–n** with methyl or ethyl diazopyruvate in 32–58% yield. The monomers **1a–n** were characterized by ^{1}H, ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. The radical homopolymerizations of **1a–n** were carried out with 2,2′-azabisisobutyronitrile (AIBN) as initiator in chlorobenzene at 65 °C. The highest polymer yields were obtained in the polymerizations of **1f** and **1h** or **1k** and **1l**, i.e. from monomers with an annelated five- or six-membered ring. In the case of **1h** and **1k**, both the polymer yields (99 and 98%, respectively) and the glass transition temperatures (T_g) of 57 and 93 °C were significantly higher than those observed for the polymer from 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (**DECVCP**), which was used as a benchmark for the monomer reactivities in the radical polymerizations of all the vinylcyclopropane derivatives **1a–n**. The bicyclic monomers **1h** and **1k** also demonstrated drastically improved reactivities in the radical copolymerization with methyl methacrylate when compared to **DECVCP**.

Introduction

2-Vinylcyclopropane-1,1-dicarboxylates are interesting monomers because they demonstrate less polymerization shrinkage than other vinyl monomers, such as methacrylates.[1,2] They undergo radical ring-opening polymerization, resulting in polymers which mainly contain 1,5-disubstituted pent-2-enyl subunits. Low polymerization shrinkage makes such cyclic monomers attractive as components of dental adhesives or filling composites. For an application in dental composites the monomers should, among other properties, exhibit a high rate of polymerization and improved mechanical properties.[3] For the latter, it is important that the corresponding homopolymers of the cyclic monomers attain both a high molecular weight and a glass transition temperature (T_g) higher than ca. 60 °C. In contrast to other ring-opening low-shrinkage monomers, such as spiro-orthocarbonates or cyclic ketene acetals, the 2-vinylcyclopropane-1,1-dicarboxylates are stable in the presence of humidity, acidic and basic impurities, and inorganic fillers. In addition, they show a greater tendency to undergo radical copolymerization with other vinyl monomers. However, in comparison with methacrylates, 2-vinylcyclopropane-1,1-dicarboxylates are less reactive in the radical copolymerization,[4] and this restricts their practical application. The reactivities of the vinylcylopropanes in the radical polymerization depend on their structure and therefore can be influenced by the number and type of substituents or the introduction of bicyclic structural units.[2]

Previously, we reported on the synthesis and polymerization of methyl 2-(bicyclo[3.1.0]hex-1-yl)acrylate, whose reactivity in radical copolymerization was found to be higher than that of methyl methacrylate.[1] Here we describe the synthesis and radical polymerization of both methyl and ethyl 2-cyclopropylacrylates bearing various substituents (**1a−e**,**g**) as well as bicyclic methyl or ethyl 2-cyclopropylacrylates (**1f**,**h−n**) with variation in the size of the second ring (Scheme 1).

[‡] Polymerization of cyclic monomers, 11. Part 10: Ref.[1] For one of us (A. d. M.), this is to be considered as Part 98 in the series "Cyclopropyl Building Blocks for Organic Synthesis". Part 97: S. Wiedemann, K. Rauch, I. Marek, A. de Meijere, *Eur. J. Org. Chem.* **2003**, 631−635; Part 96: S. I. Kozhushkov, R. Langer, D. S. Yufit, J. A. K. Howard, H. Schill, D. Demus, K. Miyazawa, A. de Meijere, *Eur. J. Org. Chem.* **2004**, 289−303.

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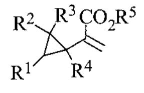


1a–n

1	R^1	R^2	R^3	R^4	R^5
a	H	H	H	H	Me
b	H	CH_2=		H	Me
c	H	▷=		H	Me
d	CO_2Me	H	H	H	Me
e	H	CO_2Et	CO_2Et	H	Et
f	$(CH_2)_3$		H	CO_2Me	Me
g	CH_2=CH	H	H	H	Et
h	$(CH_2)_3$		H	H	Me
i	$(CH_2)_3$		H	H	Et
j	CH_2CMe_2		H	H	Et
k	$(CH_2)_4$		H	H	Me
l	$(CH_2)_4$		H	H	Et
m	$(CH_2)_2$CH=CH		H	H	Et
n	$(CH_2)_6$		H	H	Et

Scheme 1. Variously substituted cyclopropylacrylates **1a**−**n** synthesized in this work

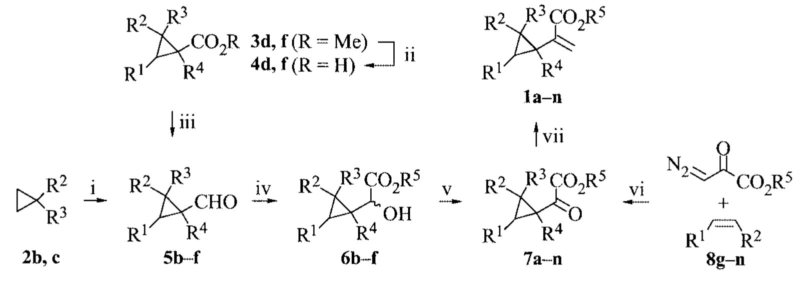
Results and Discussion

Synthesis of New Monomers

The unsubstituted and the cyclopropane ring-substituted alkyl 2-cyclopropylacrylates **1a**−**n** were prepared by Wittig methylenation of the corresponding alkyl 2-cyclopropyl-2-oxoacetates, which were synthesized by two different methods (Scheme 2) depending on the substitution pattern of the cyclopropane ring.

The first route relies on transformations of functional groups, which are already attached to the cyclopropane ring. The key precursors to compounds **7a**−**f**, such as potassium cyclopropyloxoacetate,[5] which is smoothly converted into the methyl ester **7a** upon heating with methyl iodide in acetone, or the substituted formylcyclopropanes **5b**−**f**, are accessible on large scales. The aldehydes **5b**,**c** were prepared on a 0.2-mol scale by formylation of the lithiated methylenecyclopropanes **2b**,**c** with DMF,[6] according to an improved protocol, in good yields (82 and 66%, respectively). The aldehyde **5e** was prepared in 83% yield according to a previously reported procedure.[7] For the preparation of aldehydes **5d**,**f** a new saponification protocol for dimethyl cyclopropanedicarboxylates **3d**,**f** leading to half-esters **4d**,**f** in high yields and, in the case of **3f**, with excellent regioselectivity, was developed. Thus, the bicyclic *gem*-diester **3f** was hydrolyzed with lithium hydroxide monohydrate, suspended in a mixture of tetrahydrofuran and methanol (4:1), to give only the *exo*-carboxylic acid **4f** in 83% yield, the configuration of which was also confirmed by an X-ray crystal structure analysis.[8] The obtained half-esters **4d**,**f** were smoothly converted into the corresponding aldehydes **5d**,**f** by catalytic hydrogenation of the corresponding acyl chlorides in the presence of 10% Pd/C and equimolar amounts of 2,6-lutidine according to an adopted protocol for a Rosenmund reduction.[9] The aldehydes **5b**−**f** were transformed via the respective cyanohydrins, prepared as described previously,[10] to the corresponding alkyl 2-cyclopropyl-2-hydroxyacetates **6b**−**f**. The cyanohydrins, derived from **5b**,**c** which could undergo acid-catalyzed side reactions, required milder methanolysis conditions (General Procedure 2A)[1,11] to yield the respective 2-hydroxyacetates **6b**,**c** in good yields, while the less sensitive cyanohydrins prepared from **5d**−**f** were smoothly converted into the α-hydroxy esters **6d**−**f** by treatment with anhydrous methanol saturated with dry HCl at −20 °C (General Procedure 2B). It should also be noted that hydrolysis of the intermediate imino ester hydrochlorides usually required 1−2 h, while overnight stirring at ambient temperature was necessary to completely solvolyze the respective imino ester hydrochloride to the α-hydroxy ester **6f**. This might be caused by formation of an intermediate pyrroline derivative, which would undergo hydrolysis more slowly than the corresponding imino ester hydrochloride.

The synthesized alkyl 2-cyclopropyl-2-hydroxyacetates were oxidized with active manganese dioxide according to a previously reported protocol,[1,12] to give the respective α-oxoacetates **7b**−**f** in good yields (71−88%).



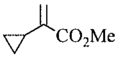
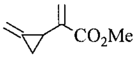
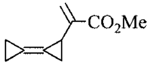
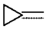
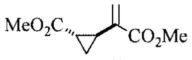
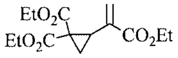
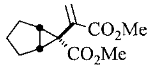
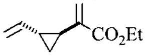
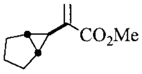
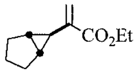
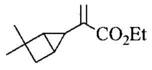
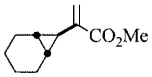
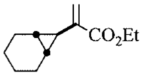
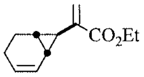
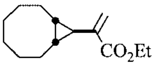
Scheme 2. Synthesis of substituted cyclopropylacrylates **1a**−**n**; reagents and conditions: i. 1) *n*BuLi, THF, 0 °C, 1 h, 2) DMF, −78 → 0 °C, 30 min, 3) 2 M H_2SO_4, 0 → 20 °C; ii. $LiOH{\cdot}H_2O$, MeOH, THF, 20 °C, 24 h; iii. 1) $(COCl)_2$, C_6H_6, 2 h, 20 °C, 2) H_2, 10 wt.% Pd/C, 2,6-lutidine, THF, 12 h, 20 °C; iv. 1) NaCN, NH_4Cl, Et_2O, H_2O, 10 °C, 40 min, 2) HCl, R^5OH, Et_2O, 2 °C, 16 h (GP 2A) or HCl, R^5OH, −10 → 20 °C, 2 h (GP 2B); v. MnO_2, Et_2O, 20 °C, 6 h; vi. 0.2 mol % $[Rh_2(OAc)_4]$, CH_2Cl_2, 16 h; vii. CH_3PPh_3Br, *n*BuLi, *i*Pr_2NH (GP 5A) or 10 mol % *i*Pr_2NH (GP 5B), THF, −78 → 20 °C, 12 h or CH_3PPh_3Br, *t*BuOK, THF, −30 → 20 °C, 16 h (GP 5C); for substituents R^1−R^5 see Scheme 1

The α-oxoacetates **7g−n** were prepared by a different route in moderate yields (32−58%) by rhodium(II) acetate catalyzed addition of alkyl diazopyruvates to the corresponding alkenes **8g−n**, according to a protocol adopted from Wenkert at al.[13]

The methylenation of α-oxoacetates was tested on **7a** as a model compound, by applying various Wittig olefination protocols. Thus, the ylide generated from methyltriphenylphosphonium bromide with bases such as sodium hydride in tetrahydrofuran, or with *n*-butyllithium in tetrahydrofuran or diethyl ether,[5] led only to partial conversion of **7a** providing the α-methyleneacetate **1a** in moderate yields (< 55%). This may be attributed to partial enolization, since about 40% of **7a** could be recovered from the reaction mixture. Reaction of **7a** with the ylide generated from methyltriphenylphosphonium bromide with sodium hydride in dimethyl sulfoxide or with potassium *tert*-butoxide in tetrahydrofuran gave only mixtures of products. It was found that only the ylide generated with lithium diisopropylamide (LDA) in tetrahydrofuran according to the protocol of Wenkert at al.,[13] which had previously been successfully applied for the methylenation of **7g** to **1g**, converted smoothly compounds **7a−c**,**m** to the respective acrylates **1a−c**,**m** in good yields (65−80%, Table 1).

However, even this method has some drawbacks. Generation of the ylide with LDA required 2 h of stirring at low temperature (−40 °C) and 2 h at ambient temperature. Moreover, methylenation of α-oxo esters with an additional alkoxycarbonyl group turned out to be problematic. Thus, attempts to methylenate **7d** according to this protocol gave the desired product **1d** only in moderate yield (44%). Therefore, an improved methylenation protocol was developed. It turned out that generation of the ylide from methyltriphenylphosphonium bromide with *n*-butyllithium in the presence of 5−10 mol % of diisopropylamine proceeds at the same rate as without it, and provides a homogeneous ylide solution just upon warming the reaction mixture from −78 °C to ambient temperature over 1 h. On the other

Table 1. The various 2-cyclopropylacrylates **1a−n** prepared; for details see Schemes 1 and 2

Product, **1a-n**		R^1	R^2	R^3	R^4	R^5	Product, Yield (%)			
							5	**6**	**7**	**1**
	**a**	H	H	H	H	Me	–	–	59	74[a]
	**b**	H	CH_2=		H	Me Et	82	62 –	88 –	65[a] 75[b]
	**c**	H			H	Me	66	76	75	80[a]
	**d**	CO_2Me	H	H	H	Me	85	A, 44 B, 63	71	44[a] 79[b]
	**e**	H	CO_2Et	CO_2Et	H	Et	83	A, 51 B, 82	78	81[b]
	**f**	$(CH_2)_3$		H	CO_2Me	Me	88	B, 94	84	19[b] 78[c]
	**g**	CH_2=CH	H	H	H	Et	–	–	32	79[a]
	**h**	$(CH_2)_3$		H	H	Me	–	–	49	85[b]
	**i**	$(CH_2)_3$		H	H	Et	–	–	48	86[b]
	**j**	CH_2CMe_2		H	H	Et	–	–	35	66[b]
	**k**	$(CH_2)_4$		H	H	Me	–	–	55	92[b]
	**l**	$(CH_2)_4$		H	H	Et	–	–	49	92[b]
	**m**	$(CH_2)_2$CH=CH		H	H	Et	–	–	58	76[a]
	**n**	$(CH_2)_6$		H	H	Et	–	–	35	77[b]

[a] Method A: CH_3PPh_3Br, *n*BuLi, *i*Pr_2NH (GP 5A). [b] Method B: 10 mol % *i*Pr_2NH, THF, −78 → 20 °C, 12 h (GP 5B). [c] Method C: CH_3PPh_3Br, *t*BuOK, THF, −30 → 20 °C, 16 h (GP 5C).

hand, the ylide thus generated smoothly reacts with an oxo group at −50 °C, while ester groups are completely inert under these conditions. Apparently, a catalytic amount (5−10 mol %) of diisopropylamine is sufficient to reprotonate the enolate formed by deprotonation of the α-oxo ester. It is remarkable that the added amine did not lead to any side reactions such as a Michael addition to the resulting acrylate, or aminolysis of the ester group, and the yield of **1d** was increased to 79%.

Of course, this improved protocol may be used for the methylenation of compounds **7a−c**,**g**,**m** to furnish better yields of **1a−c**,**g**,**m**, which had been synthesized before the new procedure was developed. Thus, ethyl 2-methylenecyclopropylacrylate **1b** (R^5 = Et) was obtained in 75% yield from oxo ester **7b** (R^5 = Et) by this improved procedure compared to the 65% yield obtained for the methyl ester **7b** (R^5 = Me), achieved with the previously applied protocol.

In this respect, the attempted methylenation of **7f** gave an unusual result in that recovery of the starting material was predominant. Most probably, complexation of the oxo carbonyl and the *endo*-methoxycarbonyl groups of **7f** with a lithium cation, forming a six-membered cyclic chelate, leads to an orientation of the oxo carbonyl group which sterically disfavors addition of the bulky ylide. Indeed, methylenation of **7f** was successful (78% yield) with so-called "salt-free" ylide, generated from methyltriphenylphosphonium bromide with potassium *tert*-butoxide in tetrahydrofuran.

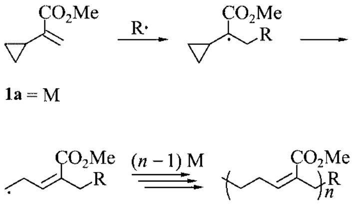
Radical Polymerizations of 2-Cyclopropylacrylates 1a−n

The polymerization of monomers **1a−e**,**g** was carried out in chlorobenzene solution using AIBN as the initiator. The results show (Table 2) that polymers formed from **1a** and **1c** have number-average molecular weights ($\bar{M}_n$) of 118900 and 86300 g/mol, and T_g of 98 and 118 °C, respectively, while the radical polymerizations of **1b** and **1e** lead to the formation of oligomeric products only. The ^{1}H and ^{13}C NMR spectra of the obtained poly-**1a** confirmed the opening of the cyclopropane ring with formation of a 1,5-disubstituted ring-opened unit (Scheme 3). This ring-opening polymerization which occurs instead of a simple vinyl-group polymerization, is typical for vinylcyclopropanes.[2] Monomer **1g** resulted in an insoluble cross-linked polymer, which was expected on the basis of the bifunctionality of this monomer. In contrast to this, poly-**1d** was also insoluble in tetrahydrofuran, but could be dissolved in other solvents, such as chloroform or chlorobenzene. Unfortunately, the polymerization of **1a−e**,**g** resulted in significantly lower polymer yields in comparison to the 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane **DECVCP**, which was used as a benchmark for the reactivity in the radical polymerization of the vinylcyclopropane derivatives. The low polymer yield and $\bar{M}_n$ value of monomer **1b** indicate that a methylene substituent affects adversely the formation of high molecular weight polymers. This was also confirmed by the fact[14] that 1,1-bis(ethoxycarbonyl)-2-methylenecyclopropane did not form polymers in dichlorobenzene in the presence of AIBN after 15 h. The polymerization behavior of **1c** can be also explained on this basis. The replacement of the methylene hydrogen atoms in **1b** by an ethylene bridge leads to monomer **1c** in which the former radical-accessible methylene group is changed to the corresponding tetrasubstituted double bond. In contrast to a vinyl group, tetrasubstituted double bonds are not usually capable of adding initiating radicals and could be therefore detected in poly-**1c** by ^{1}H and ^{13}C NMR spectroscopy.

Table 2. Polymerization of monomers **1a−e**,**g** and **DECVCP** (2.0 mol/L) in chlorobenzene and in the presence of AIBN (2.0 mol %) at a temperature of 65 °C with a polymerization time (t_P) of 15 h

Monomer	Polymer yield (%)	$\bar{M}_n$ [g/mol]	$\bar{M}_w$ [g/mol]	T_g [°C]
1a	71	118900[a]	419000	98
1b	15	5300	7800	54
1c	43	86300	156100	118
1d	67[b]	–[c]	–	53
1e	17	2900	8500	–
1g	42[b]	–	–	62
DECVCP	95	67500	128700	40

[a] Polymer was not completely soluble in THF. [b] Polymer was not soluble in THF. [c] Not determined.



Scheme 3. Ring-opening polymerization of methyl 2-cyclopropylacrylate (**1a**)

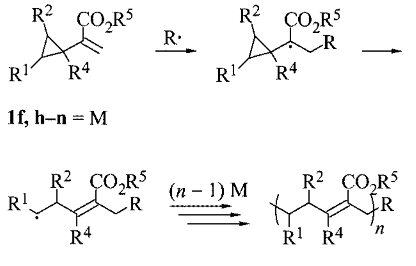
Polymerizations of the bicyclic monomers **1f**,**h**,**i** and **1j−n** were also carried out in chlorobenzene solutions with AIBN as the initiator. These promising results demonstrate (Table 3) a significant influence of the size of the second ring on the radical polymerization of the bicyclic monomers. The highest polymer yields were obtained from the polymerizations of **1f** and **1h** or **1k** and **1l**, i.e. of monomers with an annelated five- or six-membered ring. In the case of **1h** and **1k** both the polymer yields (99 and 98%, respectively) and the glass transition temperatures (T_g) of 57 and 93 °C were significantly higher than those observed for **DECVCP**. According to these results, the monomers **1h** and **1k** meet the requirements for dental applications mentioned above, and can be considered as leads for further structure optimization. In contrast to this, the bicyclo[2.1.0]pentyl and bicyclo[6.1.0]nonyl groups containing monomers **1j** and **1n**, respectively, gave low or even very low polymer yields. In comparison to **1f** and **1h**, compounds **1j** and **1n** showed a significant reduction of both the polymer yield and $\bar{M}_n$ value. It is well documented[2] that the introduction of a second substituent at the same position of the cyclopropane ring, such as the vinyl group, may cause a significant decrease of the monomer reactivity in the radical polymerization because of steric interactions. In comparison to

1l, the drastically lower polymer yield in the radical polymerization of **1m**, which contains an annelated cyclohexene ring, can probably be attributed to the presence of allylic hydrogen atoms in the monomer structure. Generally, this causes a degradative chain transfer in the radical polymerization with formation of less reactive and therefore more slowly propagating radicals.[15] The ^{1}H and ^{13}C NMR spectra of the polymers obtained, for example, in the radical polymerization of the bicyclic monomers **1h** or **1k** confirmed the opening of the cyclopropane rings with formation of 1,5-disubstituted ring-opened units containing the unchanged second ring (Scheme 4).

Table 3. Polymerization of bicyclic monomers **1f**,**h**−**n** (2.0 mol/L) in chlorobenzene and in the presence of AIBN (2.0 mol %) at a temperature of 65 °C, with t_P = 15 h

Monomer	Polymer yield (%)	$\bar{M}_n$ [g/mol]	$\bar{M}_w$ [g/mol]	T_g [°C]
1f	30	14600	23100	55
1h	99	113000	380800	57
1i	91	181300	204600	40
1j	37	21000	30900	46
1k	98	58500	124100	93
1l	94	−[a]	−	53
1m	27	19800	22400	−
1n	2	−	−	−

[a] Not determined



Scheme 4. Ring-opening polymerization of bicyclic monomers **1f**,**h**−**n**; for substituents R^1, R^2, R^4 and R^5 see Scheme 1

As mentioned above, 2-vinylcyclopropane-1,1-dicarboxylates are less reactive in the radical copolymerization with methacrylates. In order to elucidate this feature, the radical copolymerizations of MMA with **1a**, **1h**, or **1k** were carried out in chlorobenzene solutions in the presence of AIBN (Table 4). The composition of the copolymers formed could be determined by ^{1}H NMR spectroscopy, using the intensity ratio of the peaks at δ = 3.69 ppm assigned to the OCH$_3$ protons of **1a**, **1h**, or **1k** and at δ = 3.60 ppm assigned to the OCH$_3$ protons of the MMA units. The copolymers formed with **1h** and **1k** contained visibly fewer units derived from MMA in comparison with the copolymer of **1a**. Taking into consideration the fact that the molar composition of a copolymer of **DECVCP** and MMA obtained under similar conditions[4] was 0.09:1.00, it can be concluded that the 2-cyclopropylacrylates, especially the bicyclic monomers **1h** and **1k**, demonstrate a drastically improved reactivity in the radical polymerization when compared to **DECVCP**.

Table 4. Copolymerization of MMA (1.0 mol/L) with **1a**,**h**,**k** (1.0 mol/L) in chlorobenzene and in the presence of AIBN (2.0 mol %) at a temperature of 65 °C with t_P = 2 h

Comonomer	Polymer yield (%)	$\bar{M}_n$ [g/mol]	F_{MMA}[a]	T_g [°C]
1a	8.6	13300	0.20	−[b]
1h	27.7	34300	0.71	62
1k	10.1	17900	0.91	95

[a] Molar composition of the copolymer: [Comonomer]/[MMA]. [b] Not determined

Experimental Section

General: ^{1}H NMR spectra were recorded with Bruker AM 250 (250 MHz), Varian Unity 300 (300 MHz) or Bruker DPX-400 (400 MHz) spectrometers. ^{13}C NMR spectra were recorded with Mercury 200 (50.3 MHz), Bruker AM 250 (62.9 MHz) or Bruker DPX-400 (100.6 MHz) spectrometers. Multiplicities were determined by DEPT (Distortionless Enhancement by Polarization Transfer) or APT (Attached Proton Test) measurements. Tetramethylsilane, hexamethyldisilane (HMDS) or residual CHCl$_3$ were used as internal standards. IR spectra were recorded with a Bruker IFS 66 (FT-IR) spectrophotometer, as KBr pellets or as neat oils sandwiched between KBr plates. Mass spectra (EI, 70 eV) were measured using a Finnigan MAT 95 spectrometer. Melting points were obtained using a Büchi 510 capillary melting point apparatus and are uncorrected. TLC: Macherey−Nagel pre-coated sheets, 0.25 mm Sil G/UV$_{254}$. Column chromatography: Merck silica gel, grade 60, 70−230 mesh. Flash chromatography: Merck silica gel, grade 60 230−400 mesh; a dry column technique[16] was applied. The number-average molecular weights of polymers ($\bar{M}_n$) were determined by gel permeation chromatography (GPC) using THF as eluent, a Spektra 100 UV-detector and columns calibrated with poly(methyl)methacrylate standards. Differential scanning calorimetry (DSC) measurements were performed with a Perkin−Elmer DSC-7 thermal analyzer employing a scan rate of 10 °C/min. The elemental analyses were performed in Göttingen by the Mikroanalytisches Laboratorium with an elemental analyzer CHN-2000 (Leco). Solvents diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone. Diisopropylamine, 2,6-lutidine and dimethyl sulfoxide were distilled from calcium hydride under nitrogen. Anhydrous methanol and ethanol were distilled from the corresponding magnesium alkoxides under nitrogen. Anhydrous dichloromethane was distilled from phosphorus pentoxide under nitrogen. Benzene, cyclopentene, cyclohexene, chlorobenzene and dimethylformamide were dried with molecular sieves (4 Å). Pentane, hexane, 1,3-cyclohexadiene, *tert*-butyl methyl ether, oxalyl chloride, methyl and ethyl chlorooxalate, lithium hydroxide monohydrate, sodium cyanide, activated manganese(IV) oxide, 10 wt.-% Pd/C, dirhodium tetraacetate, methyltriphenylphosphonium bromide, potassium *tert*-butoxide, *n*-butyllithium solution in hexane, 2,6-di-*tert*-butyl-4-methylphenol (BHT), dimethyl *trans*-cyclopropane-1,2-dicarboxylate (**3d**) and aliphatic urethane dimethacrylate (UDMA, Ivoclar Vivadent, from 2-hydroxyethyl methacrylate and 2,2,4-trimethylhexamethylenediisocyanate) were used as supplied without further purification. 1,1-Bis(ethoxycarbonyl)-2-vinylcyclopropane[17] (**DECVCP**), methylenecyclopropane[18] (**2b**), bicyclopropylidene[19] (**2c**), dimethyl bicyclo[3.1.0]hexane-6,6-dicarboxylate[20] (**3f**), diethyl 2-formylcyclopropane-1,1-dicarboxylate[7] (**5e**), potassium cyclopropyloxoacetate,[21] methyl and ethyl diazopyruvate,[22] 3,3-dimethylcyclobutyl bromide,[23] ethyl *trans*-(2-ethenylcyclopropyl)oxoacetate (**7g**) and ethyl *trans*-2-(2-ethenylcyclopropyl)propenoate[13] (**1g**) were prepared as described previously. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Methyl methacrylate (MMA) was washed with a 5.0 wt.-% NaOH solution, dried with anhydrous sodium sulfate, and distilled from calcium hydride under argon.

Syntheses

3,3-Dimethylcyclobut-1-ene (8j): 1-Bromo-3,3-dimethylcyclobutane (49.3 g, 302 mmol) was added in one portion to a stirred solution of *t*BuOK (52 g, 463 mmol) in anhydrous DMSO (460 mL), kept at 20 °C (cold water bath) under nitrogen. The mixture was stirred at ambient temperature for 20 min, the volatile material was bulb-to-bulb-distilled (T_{bath} 50 °C/20 Torr) into a −78 °C (dry ice/acetone bath) cold, pointed-bottom Schlenk flask. After the distillation was complete, the crude product was transferred by cannula from the cooled collecting flask into a separating funnel, washed with water (2 × 20 mL), brine (10 mL) and placed in a storage bottle containing a small amount of BHT (ca. 10 mg) and molecular sieves (4 Å) (ca. 1 g). The colorless liquid weighed 21.9 g (88%). It was pure 3,3-dimethylcyclobut-1-ene according to its ^{1}H NMR spectrum. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.19$ (s, 6 H, 2 CH_3), 2.25 (d, $J = 1$ Hz, 2 H, CH_2), 5.99 [dt, $J = 2.8, 1$ Hz, 1 H, C(1)−H], 6.09 [d, $J = 2.8$ Hz, 1 H, C(2)−H] ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 26.5$ (2 CH_3), 44.6 (CH_2), 44.9 (C), 132.0 (CH), 146.5 (CH) ppm.

Partial Hydrolysis of Diesters 3d,f with Lithium Hydroxide: A solution of $LiOH{\cdot}H_2O$ (4.2 g, 100 mmol) in anhydrous methanol (100 mL) was added dropwise over a 30-min period to a vigorously stirred solution of the respective diester (100 mmol) in anhydrous THF (400 mL) at ambient temperature, and the mixture was stirred for an additional 24 h. Then the solvents were completely evaporated under reduced pressure ($T_{\text{bath}} = 40$ °C), the residue was dissolved in a minimal amount of water (ca. 100 mL) and extracted with diethyl ether (2 × 50 mL). The aqueous phase was acidified with 12 N HCl, saturated with NaCl and extracted with diethyl ether (5 × 100 mL). The combined extracts were dried with Na_2SO_4, and the solvents evaporated under reduced pressure to give a crude product, which was purified by distillation under reduced pressure or recrystallized from an appropriate solvent.

***trans*-2-(Methoxycarbonyl)cyclopropanecarboxylic Acid (4d):** A crude mixture (25 g) obtained after hydrolysis of the diester **3d** (31 g, 196 mmol) with LiOH, was bulb-to-bulb-distilled under reduced pressure ($T_{\text{bath}} = 100-110$ °C/0.1 Torr) to give pure ester **4d** (20 g, 70%), the physical properties and ^{1}H NMR spectra of which are identical to those reported in the literature.[24] IR (film): $\tilde{\nu}$ = 3116, 3078, 3018, 2958, 2751, 2702, 2658, 2560, 1731, 1698, 1436, 1376, 1327, 1305, 1207, 1175, 1115, 1087, 1055, 1006, 918, 853, 820, 744, 651, 629 cm^{-1}. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 15.8$ (CH_2), 22.0 (CH), 22.7 (CH), 52.3 (CH_3), 171.8 (C), 178.1 (C) ppm. MS (70 eV, EI): m/z (%) = 144 (1) [M^+], 143 (1) [$M^+ - H$], 127 (4) [$M^+ - OH$], 126 (4) [$M^+ - H_2O$], 113 (100) [$M^+ - OCH_3$], 112 (54) [$M^+ - CH_3OH$], 99 (23) [$M^+ - CO_2 - H$], 98 (58) [$M^+ - CO - H_2O$], 95 (6), 85 (27) [$M^+ - CO_2Me$], 84 (51) [$M^+ - CO_2Me - H$], 71 (4), 69 (10), 68 (20), 67 (6), 59 (32), 57 (16), 55 (18), 45 (16), 43 (6), 42 (6), 41 (20). $C_6H_8O_4$ (144.13): calcd. C 50.00, H 5.59; found C 49.74, H 5.36.

***exo*-6-(Methoxycarbonyl)bicyclo[3.1.0]hexane-6-carboxylic Acid (4f):**[8] The colorless solid (15.53 g) obtained after hydrolysis of diester **3f** with LiOH, was recrystallized from a mixture of toluene and cyclohexane (1:2; 250 mL) to yield 13.92 g of pure **4f** as colorless prisms. A second crop (1.29 g) was obtained after concentration of the mother liquor and recrystallization of the residue from the same solvent (ca. 25 mL). The overall yield was 15.21 g (83%), m.p. 137−137.5 °C. IR (KBr): $\tilde{\nu}$ = 3450, 3045, 3023, 2968, 2875, 1747, 1700, 1443, 1371, 1316, 1283, 1233, 1193, 1162, 1110, 1050, 1022, 938, 872, 806, 768 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.83$ [m, 1 H, C(3)−H], 1.67 [m, 1 H, C(3)−H], 1.85−2.10 (m, 4 H, 2 CH_2), 2.20 (m, 2 H, 2 CH), 3.73 (s, 3 H, OCH_3), 11.22 (br. s, 1 H, OH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 21.3$ (CH_2), 26.4 (2 CH_2), 35.7 (2 CH), 35.8 (C), 52.7 (CH_3), 167.6 (C), 176.8 (C) ppm. MS (70 eV, EI): m/z (%) = 184 (22) [M^+], 166 (96) [$M^+ - H_2O$], 155 (21) [$M^+ - H - C_2H_4$], 153 (73) [$M^+ - CH_3O$], 152 (70) [$M^+ - CH_3OH$], 138 (36) [$M^+ - CO - H_2O$], 134 (100) [$M^+ - CH_3OH - H_2O$], 124 (78), 107 (21), 106 (36), 93 (15), 79 (90), 77 (34) [$C_6H_5^+$], 67 (27), 53 (12), 41 (19) [$C_3H_5^+$]. $C_9H_{12}O_4$ (184.19): calcd. C 58.69, H 6.57; found C 58.89, H 6.83.

General Procedure for the Two-Step Synthesis of Aldehydes 5d,f from Carboxylic Acids by Rosenmund Reduction of Acid Chlorides (GP 1):[9] Anhydrous DMF (0.1 mL) and oxalyl chloride (15.2 g, 10.3 mL, 120 mmol) were added at ambient temperature to a stirred solution of the respective carboxylic acid (100 mmol) in anhydrous CH_2Cl_2 (50 mL), and the mixture was stirred until the gas evolution had ceased (1−2 h). Then the solvent was evaporated under reduced pressure (15−20 Torr) without heating until the temperature of the reaction flask had reached ca. 20 °C, anhydrous benzene (50 mL) was added to the residue and solvent evaporation was repeated under the same conditions. The resulting crude acyl chloride was used for the next step without additional purification. Freshly distilled 2,6-lutidine (10.7 g, 11.6 mL, 100 mmol) and the crude acyl chloride were added at ambient temperature to a vigorously stirred suspension of 10% Pd/C (1.5 g, 1.4 mmol) in anhydrous degassed THF (500 mL) under hydrogen (1 bar). The reaction mixture was stirred until the hydrogen absorption had ceased (2−12 h), then the solvent was evaporated under reduced pressure at ambient temperature. The residue was triturated with anhydrous ether (100 mL), the solution diluted with pentane (200 mL) whilst stirring, and filtered through Celite® which was subsequently washed with a 2:1 mixture of ether/pentane (2 × 50 mL). The filtrate was concentrated under reduced pressure at ambient temperature to give the crude aldehyde, which was purified by distillation under reduced pressure.

Methyl *trans*-2-Formylcyclopropanecarboxylate (5d): According to GP 1, the half-ester **4d** (15.1 g, 105 mmol), after distillation of the crude product, gave 11.4 g (85%) of pure **5d** as a colorless oil, b.p. 81−82 °C (12 Torr), ^{1}H and ^{13}C NMR spectra of which are identical to those reported in the literature.[26] IR (film): $\tilde{\nu}$ = 3105, 3062, 3013, 2958, 2849, 2740, 1736, 1715, 1436, 1387, 1322, 1284, 1207, 1175, 1082, 1060, 1022, 946, 913, 864, 850, 820, 749, 735, 667 cm^{-1}. MS (70 eV, EI): m/z (%) = 128 (4) [M^+], 113 (1) [$M^+ - CH_3$], 99 (4) [$M^+ - CHO$], 97 (19) [$M^+ - OCH_3$], 96 (20) [$M^+ - CH_3OH$], 85 (2), 71 (6), 69 (53) [$M^+ - CO_2CH_3$], 68 (33) [$M^+ - CH_3OH - CO$], 59 (18), 55 (9), 45 (2), 43 (5), 42 (9), 41 (100) [$C_3H_5^+$], 40 (22) [$C_3H_4^+$].

Methyl *exo*-6-Formylbicyclo[3.1.0]hexane-6-carboxylate (5f): According to GP 1, the half-ester **4f** (14.7 g, 80 mmol), after distillation of the crude product, gave pure **5f** (11.8 g, 88%) as a colorless oil, b.p. 66−67 °C (7 mbar). IR (film): $\tilde{\nu}$ = 2955, 2918, 2894, 2866, 2791, 2753, 2716, 1739, 1701, 1480, 1438, 1405, 1372, 1330, 1293, 1232, 1199, 1156, 1109, 1091, 1054, 1030, 987, 964, 945, 893, 870, 832, 809, 757 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.93-1.14$

[m, 1 H C(3)−H], 1.66−1.80 [m, 1 H C(3)-H], 1.91−2.12 (m, 4 H, 2 CH_2), 2.20−2.26 [m, 2 H, 2 CH], 3.78 (s, 3 H, CH_3), 9.15 (s, 1 H, CHO) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.3 (CH_2), 26.2 (2 CH_2), 35.3 (2 CH), 45.2 (C), 52.5 (CH_3), 168.6 (C), 195.5 (CH) ppm. MS (70 eV, EI), *m/z* (%) = 168 (9) [M^+], 167 (100) [$M^+ - H$], 135 (13), [$M^+ - CH_3OH - H$], 108 (3) [$M^+ - CO_2CH_3$], 107 (4) [$M^+ - CO_2CH_3 - H$], 79 (5) [$C_6H_7^+$], 67 (6). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 64.07, H 7.03.

General Procedure for the Two-Step Synthesis of α-Hydroxycarboxylic Esters from Aldehydes (GP 2): A solution of NaCN (11.3 g, 230 mmol) in water (25 mL) was added with cooling (ice/water bath) during a period of 20 min to a stirred suspension of NH_4Cl (13.9 g, 260 mmol) and the respective aldehyde (200 mmol) in 70 mL of a 1:1 mixture of water/diethyl ether so that the temperature of the mixture was kept at 10 °C. After the addition was complete, the mixture was stirred at this temperature for an additional 20 min. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine (2 × 50 mL), acidified with a few drops of *ortho*-phosphoric acid, dried with $MgSO_4$, filtered and concentrated under reduced pressure at ambient temperature to give the crude product,[1,10] which was converted into the alkyl α-hydroxyacetates **6b−f** by two different methods. **Method A:** Anhydrous MeOH (16 mL, 400 mmol) and diethyl ether (25 mL) were added under nitrogen to the crude cyanohydrin. This mixture was added in one portion with stirring to a pre-cooled (−10 °C, ice/salt bath) solution prepared by saturating anhydrous diethyl ether (100 mL) at 0 °C with dry HCl and subsequent dilution with the same solvent (175 mL). The mixture was stirred at 0−2 °C for 18 h, then the solid was filtered off, washed with anhydrous diethyl ether (50 mL) and dried under reduced pressure at ambient temperature to give a slightly gray powder, which was then added with stirring to water (100 mL) and kept at 0 °C (ice bath). The mixture was stirred at 0 °C for 30 min and at ambient temperature for 1 h. The aqueous phase was saturated with NaCl and extracted with ethyl acetate (4 × 50 mL). The combined organic layers were washed with brine (50 mL) and dried with $MgSO_4$. The solvent was evaporated, and the residue distilled under reduced pressure, or was used in the next step without additional purification.[1,11] **Method B:** A three-necked pointed-bottom 250-mL flask was equipped with a septum, thermometer and gas inlet tube, which almost reached the bottom of the flask. The outer neck of the inlet tube was fitted with a bubbler charged with paraffin, and this in turn was connected to a $CaCl_2$ drying tube. The reaction flask was immersed in a dry ice/acetone bath, and a slow stream of dry hydrogen chloride was passed through the system. Then a solution of the crude cyanohydrin (200 mmol) in the respective anhydrous alcohol (100 mL) was added by syringe at such a rate as to keep the temperature of the reaction mixture below −10 °C (ca. 20 min, cooling with dry ice/acetone bath). At the same time the stream of HCl was adjusted so as to keep the pressure in the reaction flask slightly above ambient (controlled by the bubbler). After the addition of the solution was complete, the mixture was saturated with hydrogen chloride at −20 °C and the cooling bath was removed. After stirring at ambient temperature for an additional 2 h, the solvents were evaporated under reduced pressure at ambient temperature. Ice/water (100 mL) was added to the stirred residue at 0 °C, and the mixture was stirred at this temperature for an additional 30 min. The ice bath was removed, and the mixture was stirred at ambient temperature for an additional time (1 h or 16 h for *gem*-alkoxycarbonyl-substituted cyanohydrins). The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (4 × 50 mL). The combined organic phases were washed with brine (50 mL) and dried with $MgSO_4$. The crude product obtained after evaporation of the solvent was distilled under reduced pressure or used in the next step without further purification.

Methyl *exo*-(6-Methoxycarbonylbicyclo[3.1.0]hex-6-yl)hydroxyacetate (6f): According to GP 2B, the crude cyanohydrin (13.6 g, 69.6 mmol) obtained from the aldehyde **5f** (11.8 g, 70.2 mmol) after workup (the imino ester hydrochloride was hydrolyzed by stirring the aqueous mixture at ambient temperature for 16 h) gave crude **6f** (14.9 g, 94%) as a colorless oil, which was used for the next step without additional purification. Flash chromatography of the crude product (0.71 g), eluting with pentane/diethyl ether (10:1 to 5:1) and subsequent kugelrohr distillation, gave an analytical sample **6f** (0.60 g, 84%) as colorless oil. IR (film): $\tilde{\nu}$ = 3487, 3029, 2953, 2865, 1736, 1436, 1393, 1349, 1295, 1267, 1202, 1153, 1137, 1098, 1060, 1027, 989, 946, 853, 842, 706 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91−1.11 [m, 1 H, C(3)-H], 1.58−1.72 [m, 1 H, C(3)-H], 1.75−1.90 (m, 5 H, 2 CH_2 + CH), 1.92−2.05 (m, 1 H, CH), 3.02 (br. s, 1 H, OH), 3.60 (s, 1 H, CH), 3.65 (s, 3 H, CH_3), 3.79 (s, 3 H, CH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 23.2 (CH_2), 25.9 (CH_2), 26.3 (CH_2), 30.0 (CH), 30.3 (CH), 36.9 (C), 52.0 (CH_3), 52.7 (CH_3), 75.3 (CH), 170.3 (C), 173.4 (C) ppm. MS (70 eV, EI): *m/z* (%) = 228 (2) [M^+], 227 (3) [$M^+ - H$], 197 (2) [$M^+ - CH_3O$], 178 (10), 169 (33) [$M^+ - CO_2CH_3$], 159 (11), 137 (100), 118 (11), 109 (21), 91 (15), 81 (24) [$C_6H_9^+$], 79 (22) [$C_6H_7^+$], 77 (8) [$C_6H_5^+$], 72 (11), 67 (30), 53 (6), 41 (5). $C_{11}H_{16}O_5$ (228.24): calcd. C 57.88, H 7.07; found C 57.60, H 6.85.

General Procedure for the Oxidation of α-Hydroxy Esters 6b−f to α-Oxo Esters 7b−f with Active Manganese Dioxide (GP 3):[1,12] Active MnO_2 (Fluka®) (2 × 40 g) was added, in two portions with an interval of 2 h, to a well-stirred solution of the respective α-hydroxy ester (80 mmol) in anhydrous diethyl ether (500 mL). The suspension was stirred at ambient temperature (2−4 h) until the starting material had been completely consumed (TLC monitoring). The mixture was filtered through Celite®, which was subsequently washed with diethyl ether (2 × 150 mL). The solvent was evaporated from the combined filtrates under reduced pressure to give sufficiently pure (> 95% according to GC) α-oxo ester, which could be used without additional purification.

Methyl *exo*-(6-Methoxycarbonylbicyclo[3.1.0]hex-6-yl)oxoacetate (7f): Oxidation of crude **6f** (11.7 g, 51 mmol) according to GP 3 gave a colorless oil (9.8 g, 84%), which was pure according to its ^1H NMR spectroscopic data. An analytical sample was obtained by kugelrohr distillation of crude **7f**. IR (film): $\tilde{\nu}$ = 3034, 2957, 2869, 1739, 1701, 1437, 1360, 1311, 1289, 1234, 1196, 1152, 1075, 1031, 1004, 982, 949, 905, 878, 856, 846, 817, 779, 751, 718 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.02−1.22 [m, 1 H, C(3)-H], 1.66−1.81 [m, 1 H, C(3)-H], 1.93−2.16 (m, 4 H, 2 CH_2), 2.32−2.38 (m, 2 H, 2 CH), 3.75 (s, 3 H, CH_3), 3.83 (s, 3 H, CH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.4 (CH_2), 26.7 (2 CH_2), 41.5 (2 CH), 43.3 (C), 52.5 (CH_3), 53.0 (CH_3), 161.7 (C), 168.3 (C), 189.0 (C) ppm. MS (70 eV, DCI, NH_3): *m/z* (%) = 470 (1) [$2M + NH_4^+$], 244 (100) [$M + NH_4^+$]. $C_{11}H_{14}O_5$ (226.23): calcd. C 58.40, H 6.24; found C 58.15, H 5.95.

General Procedure for the Synthesis of Alkyl Oxoacetates 7h−n by [$Rh_2(OAc)_4$]-Catalyzed Addition of Alkyl 3-Diazopyruvates to Cyclic Alkenes (GP 4): A solution of the corresponding alkyl 3-diazopyruvate[22] (200 mmol) in anhydrous degassed CH_2Cl_2 (400 mL) was added to a well-stirred solution of [$Rh_2(OAc)_4$] (0.14−0.39 mol %) and the respective cycloalkene (200−500 mmol) in the same solvent (400 mL) during 16 h. After the addition was complete, the solvents were evaporated under reduced pressure at ambient temperature. The residue was triturated with pentane (110 mL), passed through a pad (diameter 65 × 30 mm) of silica gel used for flash chromatography and washed with pentane/diethyl ether (10:1; 3 × 150 mL). The slightly yellow oil obtained after evaporation of the solvent was purified by column chromatography on silica gel.

Methyl *exo*-(Bicyclo[3.1.0]hex-6-yl)oxoacetate (7h): Addition of methyl diazopyruvate[22] (19.8 g, 155 mmol) to cyclopentene (27 mL, 308 mmol) in the presence of 0.26 mol % of $Rh_2(OAc)_4$ (176 mg, 0.4 mmol) according to GP 4 gave a slightly yellow oil (25.7 g), which was subjected to chromatography on silica gel (2 L) eluting with pentane/diethyl ether (10:1) to give pure **7h** (12.7 g, 49% yield, > 98% purity according to GC) as a colorless oil. B.p. 80−82 °C (2 mbar). IR (film): $\tilde{\nu}$ = 3037, 2956, 2886, 2865, 1735, 1706, 1448, 1438, 1406, 1327, 1290, 1249, 1227, 1169, 1100, 1074, 1044, 1017, 992, 976, 935, 887, 843, 804, 754 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 [dtt, *J* = 13.3, 10.8, 9 Hz, 1 H, C(3)-H_{exo}], 1.60−1.94 (m, 5 H), 2.10−2.13 (m, 2 H, 2 CH), 2.57 (t, *J* = 2.8 Hz, 1 H, CH), 3.85 (s, 3 H, CH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 19.9 (CH_2), 27.4 (CH), 27.5 (2 CH_2), 35.9 (2 CH), 52.9 (CH_3), 161.6 (C), 192.6 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 168 (2) [M^+], 109 (100) [$M^+ - CO_2CH_3$], 85 (2), 81 (26) [$M^+ - C_2H_3O_2 - CO$], 79 (8) [$C_6H_7^+$], 71 (3), 67 (2), 55 (3), 53 (7), 41 (6). $C_9H_{12}O_3$ (168.19): calcd. C 64.27, H 7.19; found C 64.51, H 6.92.

Ethyl (2,2-Dimethylbicyclo[2.1.0]pent-5-yl)oxoacetate (7j): Addition of ethyl diazopyruvate[22] (24.4 g, 172 mmol) to 3,3-dimethylcyclobutene (**8j**; 25 mL, 215 mmol) in the presence of 0.39 mol % of [$Rh_2(OAc)_4$] (300 mg, 0.68 mmol) according to GP 4 gave a crude product (29.1 g) as a yellow oil, which was separated by column chromatography on silica gel (2 L), eluting with hexane/*t*BuOMe (20:1) to yield an intermediate fraction (2.27 g) containing about 70% of **7j** and pure **7j** (11.7 g, 35%, purity > 98% according to GC) as a 3.8:1 mixture of *exo*/*endo* isomers. A small amount (250 mg) of pure *exo*-**7j** was isolated by column chromatography of an aliquot of the mixture of *exo*/*endo* isomers (2 g) on 200 g of silica gel under the same conditions as above, but only from the latest fractions. IR (film): $\tilde{\nu}$ = 3039, 2959, 2930, 2867, 1733, 1712, 1465, 1443, 1385, 1368, 1303, 1271, 1240, 1146, 1082, 1030, 1015, 986, 938, 914, 880, 834, 790, 739 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.37 (t, *J* = 7 Hz, 3 H, CH_3), 1.42 [d, *J* = 11.5 Hz, 1 H, C(3)-H], 1.79 [dd, *J* = 11.5, 4 Hz, 1 H, C(3)-H], 2.10 (d, *J* = 4.8 Hz, 1 H, CH), 2.17 (dd, *J* = 4.8, 4 Hz, 1 H, CH), 3.05 (s, 1 H, CH), 4.33 (q, *J* = 7 Hz, 2 H, CH_2) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (CH_3), 23.3 (CH_3), 26.4 (CH), 29.5 (CH_3), 34.1 (CH), 36.3 (C), 38.1 (CH_2), 41.8 (CH), 62.4 (CH_2), 161.0 (C), 192.3 (C) ppm. MS (70 eV, DCI, NH_3): *m*/*z* (%) = 410 (4) [$2M + NH_4^+$], 231 (19) [$M + NH_3 + NH_4^+$], 214 (100) [$M + NH_4^+$], 185 (1) [$M + NH_4^+ - C_2H_5^+$], 135 (2), 95 (1), 79 (9), 77 (5), 67 (23), 55 (17), 53 (6), 41 (10). $C_{11}H_{16}O_3$ (196.24): calcd. C 67.32, H 8.22; found C 67.19, H 7.96.

Methyl *exo*-(Bicyclo[4.1.0]hept-7-yl)oxoacetate (7k): Addition of methyl diazopyruvate[22] (25.6 g, 200 mmol) to cyclohexene (50 mL, 500 mmol) in the presence of 0.31 mol % of [$Rh_2(OAc)_4$] (0.28 g, 0.63 mmol) according to GP 4 gave a crude product (31 g) as a yellow oil, which was separated into four fractions by column chromatography on silica gel (2 L), eluting with hexane/*t*BuOMe (10:1) as analyzed by GC. Fraction I: methyl 3-(cyclohexene-1-yl)pyruvate (2.16 g, 92% purity); fraction II: **7k** contaminated with some unidentified products (1 g, 50% purity); fraction III: **7k** (2.8 g, 73% purity); fraction IV: pure **7k** (19.9 g, 55%, > 99.5% purity). IR (film): $\tilde{\nu}$ = 3011, 2935, 2860, 1734, 1703, 1449, 1413, 1306, 1259, 1203, 1172, 1152, 1100, 1077, 1037, 1017, 973, 950, 890, 843, 779, 755, 720 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.24−1.36 (m, 4 H), 1.68−1.79 (m, 2 H), 1.85−1.95 (m, 4 H), 2.58 (t, *J* = 3.4 Hz, 1 H, CH), 3.86 (s, 3 H, CH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 20.7 (2 CH_2), 23.1 (2 CH_2), 30.5 (2 CH), 32.1 (CH), 52.9 (CH_3), 161.7 (C), 193.1 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 182 (1) [M^+], 123 (100) [$M^+ - CO_2CH_3$], 95 (45) [$C_7H_{11}^+$], 93 (4) [$C_7H_9^+$], 91 (3) [$C_7H_7^+$], 81 (19) [$C_6H_9^+$], 79 (19) [$C_6H_7^+$], 77 (6) [$C_6H_5^+$], 67 (39), 66 (5), 65 (5), 59 (4), 55 (61), 53 (20), 51 (4), 41 (42). HRMS (EI): calcd. for ($C_{10}H_{14}O_3$) [M^+] 182.0943, found 182.0943.

Ethyl *exo*-(Bicyclo[4.1.0]hept-2-en-7-yl)oxoacetate (7m): Addition of ethyl diazopyruvate[22] (10.0 g, 70 mmol) to 1,3-cyclohexadiene (13 mL, 137 mmol) in the presence of 0.32 mol % of [$Rh_2(OAc)_4$] (100 mg, 0.22 mmol) according to GP 4 gave a crude product (10.7 g) as a yellow oil, which was subjected to chromatography on silica gel (1 L), eluting with hexane/*t*BuOMe (20:1) to yield pure **7m** (7.9 g, 58%). IR (film): $\tilde{\nu}$ = 3039, 2985, 2936, 2852, 1728, 1703, 1638, 1473, 1445, 1420, 1393, 1370, 1295, 1258, 1236, 1196, 1089, 1043, 1015, 961, 928, 858, 802, 757, 746, 684 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, *J* = 7 Hz, 3 H, CH_3), 1.63−2.23 (m, 6 H), 3.02 (dd, *J* = 4.2, 3.5 Hz, 1 H, CH), 4.31 (q, *J* = 7 Hz, 2 H, CH_2), 5.58−5.66 (m, 1 H, CH), 5.92−5.60 (m, 1 H, CH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (CH_3), 17.9 (CH_2), 20.3 (CH_2), 28.3 (CH), 30.1 (CH), 30.9 (CH), 62.4 (CH_2), 124.9 (CH), 126.3 (CH), 161.0 (C), 191.8 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 194 (7) [M^+], 179 (2) [$M^+ - CH_3$], 165 (4) [$M^+ - C_2H_5$], 148 (6), 147 (7), 121 (73), 120 (48), 116 (15), 103 (14), 93 (100), 91 (64), 79 (34) [$C_6H_7^+$], 77 (57) [$C_6H_5^+$], 65 (13), 55 (27), 41 (7). HRMS (EI): calcd. for ($C_{11}H_{14}O_3$) [M^+] 194.0943, found 194.0943.

General Procedure for the Wittig Methylenation of Oxo Esters 7d−n to 2-Substituted Alkyl Acrylates 1d−n (GP 5B): First diisopropylamine (1.4 mL, 10 mmol), then a 2.5 M *n*BuLi solution in hexane (40 mL, 100 mmol) were added to a well-stirred suspension of methyltriphenylphosphonium bromide (37.5 g, 105 mmol) in anhydrous THF (250 mL), kept at −78 °C (dry ice/acetone bath) under nitrogen. After the slight warming of the reaction mixture had ceased, the cooling bath was removed, and the mixture was warmed up to ambient temperature (about 1 h), then cooled to −78 °C again, and a solution of the respective carbonyl compound (100 mmol) in anhydrous THF (20 mL) was added with vigorous stirring so that the temperature did not exceed −50 °C. After stirring for an additional 30 min at this temperature, the cooling bath was removed, the reaction mixture was stirred overnight (12 h) and then acidified with 5% aqueous H_2SO_4 (10 mL). Brine (50 mL) was then added, the organic phase was separated and the aqueous phase was extracted with diethyl ether (2 × 100 mL). The combined organic layers were washed with brine (2 × 100 mL) and dried with $MgSO_4$. BHT (10 mg) was added, and a major proportion of the solvents was removed at ambient temperature in a rotary evaporator until the volume of the residue had been reduced to 50−60 mL. Pentane (500 mL) was gradually added to the stirred liquid residue (a spontaneously solidified residue may be homogenized by adding a minimal amount of warm dichloromethane), and the stirring continued at 0 °C until the $OPPh_3$ crystallization was complete. Then the solid was filtered off and washed with pentane/ether (10:1; 2 × 50 mL). The combined filtrates were concentrated under reduced pressure at ambient temperature. In the cases of the relatively low-boiling compounds **1a**, **1b** and **1g**, the solvents were distilled off at ambient pressure at a bath temperature < 60 °C, and the remaining solvent was removed under reduced pressure (ca. 10 Torr) at ambient temperature (the evaporation was stopped as soon as the contents of the distillation flask had reached room temperature). The obtained crude product was purified by column chromatography or distilled under reduced pressure.

Methyl *exo*-2-(6-Methoxycarbonylbicyclo[3.1.0]hex-6-yl)propenoate (1f): Methylenation of the oxo ester **7f** (7.9 g, 35 mmol) according to GP 5B yielded only 1.5 g (19%) of **1f**, most of the starting material being recovered. Therefore, an improved protocol (GP 5C) to methylenate **7f** was developed. **GP 5C:** A freshly prepared solution of *t*BuOK (0.25 g, 2.2 mmol) in anhydrous THF (10 mL) was added all at once with stirring into an oven-dried 25-mL flask charged with methyltriphenylphosphonium bromide (0.82 g, 2.3 mmol) under argon at ambient temperature. After additional stirring at room temperature for 1 h, the ylide solution was cooled to −30 °C and oxo ester **7f** (0.45 g, 2 mmol) dissolved in the same solvent (2 mL) was added dropwise, keeping the temperature of the reaction mixture below −20 °C, and stirring continued at this temperature for an additional 1 h. Then, the cooling bath was removed, and stirring was continued at ambient temperature for 16 h. The reaction was quenched by addition of a few drops of acetic acid. Most of the solvent was removed under reduced pressure at ambient temperature. The residue was suspended in *t*BuOMe (10 mL) whilst stirring, poured into pentane (20 mL), and the mixture was filtered. The residue obtained after evaporation of the solvents from the filtrate was subjected to chromatography on silica gel (50 mL), eluting with hexane/*t*BuOMe (10:1) to give pure **1f** (0.35 g, 78%). IR (film): $\tilde{\nu}$ = 3111, 3023, 2952, 2869, 1734, 1635, 1437, 1371, 1295, 1233, 1196, 1152, 1102, 1048, 1026, 993, 954, 916, 867, 845, 812, 768, 685 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34−1.52 [m, 1 H, C(3)-H], 1.64−2.06 (m, 7 H), 3.58 (s, 3 H, CH_3), 3.69 (s, 3 H, CH_3), 5.62 (d, *J* = 0.8 Hz, 1 H), 6.19 (d, *J* = 0.8 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 25.5 (CH_2), 26.4 (2 CH_2), 34.9 (2 CH), 35.9 (C), 51.7 (CH_3), 51.9 (CH_3), 126.8 (CH_2), 140.9 (C), 166.6 (C), 170.6 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 224 (2) [M^+], 192 (100) [$M^+ - CH_3OH$], 177 (1), 164 (21) [$M^+ - CH_3OH - CO$], 160 (30), 151 (8), 149 (6), 136 (12), 133 (23), 132 (23), 121 (4), 105 (42), 91 (9), 79 (15), 77 (15), 67 (16), 65 (6), 59 (9), 55 (2), 53 (3), 51 (4), 45 (2), 41 (4). $C_{12}H_{16}O_4$ (224.25): calcd. C 64.27, H 7.19; found C 64.21, H 7.00.

Methyl *exo*-2-(Bicyclo[3.1.0]hex-6-yl)propenoate (1h): Methylenation of the oxo ester **7h** (11.44 g, 68 mmol) according to GP 5B gave a crude product (12.38 g) as a yellow oil, which was subjected to chromatography on silica gel (1 L), eluting with pentane/diethyl ether (20:1) to yield pure **1h** (9.6 g, 85%) as a colorless liquid. IR (film): $\tilde{\nu}$ = 3105, 3026, 2952, 2861, 1724, 1624, 1437, 1408, 1336, 1294, 1280, 1252, 1229, 1193, 1174, 1137, 1081, 1053, 998, 926, 887, 844, 812 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.13−1.30 [m, 1 H, C(3)-H], 1.37 (dd, *J* = 3.7, 3.5 Hz, 2 H, 2 CH), 1.56 (t, *J* = 3.7 Hz, 1 H, CH), 1.59−1.77 (m, 3 H), 1.85 (dd, *J* = 12.4, 8 Hz, 2 H), 3.75 (s, 3 H, CH_3), 5.18 (d, *J* = 1 Hz, 1 H), 5.93 (d, *J* = 1 Hz, 1 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 18.9 (CH), 20.9 (CH_2), 27.7 (2 CH_2), 28.5 (2 CH), 51.8 (CH_3), 119.5 (CH_2), 141.9 (C), 167.7 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 166 (37) [M^+], 151 (15) [$M^+ - CH_3$], 138 (13) [$M^+ - C_2H_4$], 135 (22) [$M^+ - CH_3O$], 134 (70) [$M^+ - CH_3OH$], 125 (8), 107 (46) [$M^+ - CH_3O - CO$], 106 (74) [$M^+ - CH_3OH - CO$], 105 (36) [$M^+ - CH_3OH - CO - H$], 100 (6), 93 (16), 91 (51) [$C_7H_7^+$], 79 (70) [$C_6H_7^+$], 77 (31) [$C_6H_5^+$], 67 (100), 65 (21), 59 (20), 53 (20), 51 (12), 43 (42), 41 (40). $C_{10}H_{14}O_2$ (166.22): calcd. C 72.26, H 8.49; found C 72.09, H 8.20.

Ethyl 2-(2,2-Dimethylbicyclo[2.1.0]pent-5-yl)propenoate (1j): Methylenation of a 3.8:1 mixture of *exo*/*endo* isomers of **7j** (8.3 g, 42 mmol) according to GP 5B gave a crude mixture of diastereomers of **1j** (6.7 g), which was purified by column chromatography on silica gel (700 mL), eluting with pentane/ether (50:1) to give pure *exo*-**7j** (5.2 g, *exo*/*endo* ratio 94:2 according to GC) contaminated with some by-product (4%) and pure *endo*-**7j** (210 mg). Total yield 66%. ***exo*-7j:** Colorless oil. IR (film): $\tilde{\nu}$ = 3111, 3045, 3023, 2957, 2924, 2864, 2721, 1723, 1624, 1465, 1465, 1443, 1410, 1384, 1366, 1311, 1262, 1212, 1152, 1124, 1108, 1026, 997, 872, 812, 784, 675 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.31 (t, *J* = 7 Hz, 3 H, CH_3), 1.42 (d, *J* = 11 Hz, 1 H), 1.47 (d, *J* = 4.5 Hz, 1 H, CH), 1.59 (dd, *J* = 4.5, 4.5 Hz, 1 H, CH), 1.67 (dd, *J* = 11, 4.5 Hz, 1 H), 2.17 (s, 1 H, CH), 4.23 (q, *J* = 7 Hz, 2 H, CH_2), 5.04 (s, 1 H), 5.90 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.2 (CH_3), 19.4 (CH), 23.3 (CH_3), 26.7 (CH), 30.3 (CH_3), 35.0 (C), 36.1 (CH), 37.7 (CH_2), 60.7 (CH_2), 119.2 (CH_2), 140.6 (C), 167.1 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 194 (1) [M^+], 179 (17) [$M^+ - CH_3$], 165 (51) [$M^+ - C_2H_5$], 151 (10), 149 (12) [$M^+ - C_2H_5O$], 148 (10) [$M^+ - C_2H_5OH$], 147 (12), 133 (39), 123 (6), 121 (38) [$M^+ - CO_2C_2H_5$], 120 (22), 119 (29), 105 (100), 95 (8), 93 (28), 91 (32), 81 (6), 79 (43) [$C_6H_7^+$], 77 (28) [$C_6H_5^+$], 67 (14), 65 (9), 55 (13), 53 (14), 51 (6), 43 (9), 41 (32). $C_{12}H_{18}O_2$ (194.27): calcd. C 74.19, H 9.34; found C 74.42, H 9.02. ***endo*-7j:** Colorless oil. IR (film): $\tilde{\nu}$ = 3105, 3037, 3016, 2985, 2953, 2936, 2902, 2865, 1722, 1628, 1464, 1446, 1383, 1364, 1300, 1275, 1249, 1188, 1163, 1110, 1030, 982, 946, 899, 855, 819, 777, 743 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.65 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.30 (t, *J* = 7 Hz, 3 H, CH_3), 1.42 (d, *J* = 11.3 Hz, 1 H), 1.56 (dd, *J* = 11.3, 4.5 Hz, 1 H), 1.63−1.83 (m, 3 H, 3 CH), 4.23 (q, *J* = 7 Hz, 2 H, CH_2), 5.73 (t, *J* = 2 Hz, 1 H), 6.38 (t, *J* = 2 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 11.9 (CH), 14.3 (CH_3), 23.4 (CH_3), 27.7 (CH), 31.0 (CH), 32.0 (CH_2), 32.4 (CH_3), 33.5 (C), 60.4 (CH_2), 127.8 (CH_2), 137.1 (C), 167.8 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 194 (1) [M^+], 179 (15) [$M^+ - CH_3$], 165 (88) [$M^+ - C_2H_5$], 151 (8), 149 (13) [$M^+ - C_2H_5O$], 148 (19) [$M^+ - C_2H_5OH$], 147 (21), 133 (41), 121 (47) [$M^+ - CO_2C_2H_5$], 120 (28), 119 (38), 105 (100), 95 (19), 93 (29), 91 (30), 79 (41) [$C_6H_7^+$], 77 (21) [$C_6H_5^+$], 67 (14), 65 (7), 55 (14), 53 (9), 43 (8), 41 (24). $C_{12}H_{18}O_2$ (194.27): calcd. C 74.19, H 9.34; found C 73.96, H 9.23.

Methyl *exo*-2-(Bicyclo[4.1.0]hept-7-yl)propenoate (1k): Methylenation of the oxo ester **7k** (18.2 g, 100 mmol) according to GP 5B gave a crude product (18.4 g), which was subjected to chromatography on silica gel (1.5 L), eluting with hexane/*t*BuOMe (20:1) to yield pure **1k** (16.5 g, 92%). IR (film): $\tilde{\nu}$ = 3107, 2996, 2927, 2852, 1721, 1627, 1435, 1403, 1355, 1322, 1264, 1193, 1140, 1082, 1028, 1014, 1001, 916, 872, 842, 813, 773, 734 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.03 (ddd, *J* = 5, 4, 1 Hz, 2 H, 2 CH), 1.20−1.28 (m, 4 H), 1.48 (t, *J* = 5 Hz, 1 H, CH), 1.64−1.75 (m, 2 H), 1.80−1.93 (m, 2 H), 3.76 (s, 3 H, CH_3), 5.16 (s, 1 H), 5.91 (d, *J* = 1 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.0 (2 CH), 21.2 (2 CH_2), 23.3 (2 CH_2), 24.0 (CH), 51.9 (CH_3), 118.8 (CH_2), 142.9 (C), 168.0 (C) ppm. MS (70 eV, EI): *m*/*z* (%) = 180 (24) [M^+], 165 (6) [$M^+ - CH_3$], 149 (9) [$M^+ - CH_3O$], 148 (18) [$M^+ - CH_3OH$], 137 (6), 121 (27) [$M^+ - CO_2Me$], 120 (37) [$M^+ - CH_3OH - CO$], 120 (28), 111 (3), 105 (17), 93 (29), 92 (36), 91 (70), 81 (100) [$C_6H_9^+$], 79 (86) [$C_6H_7^+$], 77 (51) [$C_6H_5^+$], 67 (34), 65 (15), 59 (15), 55 (10), 53 (17), 51 (6), 41 (79). HRMS (EI): calcd. for ($C_{11}H_{16}O_2$) [M^+] 180.1150, found 180.1150.

Ethyl *exo*-2-(Bicyclo[4.1.0]hept-2-en-7-yl)propenoate (1m): Methylenation of the oxo ester **7m** (7.6 g, 39 mmol) according to GP 5A gave after flash chromatography of the crude product on flash silica gel (120 mL), eluting with pentane/ether (20:1), pure **1m** (5.7 g, 76%) as a slightly yellow liquid. IR (film): $\tilde{\nu}$ = 3032, 2981, 2928, 2853, 1718, 1624, 1457, 1444, 1409, 1395, 1368, 1339, 1301, 1260, 1174, 1140, 1099, 1061, 1044, 1027, 940, 923, 861, 845, 811, 789, 724, 696 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.29$ (t, $J = 7$ Hz, 3 H, CH_3), 1.29−1.36 (m, 1 H), 1.43−1.66 (m, 2 H), 1.77−2.08 (m, 4 H), 4.20 (q, $J = 7$ Hz, 2 H, CH_2), 5.26 (dd, $J = 1$, 1 Hz, 1 H), 5.49 (ddd, $J = 9.5$, 6.5, 2.5 Hz, 1 H, CH), 5.98 (d, $J = 1$ Hz, 1 H), 6.01−6.08 (m, 1 H, CH) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 14.1$ (CH_3), 17.9 (CH_2), 20.7 (CH), 20.8 (CH_2), 23.8 (2 CH), 60.6 (CH_2), 119.8 (CH_2), 123.8 (CH), 127.0 (CH), 141.6 (C), 167.0 (C) ppm. MS (70 eV, EI): m/z (%) = 192 (9) [M^+], 164 (2) [$M^+ - C_2H_4$], 163 (12) [$M^+ - C_2H_5$], 147 (15) [$M^+ - C_2H_5O$], 146 (40) [$M^+ - C_2H_5OH$], 145 (47), 131 (7), 119 (5) [$M^+ - CO_2C_2H_5$], 118 (44) [$M^+ - CO_2C_2H_5 - H$], 117 (98), 114 (100), 105 (7), 103 (6), 91 (66), 86 (42), 79 (87) [$C_6H_7^+$], 78 (51), 77 (61) [$C_6H_5^+$], 65 (11), 53 (5), 51 (4), 41 (14). $C_{12}H_{16}O_2$ (192.25): calcd. C 74.97, H 8.39; found C 74.71, H 8.32.

Polymerizations: The polymerizations were carried out in sealed glass tubes as described previously.[2] The polymers were reprecipitated from THF/methanol and dried under vacuum to a constant weight.

Poly-1f: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.1-2.6$ (br., 8 H), 2.63 (s, 2 H, $CH_2{-}C{=}$), 3.71 (m, 6 H, 2 CH_3) ppm.

Poly-1h: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.25-1.80$ (br., 7 H), 2.19 (s, 1 H, $CH{-}CH{=}$), 2.36 (s, 2 H, $CH_2{-}C{=}$), 3.70 (s, 3 H, CH_3), 6.62 (s, 1 H, $-CH{=}$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 23.9$ (CH_2), 31.0 (CH_2), 31.8 (CH_2), 32.0 (CH_2) 46.2 (CH), 47.8 (CH), 51.2 (CH_3), 131.0 (C), 147.1 (CH), 168.4 (C) ppm.

Poly-1i: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.25-1.55$ (m, 4 H, CH, CH_3), 1.6−1.8 (br., 6 H), 2.17 (s, 1 H, $CH{-}CH{=}$), 2.39 (s, 2 H, $CH_2{-}C{=}$), 4.14 (m, 2 H, CH_2), 6.61 (s, 1 H, $-CH{=}$) ppm.

Poly-1k: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.84-2.68$ (br., 12 H), 3.74 (s, 3 H, CH_3), 6.7−7.1 (br., 1 H, $-CH{=}$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 23.7$ (CH_2), 25.9−26.4 (2 CH_2), 31.1 (CH_2), 32.4 (CH_2), 39.2 (CH), 42.7 (CH), 51.6 (CH_3), 130.6 (C), 148.0 (CH), 168.5 (C) ppm.

Poly-1l: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.95-1.7$ (br., 12 H), 2.27−2.67 (br., 3 H), 4.19 (m, 2 H, CH_2), 6.7−7.1 (br., 1 H, $-CH{=}$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 14.3$ (CH_3), 25.6−26.1 (3 CH_2), 31.0 (CH_2), 32.4 (CH_2), 39.2 (CH), 42.5 (CH), 60.3 (CH_2), 130.7 (C), 148.0 (CH), 168.1 (C) ppm.

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