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Cyclopropyl Building Blocks for Organic Synthesis, 139.[1] Ethyl Cyclopropylidenepyruvate as a Novel Multifunctional Cyclopropyl Building Block: Facile Preparation and Basic Reaction Patterns

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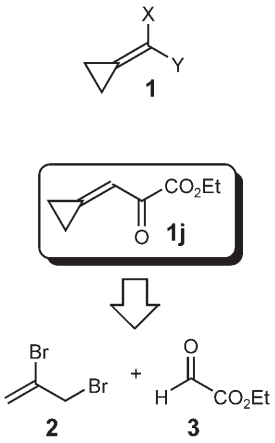
Abstract: Tin(II) chloride-mediated Barbier-type coupling of ethyl glyoxylate with 2,3-dibromopropene followed by Simmons–Smith cyclopropanation and subsequent Dess–Martin oxidation, afforded ethyl 3-(1-bromocycloprop-1-yl)-2-oxopropionate (**5**), a stable precursor of ethyl cyclopropylidenepyruvate (**1j**), in good overall yield (65%), even on a multi-gram scale. The potentially rich chemistry of this novel cyclopropyl building block was illustrated by some basic transformations such as Michael additions of N-, S-, O- and C-nucleophiles (10–91% yields), Diels–Alder reactions with cyclopentadiene (65%) and 2,3-dimethylbuta-1,3-diene (66%) as well as [4+2] cycloadditions across the enone moiety of **1j** (hetero-Diels–Alder reactions) with furan and enol ethers (65–79%), thus opening up a ready access to a wide range of new variously functionalized cyclopropane derivatives.

Keywords: bicyclic compounds; cycloadditions; Diels–Alder reactions; methylenecyclopropanes; Michael addition; spiro compounds

Introduction

In view of the wide variety of biologically active compounds containing a cyclopropane moiety, not only have cyclopropanations of alkenes gained increasing importance, but also the applications of highly functionalized molecular building blocks already containing a cyclopropane ring, which will be retained in the target structures. A series of 1′-substituted methylenecyclopropane derivatives **1** (Scheme 1) has demonstrated a range of reactivity patterns potentially useful for the synthesis of certain natural products and spirocyclopropanated analogues of biologically active compounds.[2,3] For example, bicyclopropylidene (**1a**) has been employed in various palladium-catalyzed cascade reactions,[2] and (benzyloxymethylene)-cyclopropane (**1b**) was used in the synthesis of a spirocyclopropane-annelated sugar[4] as well as interesting azetidine derivatives.[5] Several previously prepared acceptor-substituted methylenecyclopropanes **1c**–**h** come along with a particularly broad spectrum of applications.[3] Ethyl cyclopropylideneacetate (**1c**, R = Et) has recently been employed in new assemblies of the skeletons of the highly cytotoxic illudines[6] as well as other natural products,[7,8] and methyl 2-halo-2-cyclopropylideneacetates **1g**, **h** have been used to prepare a large variety of spirocyclopropanated carbo- and heterocyclic compounds[3,9] including a penicillin analogue[10] as well as cyclopropyl-group containing amino acids.[11]



1	X	Y	Ref.
a	–(CH$_2$)–		[2]
b	OBn	H	[4,5]
c	CO$_2$R	H	[12,13]
d	COMe	H	[12b,14]
e	CHO	H	[14,15]
f	CN	H	[16]
g	CO$_2$Me	Cl	[13,17]
h	CO$_2$Me	Br	[10,13]
i	CO$_2$Et	CO$_2$Et	[18]
j	COCO$_2$Et	H	this work

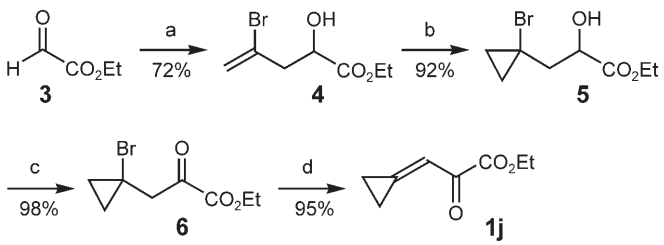
Scheme 1. Previously known methylenecyclopropanes **1a**–**i** with functionalities on the methylene group and retrosynthetic considerations concerning the newly conceived cyclopropylidenepyruvate **1j**.

In line with our long-standing interest in the design and development of new cyclopropyl building blocks for organic synthesis, we envisaged an enhanced reactivity of an alkyl cyclopropylidenepyruvate like **1j** in which the methylenecyclopropane double bond would be activated by the α-oxo ester moiety, and we here report the first synthesis of ethyl cyclopropylidenepyruvate (**1j**) as well as some of its potentially useful transformations.

Results and Discussion

In anticipation of the extreme reactivity of **1j**, it appeared to be most reasonable to first assemble its carbon framework and eventually elaborate the required functionalities by mild and highly efficient functional group transformations (Scheme 2). The thus conceived four-step synthesis started with an iodide-accelerated Barbier-type reductive allylation of ethyl glyoxylate (**3**) in the presence of $SnCl_2$[19] to give 4-bromo-2-hydroxypent-4-enoate (**4**) in good yield (72%). After some optimization, this procedure turned out to be easily scalable to produce **4** on a molar scale. The bromovinyl group in **4** was smoothly cyclopropanated[20] with a 3.3-fold excess of $CF_3COOZnCH_2I$ (so-called Shi's carbenoid)[21] to afford the key intermediate **5** in excellent yield (92%). Remarkably, the vinyl bromide **4** could be cyclopropanated with a significantly smaller excess of the reagent mixture than a vinyl chloride as reported by Evans et al.[22]

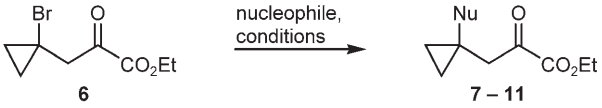
An initially attempted Swern oxidation of the 3-(1-bromocyclopropyl)-2-hydroxypropionate (**5**) failed, as it gave a complex mixture containing, along with various by-products, the target ethyl cyclopropylidenepyruvate **1j** (about 50%, according to an ^{1}H NMR spectrum of the reaction mixture), but the latter could not be isolated in pure form either by column chromatography (silica gel, Florisil® and alumina were tested) or by distillation. However, Dess–Martin[23] oxidation of **5** followed by "dry-column" flash chromatography[24] furnished sufficiently pure ethyl 3-(1-bromocyclopropyl)pyruvate (**6**). The final dehydrobromination of **6** was accomplished by stirring an ethereal solution of **6** with anhydrous sodium carbonate overnight. The obtained product showed no impurities in its ^{1}H NMR spectrum (purity > 95% according to GC) and was fully characterized by spectroscopic methods. Ethyl cyclopropylidenepyruvate (**1j**) is stable at room temperature in dilute solution, but as a neat compound irreversibly forms oligomeric products upon storage at ambient temperature even for short times. Even so, an attempted "Kugelrohr" distillation of crude **1j** afforded a pure sample albeit in poor yield (about 30%). This indicates that **1j** is thermally stable at temperatures not higher than 100 °C towards possible unimolecular processes such as rearrangements or extrusions.



Scheme 2. Synthesis of ethyl cyclopropylidenepyruvate (**1j**). *Reagents and conditions:* (a) 2,3-dibromopropene (**2**) (1.1 equivs.), $SnCl_2 \cdot 2H_2O$ (1.2 equivs.), NaI, THF, 25 °C, 24 h (1.2 equivs.); (b) Et_2Zn (3.3 equivs.), CF_3CO_2H (3.3 equivs.), CH_2I_2 (3.3 equivs.), CH_2Cl_2, −5 to 0 °C, 1.5 h, then 25 °C, 60 h; (c) Dess–Martin periodinane (1.1 equivs.), CH_2Cl_2, 25 °C, 1 h; (d) Na_2CO_3 (5 equivs.), Et_2O, 25 °C, 24 h.

The new cyclopropylidenepyruvate (**1j**) was first tested in reactions with a set of carbo- and heteronucleophiles. Because of its tendency to undergo oligomerization, **1j** is best generated *in situ* from its stable precursor, ethyl 3-(1-bromocyclopropyl)-2-oxopropionate (**6**) in the presence of the respective reaction partner. In order to achieve reasonable yields of the desired Michael adducts of **1j**, three different protocols were developed (Table 1) depending on the required base strength and on the nucleophilicity of the applied nucleophile. Thus, one additional equivalent of the nucleophile, when it is a sufficiently strong non-ionic base itself, such as a secondary aliphatic amine (Table 1, entry 1), or added triethylamine, in the case of weak bases such as phenols or mercaptans (Table 1, entry 2), were used to accomplish sequential elimination and Michael addition. With sodium azide and sodium nitrite (Table 1, entries 4 and 5), no additional base was required to eliminate hydrogen bromide from **6** thus liberating the respective conjugate acid, which in turn trapped the simultaneously formed **1j**. Whereas diethylamine, thiophenol, sodium azide and sodium nitrite gave the corresponding adducts **7**, **8**, **10**, **11** in good yields, *p*-methoxyphenol in the presence of triethylamine gave an inseparable mixture in which the respective Michael adduct was present to an extent of 10% (according to ^{1}H NMR), and Michael additions of aliphatic alcohols onto **1j** could not be achieved at all, since **1j** apparently does not tolerate hard bases such as hydroxide or alkoxide anions. Acid catalysis turned out to be ineffective, too. Treatment of **1j** or its precursor **6** with slightly basic water even for a short time caused complete loss of them. Therefore, the standard work-up procedure after the Dess–Martin oxidation, i.e., removal of the acidic by-products by washing with aqueous NaOH, had to be replaced by flash chromatography (see above).

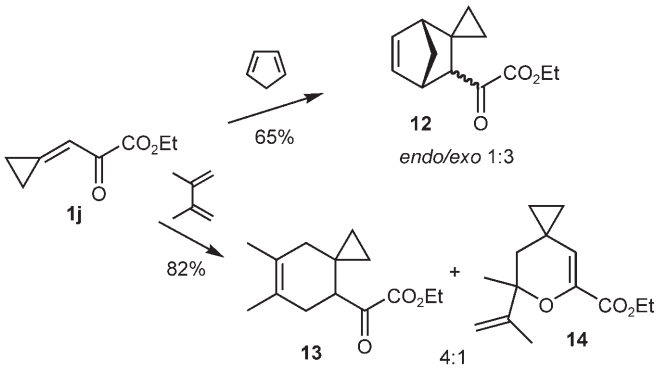
Table 1. Michael additions of various nucleophiles to ethyl cyclopropylidenepyruvate (**1j**) *in situ* generated from ethyl 3-(1-bromocyclopropyl)-2-oxopropionate (**6**).



Entry	Nucleophile	Base (equivs.)	Conditions	Product	Nu	Yield [%]
1	$HNEt_2$	$HNEt_2$ (1.1)	CH_2Cl_2, 0 °C, 1 h	**7**	Et_2N	90
2	PhSH	NEt_3 (1.1)	CH_2Cl_2, 0 °C, 1 h	**8**	PhS	91
3	$CH_2(CO_2Me_2)$	DBU (1.5)	THF, LiI (60 mol %), 25 °C, 2 h	**9**	$(MeO_2C)_2CH$	43
4	NaN_3	–	Et_2O, 18-crown-6 (5 mol %), 25 °C, 3 h	**10**	N_3	92
5	$NaNO_2$	–	Et_2O, 18-crown-6 (5 mol %), 25 °C, 3 h	**11**	O_2N	96

As Michael additions of carbon nucleophiles to 1′-acceptor-substituted methylenecyclopropanes do occur readily,[25] they were also tested for **1j**. An initially attempted reaction with sodium cyanide in DMF, EtOH or Et_2O with **6** led to a complex mixture of products, which must be due to the presence of the electrophilic carbonyl group in **6**, its dehydrobromination product **1j**, as well as the initial Michael adduct of type **7**.[26] However, the enolate of dimethyl malonate, generated with 1,8-diazabicyclo[5.3.0]undecene (DBU) in the presence of lithium iodide,[27] did provide the adduct **9**, but in moderate yield (43 %). Most probably, though, this yield may be significantly improved by appropriate modification of the reaction conditions.

The reactivity of **1j** in Diels–Alder reactions was initially tested with cyclopentadiene and 2,3-dimethylbuta-1,3-diene by dissolving **1j** in an excess of the diene and leaving the mixture at ambient temperature for 1 day (Scheme 3). The cyclopentadiene adduct **12** was obtained in 65 % yield as a 3:1 mixture of *endo*- and *exo*-diastereomers. Surprisingly, the reaction of **1j** with 2,3-dimethylbutadiene afforded in 82 % yield a 4:1 mixture of the expected [4+2] cycloadduct **13** and the 6-oxaspiro[2.5]octane derivative **14** resulting from an inverse electron-demand cycloaddition of **1j** acting as a heterodiene. Indeed, ethyl vinyl ether and 4,5-dihydrofuran also smoothly reacted with **1j** at ambient temperature to give the corresponding hetero-Diels–Alder (HDA) adducts **15** and **16** in 79 and 37 % yield, respectively. Furan furnished the spirocyclopropanated bicyclic HDA adduct **17** in good yield (65 %) as well. Being unstable towards either aqueous work-up or column chromatography, **17** underwent further transformations, affording the ring-opening product **18**, which may also be referred to as a formal Michael adduct of furan to **1j**, along with a small amount of **19** by addition of water to the dihydrofuran moiety in **17** (Scheme 4)



Scheme 3. Diels–Alder reactions of ethyl cyclopropylidenepyruvate (**1j**). *Reagents and conditions:* diene (2 mL per mmol of **1j**) neat, 25 °C, 24 h.

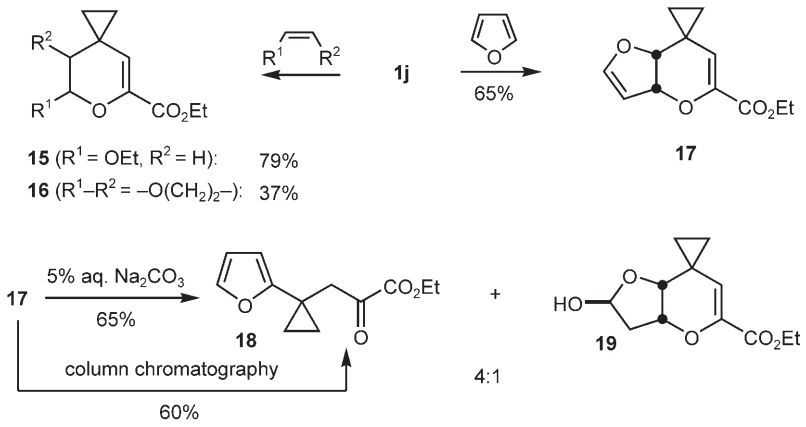
The lower yield of the cycloadduct **16** may be caused by a steric effect; thus, the slightly more sterically demanding 3,4-dihydropyran did not react with **1j** at all under the same reaction conditions. Simple cycloalkenes also did not undergo this cycloaddition.

The unexpectedly high reactivity of **1j** in inverse electron-demand HDA (no heating, no high pressure, no Lewis acid catalyst required) may originate from the preferred *s-cis* conformation of the enone moiety in **1j**.

The HDA adducts of **1j** can also be obtained by treating the stable precursor **6** of **1j** in an excess of the corresponding enol ether with triethylamine. In fact, under these conditions, the reactions were complete in significantly shorter time (1–2 h) and sometimes provided better yields of the respective adducts, (e.g., under these conditions **16** was obtained in 65 % yield), which may be due to a catalytic acceleration of the reaction by the formed triethylamine hydrobromide.

Conclusions

In conclusion, a short and highly efficient synthesis of the new multifunctional cyclopropyl building block, ethyl cyclopropylidenepyruvate (**1j**), has been developed, and the efficiency of the latter in a number of



Scheme 4. Inverse electron-demand hetero-Diels–Alder reactions of ethyl cyclopropylidenepyruvate (**1j**), and further transformations of the furan adduct of **1j**. *Reagents and conditions:* alkene (2 mL per mmol of **1j**), neat, 25 °C, 24 h.

synthetically useful transformations such as Michael additions, Diels–Alder and inverse-electron demand hetero-Diels–Alder reactions has been demonstrated. The new building block displayed a reactivity pattern, which is complementary in several aspects to those which the previously known acceptor-substituted methylenecyclopropanes feature.[28]

Experimental Section

General Remarks

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AM 250 (250 for ^{1}H, 62.9 MHz for ^{13}C) and Varian Unity 300 (300 for ^{1}H and 75.6 MHz for ^{13}C) instruments. Multiplicities were determined by DEPT (distortionless enhancement by polarization transfer; Bruker), or by APT (attached proton test; Varian) measurements. The residual signal of $CHCl_3$ served as an internal standard. IR: Bruker IFS 66 (FT-IR) spectrometer, samples were measured as KBr pellets or oils between KBr plates. MS (EI, 70 eV) or MS (70 eV, DCI, NH_3): Finnigan MAT 95 spectrometer. TLC: Macherey–Nagel precoated sheets, 0.25 mm Sil G/UV$_{254}$. Column chromatography: Merck silica gel 60 (70–230 mesh). Analytical gas chromatography: Varian CP-3800. Flash chromatography: Merck silica gel 60 230–400 mesh; the "dry column technique"[24] was applied. Elemental analyses were performed by Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen, with an elemental analyzer CHN-2000 (Leco). Starting materials and solvents: tetrahydrofuran (THF) was distilled from sodium/benzophenone. Anhydrous dichloromethane was distilled from phosphorus pentoxide under nitrogen and stored over molecular sieves 3 Å. Triethylamine was distilled from calcium hydride under nitrogen. 2,3-Dibromopropene (**3**) was prepared according to a published procedure.[29] All other chemicals were used as commercially available without further purification.

Ethyl 4-Bromo-2-hydroxypent-4-enoate (4)

To a stirred solution of $SnCl_2{\cdot}2H_2O$ (86.9 g, 385 mmol) and NaI (57.7 g, 385 mmol) in THF (600 mL) were added ethyl glyoxylate (**3**) (64 mL of a ~50% solution in toluene, ~320 mmol) and 2,3-dibromopropene (**2**) (70.4 g, 352 mmol), with occasional cooling of the reaction mixture with ice/water. After the slightly exothermic reaction had ceased, the cooling bath was removed, and the mixture was stirred at ambient temperature for 24 h, then poured into a half-saturated aqueous solution of NH_4Cl (600 mL). The organic layer was separated and the aqueous phase was re-extracted with diethyl ether (3×200 mL). The combined organic phases were washed with half-diluted brine (2× 400 mL; iodine was removed by addition of a minimal amount of crystalline $Na_2S_2O_3$ during the first washing), brine (500 mL), and dried with $MgSO_4$. Removal of the solvent left 66.4 g of a pale-yellow crude product, which was rectified under reduced pressure through a 20 cm Vigreux column, affording pure **3** as a colorless oil; yield: 51.6 g (72%); bp 62–63 °C (0.02 mbar). IR (film): $\tilde{\nu}$ = 3466, 2982, 2938, 2907, 1739, 1735, 1633, 1473, 1445, 1419, 1369, 1274, 1217, 1131, 1099, 1033, 1017, 952, 894, 863 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.2 Hz, 3H), 2.73 (ddd, J = 14.7, J = 8.3, J = 0.8 Hz, 1H), 2.88 (bs, 1H), 2.92 (dddd, J = 14.7, J = 4.0, J = 1.2, 0.5 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.45 (dd, J = 8.3, 4.0 Hz, 1H), 5.57 (dd, J = 1.8, J = 0.8 Hz, 1H), 5.74 (ddd, J = 1.8, J = 1.2, 0.5 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 14.2 (CH_3), 46.0 (CH_2), 62.1 (CH_2), 68.4 (CH), 120.4 (CH_2), 128.1 (C), 173.8 (C); MS (70 eV, DCI, NH_3): m/z (%) = 257/259 (4/5) [M + NH_3 + NH_4]$^+$, 242/240 (92/100) [M + NH_4]$^+$, 162 (2) [M + NH_4 − Br]$^+$, 143 (4) [M − Br]$^+$; anal. calcd. for $C_7H_{11}BrO_3$ (223.06): C 37.69, H 4.97; found: C 37.68, H 5.00.

Ethyl 3-(1-Bromocycloprop-1-yl)-2-hydroxypropionate (5)

To a mechanically stirred solution of $ZnEt_2$ (50 mL, 0.488 mol) in anhydrous CH_2Cl_2 (450 mL) chilled at −25 °C under nitrogen, was added trifluoroacetic acid (36 mL, 0.486 mol) within 1 h at such a rate that the temperature did not exceed 0 °C (***Caution!*** Gas evolution! Full size adapters, gas

inlets and bubblers charged with paraffin oil must be used to avoid clogging of holes with solid particles from the reaction mixture). After additional stirring at 0 °C for 15 min, CH_2I_2 (40 mL, 0.496 mol) was added all at once, keeping the temperature around 0 °C with occasional cooling (ice/salt bath), and the reaction mixture was vigorously stirred at this temperature until it had become completely homogeneous (25–30 min). To this carbenoid solution was added **4** (33 g, 0.148 mol) dropwise at 0 °C within 15 min. After stirring at this temperature for an additional 30 min, the cooling bath was removed, and the mixture was stirred at ambient temperature for 60 h (at that point, a gas chromatogram of the reaction mixture showed only about 1 % of the starting material to be left). The vigorously stirred reaction mixture was then cooled to 0 °C (ice/salt bath), and 2 M aqueous H_2SO_4 (250 mL) was gradually added (the first 50 mL was added slowly and carefully). The phases were separated and the aqueous layer was extracted with diethyl ether (3×200 mL). The combined organic phases were subsequently washed with 2 N NaOH (250 mL), brine (2×150 mL) and dried over $MgSO_4$. The residue obtained after evaporation of the solvents was distilled under reduced pressure to give pure **5** as a pale-yellow oil; yield: 32.3 g (92 %); bp 75–76 °C (0.1 mbar). IR (film): $\tilde{\nu}$ = 3485, 2983, 2939, 2908, 2874, 1735, 1473, 1465, 1458, 1448, 1419, 1370, 1272, 1224, 1149, 1108, 1045, 1023, 941, 860, 819, 772, 684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.78–0.90 (m, 1 H), 1.00–1.08 (m, 1 H), 1.12–1.26 (m, 2 H), 1.32 (t, J = 7.2 Hz, 3 H), 1.67 (dd, J = 14.8, J = 8.8 Hz, 1 H), 2.46 (ddd, J = 14.8, J = 3.5, J = 1.2 Hz, 1 H), 2.82 (bs, 1 H), 4.18–4.33 (m, 2 H), 4.54 (dd, J = 8.8, 3.5 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 14.1 (CH_3), 15.5 (CH_2), 16.4 (CH_2), 30.9 (C), 46.2 (CH_2), 61.9 (CH_2), 69.9 (CH), 174.7 (C) ppm; MS (70 eV, EI): m/z (%) = 238/236 (0.5) [M^+], 165/163 (3/3) [$M^+-C_2H_5O-CO$], 157 (18) [M^+-Br], 139 (2) [M^+-Br-H_2O], 129 (8) [$M^+-Br-C_2H_5$], 111 (13) [M^+-Br-H_2O], 104 (27) 83 (31) [$M^+-Br-C_2H_5OH-CO$], 76 (17), 75 (10), 67 (6), 55 (100), 53 (20), 45 (3); anal. calcd. for $C_8H_{13}BrO_3$ (237.09): C 40.53, H 5.53; found: C 40.50, H 5.50.

Ethyl 3-(1-Bromocycloprop-1-yl)-2-oxopropionate (6)

Compound **5** (4.74 g, 20 mmol) was added in one portion to a stirred solution of Dess–Martin periodinane (9.33 g, 22 mmol) in anhydrous CH_2Cl_2 (20 mL), and the mixture was stirred at ambient temperature until the starting material had completely disappeared (60–80 min, TLC control). The mixture was then diluted with pentane (100 mL), and the obtained suspension was passed through a short plug of flash silica gel (80 mL, Ø65 mm) eluting with hexane/EtOAc, 5:1 (5×100 mL), to afford sufficiently pure **5**; yield 4.61 g (98 %). The thus obtained product is sufficiently stable at ambient temperature in solution; the neat compound could be stored infinitely at temperatures below −20 °C. IR (film): $\tilde{\nu}$ = 3088, 3005, 2985, 2940, 2907, 2875, 1748, 1731, 1474, 1446, 1391, 1371, 1306, 1266, 1230 1143, 1097, 1068, 1028, 1015, 975, 936, 912, 860, 848, 819, 787, 763, 744, 689 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.94–1.00 (m, 2 H), 1.24–1.30 (m, 2 H), 1.38 (t, J = 7.2 Hz, 3 H), 3.29 (s, 2 H), 4.33 (q, J = 7.2 Hz, 2 H); ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 13.9 (CH_3), 16.3 (2 CH_2), 25.2 (C), 50.3 (CH_2), 62.7 (CH_2), 160.9 (C), 190.8 (C).

Ethyl Cyclopropylidenepyruvate (1j)

Compound **6** (1.18 g, 5.02 mmol) was added to a suspension of oven-dried finely powdered Na_2CO_3 (2.65 g, 25.0 mmol) in anhydrous diethyl ether (25 mL), and the mixture was stirred at ambient temperature for 24 h. Filtration and solvent evaporation at 0 °C afforded sufficiently pure **1j** as a colorless or pale-yellow liquid. IR (film): $\tilde{\nu}$ = 3055, 2986, 2940, 2908, 2876, 2855, 1745, 1733, 1677, 1476, 1466, 1448, 1401, 1394, 1371, 1315, 1268, 1250, 1175, 1143, 1102, 1037, 1016, 970, 925, 874, 814, 770, 732 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.32–1.52 (m, 4 H), 1.37 (t, J = 7.1 Hz, 3 H), 4.34 (q, J = 7.1 Hz, 2 H), 6.78 (tt, J = 1.9, 1.7 Hz, 1 H); ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 2.8 (CH_2), 5.0 (CH_2), 14.0 (CH_3), 62.4 (CH_2), 116.1 (CH), 152.9 (C), 164.3 (C), 185.6 (C); MS (70 eV, EI): m/z (%) = 154 (7) [M^+], 126 (14) [M^+-CO], 109 (2) [$M^+-C_2H_5O$], 98 (10) [M^+-2 CO], 81 (100) [$M^+-C_2H_5O-CO$], 53 (54) [$C_4H_5^+$], 51 (6) [$C_4H_3^+$], 42 (2). The neat compound thus obtained has to be used immediately, since it is extremely susceptible to undergo oligomerization.

General Procedure for Reaction of 6 with Neutral Nucleophiles (GP 1)

To an ice-cold solution of **6** (470 mg, 2.0 mmol) in anhydrous CH_2Cl_2 (4 mL) the respective nucleophile (2 mmol) was added all at once, and triethylamine (2.1 mmol, 212 mg) was gradually added within 5 min. After additional stirring at 2 °C for 1 h, the reaction mixture was diluted with anhydrous ether (20 mL), and filtered. Evaporation of the solvents left a crude product, which was purified by chromatography on silica gel.

Ethyl 3-[1-(*N,N*-Diethylamino)cycloprop-1-yl]-2-oxopropionate (7)

According to GP 1, **6** reacted with diethylamine (146 mg, 2 mmol) to afford after flash chromatography on silica gel (10 g), eluting with hexane/ethyl acetate/ethanol, 40/10/1 to 20/10/1, 409 mg of pure **7** (90 %), as a 2:1 mixture of tautomers.

Major tautomer: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.55–0.61 (m, 2 H), 0.65–0.71 (m, 2 H), 0.88 (t, J = 7.1 Hz, 3 H), 0.95 (t, J = 7.2 Hz, 6 H), 2.48 (q, J = 7.2 Hz, 4 H), 2.74 (s, 2 H), 3.88 (q, J = 7.1 Hz, 2 H); ^{13}C NMR (62.5 MHz, C_6D_6): δ = 13.5 (CH_3), 14.3 (2 CH_2), 15.0 (2 CH_3), 39.7 (CH_2), 41.5 (C), 46.9 (2 CH_2), 61.9 (CH_2), 162.5 (C), 193.9 (C).

Minor tautomer: ^1H NMR (250 MHz, $CDCl_3$): δ = 0.49–0.54 (m, 2 H), 0.70–0.75 (m, 2 H), 0.93 (t, J = 7.2 Hz, 6 H), 0.98 (t, J = 7.1 Hz, 3 H), 2.01 (q, J = 7.2 Hz, 4 H), 4.06 (q, J = 7.1 Hz, 2 H), 5.41 (s, 1 H); ^{13}C NMR (62.5 MHz, C_6D_6): δ = 13.8 (2 CH_3), 14.0 (CH_3), 14.3 (2 CH_2), 42.4 (C), 46.4 (CH_2), 60.8 (CH_2), 115.2 (CH), 145.1 (C), 164.4 (C); MS (70 eV, DCI, NH_3): m/z (%) = 455 (2) [2M+H]$^+$, 228 (100) [M+H], 154 (5) [M^+-Et_2NH]; anal. calcd. for $C_{12}H_{21}NO_3$ (227.30): C 63.41, H 9.31, N 6.16; found: C 63.15, H 9.08, N 5.99.

Ethyl 3-(1-Phenylsulfonylcycloprop-1-yl)-2-oxopropionate (8)

According to GP 1, **6** reacted with thiophenol (220 mg, 2 mmol) to afford after column chromatography on silica

gel (30 g), eluting with hexane/ethyl acetate, 8:1 to 6:1, pure **8**; yield: 480 mg (91%). IR (film): $\tilde{\nu}$ = 3077, 3060, 3003, 2985, 2965, 2939, 2903, 1750, 1728, 1584, 1479, 1440, 1392, 1370, 1294, 1261, 1241, 1172, 1158, 1092, 1069, 1058, 1025, 1015, 980, 858, 849, 828, 741, 692 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 1.01–1.09 (m, 2H), 1.12–1.20 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H, CH_3), 3.09 (s, 2H, CH_2), 4.29 (q, J = 7.2 Hz, 2H, CH_2), 7.18–7.42 (m, 5H); ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 13.9 (CH_3), 15.7 (2 CH_2), 21.3 (C), 46.3 (CH_2), 62.5 (CH_2), 126.4 (CH), 129.0 (2 CH), 129.3 (2 CH), 135.5 (C), 161.3 (C), 192.2 (C); MS (70 eV, EI): m/z (%) = 264 (16) [M^+], 246 (18) [$M^+ - H_2O$], 235 (9), 217 (2), 200 (8), 191 (41), 173 (16), 163 (62), 148 (28), 135 (100), 129 (58), 123 (26), 115 (23), 109 (57), 91 (94), 85 (8), 81 (37), 77 (28), 71 (8), 69 (13), 65 (34), 55 (13), 53 (45), 51 (24), 45 (29), 41 (5); anal. calcd. for $C_{14}H_{16}O_3S$ (264.34): C 63.61, H 6.10; found: C 63.46, H 5.93.

General Procedure for Michael Additions of β-Dicarbonyl Compounds to *in situ* Generated 1j (GP 2)

To a stirred solution of **6** (470 mg, 2 mmol), LiI (161 mg 1.2 mmol) in anhydrous THF (4 mL) and DBU (457 mg, 3 mmol) were added within 10 min keeping the mixture around 20 °C with occasional cooling (cold water). After stirring at ambient temperature for 2 h, the reaction was quenched by addition of 5% aqueous H_2SO_4 (2 mL), the organic layer was separated, and the aqueous phase was re-extracted with diethyl ether (3 × 2 mL). The combined organic phases were washed with brine (2 × 5 mL) and dried with $MgSO_4$. Solvent removal left a crude product, which was purified by chromatography on silica gel.

Dimethyl 2-[1-(3-Ethoxy-2,3-dioxopropyl)cyclopropyl]-malonate (9)

According to GP 2, **6** reacted with dimethyl malonate (264 mg, 2 mmol) to afford, after column chromatography on silica gel (50 g), eluting with hexane/ethyl acetate, 4:1, pure **9** as a viscous colorless oil; yield: 246 mg (43%). IR (film): $\tilde{\nu}$ = 3085, 3003, 2988, 2957, 2907, 2847, 1750, 1734, 1437, 1395, 1369, 1321, 1301, 1267, 1195, 1157, 1095, 1071, 1057, 1034, 949, 746 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.69–0.73 (m, 4H), 1.36 (t, J = 7.1 Hz, 3H), 3.00 (s, 1H), 3.13 (s, 2H), 3.72 (s, 6H), 4.30 (q, J = 7.1 Hz, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 12.1 (2 CH_2), 14.0 (CH_3), 15.6 (C), 43.8 (CH_2), 52.5 (2 CH_3), 57.1 (CH), 62.4 (CH_2), 160.9 (C), 168.7 (2 C), 192.7 (C); MS (70 eV, EI): m/z (%) = 286 (0.2) [M^+], 255 (12), 227 (10), 223 (8), 213 (100), 199 (8), 195 (4), 185 (16), 181 (72), 167 (4), 153 (42), 139 (5), 125 (46), 121 (17), 111 (5), 95 (7), 85 (15), 81 (5), 67 (6), 59 (13), 53 (6), 41 (4); ESI-HR-MS: m/z = 325.06841, calcd. for $C_{13}H_{18}O_7$ [M + K]$^+$: 286.10525.

General Procedure for Reactions of 6 with Nucleophilic Salts (GP 3)

To a stirred suspension of the respective salt (2.4 mmol) and 18-crown-6 (26.4 mg, 0.1 mmol) in anhydrous diethyl ether (4 mL), **6** (573 mg, 2 mmol) was added all at once and the reaction mixture was stirred at ambient temperature for 3 h. Then water (2 mL) was added, and the aqueous phase was extracted with diethyl ether (2 × 2 mL). The combined organic layers were washed with brine (4 mL) and dried with $MgSO_4$. Chromatographic purification of the residue obtained after solvent removal, afforded the pure product.

Ethyl 3-(1-Azidocycloprop-1-yl)-2-oxopropionate (10)

According to GP 3, **6** reacted with sodium azide (158 mg, 2.4 mmol) to afford, after column chromatography on silica gel (40 g), eluting with hexane/ethyl acetate, 8:1, pure **10** as a pale-yellow oil; yield: 363 mg (92%). IR (film): $\tilde{\nu}$ = 3005, 2986, 2941, 2907, 2117, 2101, 1750, 1733, 1363, 1309, 1284, 1262, 1172, 1160, 1069, 1027, 1015 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.75–0.80 (m, 2H), 1.03–1.08 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 3.11 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 12.3 (2 CH_2), 13.9 (CH_3), 39.0 (C), 45.9 (CH_2), 62.7 (CH_2), 160.7 (C), 191.7 (C); MS (70 eV, DCI, NH_3): m/z (%) = 412 (10) [2M + NH_4]$^+$, 232 (32) [M + NH_3 + NH_4]$^+$, 215 (100) [M + NH_4]$^+$, 187 (8), 170 (12)143 (5); anal. calcd. for $C_8H_{11}N_3O_3$ (197.19): C 48.73, H 5.62, N 21.31; found: C 48.68, H 5.52, N 21.10.

Ethyl 3-(1-Nitrocycloprop-1-yl)-2-oxopropionate (11)

According to GP 3, **6** (2.95 g, 12.5 mmol) reacted with sodium nitrite (1.04 g, 15 mmol) to afford, after flash chromatography on silica gel (50 mL), eluting with hexane/ethyl acetate, 8:1 to 3:1, pure **11** as a viscous colorless oil which crystallized in the refrigerator; yield: 2.43 g (96%); mp 55–56 °C. IR (film): $\tilde{\nu}$ = 3115, 2987, 2942, 2910, 2880, 1751, 1733, 1538, 1474, 1468, 1461, 1446, 1396, 1375, 1354, 1315, 1273, 1256, 1159, 1080, 1064, 1013, 991, 969, 938, 920, 878, 849, 815, 743, 729, 691, 584 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15–1.30 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.95–2.10 (m, 2H), 3.53 (s, 2H), 4.36 (q, J = 7.1 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 13.9 (CH_3), 17.9 (2 CH_2), 41.9 (CH_2), 60.1 (C), 62.9 (CH_2), 160.2 (C), 189.1 (C); MS (70 eV, DCI, NH_3): m/z (%) = 236 (34) [M + NH_3 + NH_4]$^+$, 219 (100) [M + NH_4]$^+$, 205 (67), 189 (24), 174 (65), 172 (81), 156 (2), 135 (9), 103 (4); anal. calcd. for $C_8H_{11}NO_5$ (201.18): C 47.76, H 5.51; found: C 47.80, H 5.47.

General Procedure for Diels–Alder Reactions of 1j or its Precursor 6 (GP 4)

Method A: Freshly prepared **1j** (154 mg, 1 mmol) was dissolved in the respective diene or enol ether (2 mL) and the solution was left at ambient temperature for 24 h. After the excess of the diene or enol ether had been removed under reduced pressure, the residue was purified by chromatography to give a sufficiently pure adduct.

Method B: To a stirred solution of **6** (235 mg, 1 mmol) in excess of the respective alkene (2 mL) anhydrous triethylamine (101 mg, 1 mmol) was added all at once, and the mixture was stirred at ambient temperature for 2 h. Then the reaction mixture was poured into the water (2 mL) and extracted with diethyl ether (3 × 2 mL). The combined extracts were washed with half-saturated brine (3 mL), brine (5 mL) and dried over $MgSO_4$. The residue, obtained after removal of the volatile materials under reduced pressure, was subjected to column chromatography to afford an appropriately pure adduct.

Ethyl *endo*-/*exo*-Spiro[cyclopropane-1,2′-norborn-5′-en-3′-yl]oxoacetate (12)

According to GP 4A, **1j** (154 mg, 1 mmol) reacted with cyclopentadiene (2 mL) to afford, after column chromatography on silica gel (50 mL), eluting with hexane/*t*-BuOMe, 20:1, an inseparable mixture of *endo*- and *exo*-diastereomers (*endo/exo* ratio according to ^{1}H NMR 3:1) of pure **12** as a colorless oil; yield: 143 mg (65%). IR (film): $\tilde{\nu}$ = 3065, 2978, 2940, 2908, 2871, 1747, 1726, 1653, 1558, 1457, 1331, 1270, 1255, 1215, 1159, 1117, 1075, 1017, 947, 904, 861, 716 cm^{-1}.

***endo*-12:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.45–0.64 (m, 4H), 1.35 (t, J = 7.1 Hz, 3H), 1.58–1.63 (m, 1H), 1.85–1.90 (m, 1H), 2.08–2.12 (m, 1H), 3.27–3.31 (m, 1H), 3.72 (d, J = 3.2 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 6.10 (dd, J = 5.7, 2.8 Hz, 1H), 6.31 (dd, J = 5.7, 3.2 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$, APT): δ = 7.8 (CH_2), 11.1 (CH_2), 13.9 (CH_3), 28.2 (C), 47.8 (CH), 49.2 (CH_2), 52.5 (CH), 54.4 (CH), 62.1 (CH_2), 133.6 (CH), 137.4 (CH), 162.0 (C), 194.9 (C).

***exo*-12:** ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.65–0.74 (m, 4H), 1.35 (t, J = 7.1 Hz, 3H), 1.47–1.53 (m, 1H), 1.99–2.04 (m, 1H), 2.05–2.07 (m, 1H), 2.99 (d, J = 1.6 Hz, 1H), 3.05–3.09 (m, 1H), 4.28 (q, J = 7.1 Hz, 2H), 6.27 (dd, J = 5.7, 3.0 Hz, 1H), 6.34 (dd, J = 5.7, 2.9 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$, APT): δ = 8.9 (CH_2), 9.0 (CH_2), 13.9 (CH_3), 28.6 (C), 47.0 (CH_2), 47.4 (CH), 51.6 (CH), 51.9 (CH), 62.3 (CH_2), 136.1 (CH), 138.3 (CH), 161.6 (C), 196.8 (C); MS (70 eV, EI): *m/z* (%) = 220 (2) [M$^+$], 192 (7), 174 (2), 163 (3), 147 (65), 119 (53), 117 (39), 104 (7), 91 (100), 81 (30), 79 (17), 77 (18), 66 (44), 53 (20), 51 (7), 41 (39); anal. calcd. for $C_{13}H_{16}O_3$ (220.26): C 70.89, H 7.32; found: C 70.85, H 7.07.

Reaction of 1j with 2,3-Dimethylbutadiene

According to GP 4A, **1j** (154 mg, 1 mmol) reacted with 2,3-dimethylbutadiene (2 mL) to afford, after column chromatography on silica gel (100 mL), eluting with hexane/*t*-BuOMe, 20:1, pure *ethyl (6,7-dimethylspiro[2.5]oct-6-en-4-yl)-2-oxoacetate* (**13**; yield: 156 mg, 66%) and sufficiently pure *ethyl 7-methyl-7-(1-isopropenyl)-6-oxaspiro[2.5]oct-4-ene-5-carboxylate* (**14**; yield: 38 mg, 16%). Alternatively, after **1j** (940 mg, 4 mmol) had been subjected to the GP 4B, **13** (yield: 605 mg, 64%) and **14** (yield: 39 mg, 4%) were isolated.

Compound 13: Colorless oil. IR (film): $\tilde{\nu}$ = 3075, 2989, 2911, 2883, 2862, 2827, 1746, 1725, 1464, 1445, 1427, 1384, 1369, 1298, 1268, 1230, 1121, 1074, 1040, 1022, 979, 948, 932, 905, 858, 832, 787, 766, 733 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.34–0.41 (m, 2H), 0.43–0.50 (m, 1H), 0.63–0.70 (m, 1H), 1.22–1.30 (m, 1H, 8-H), 1.36 (t, J = 7.1 Hz, 3H), 1.54–1.56 (m, 3H), 1.65–1.67 (m, 3H), 2.25–2.35 (m, 3H), 2.62 (ddd, J = 5.0, 3.7, 0.9 Hz, 1H), 4.23–4.39 (m, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 10.6 (CH_2), 13.3 (CH_2), 14.0 (CH_3), 16.9 (C), 18.8 (CH_3), 18.9 (CH_3), 30.9 (CH_2), 39.3, (CH_2), 49.0 (CH), 62.1 (CH_2), 123.4 (C), 125.2 (C), 164.1 (C), 196.9 (C); MS (70 eV, EI): *m/z* (%) = 236 (3) [M$^+$], 208 (2), 189 (2), 163 (17), 147 (6), 145 (24), 135 (66), 133 (13), 120 (27), 117 (7), 107 (100), 105 (28), 93 (39), 91 (40), 89 (6), 79 (19), 77 (15), 69 (4), 67 (5), 65 (7), 55 (13), 53 (8), 43 (8), 41 (20); anal. calcd. for $C_{14}H_{20}O_3$ (236.31): C 71.16, H 8.53; found: C 70.89, H 8.33.

Compound 14: Colorless oil. IR (film): $\tilde{\nu}$ = 3079, 2982, 2952, 2935, 2872, 1728, 1638, 1456, 1446, 1395, 1371, 1341, 1321, 1305, 1275, 1236, 1213, 1172, 1140, 1105, 1087, 1027, 981, 954, 902, 866, 854, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72–0.80 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 1.43 (s, 3H), 1.71 (d, J = 13.8 Hz, 1H), 1.78 (dd, J = 1.3, 0.6 Hz, 3H), 1.85 (d, J = 13.8 Hz, 1H), 4.14–4.34 (m, 2H), 4.86 (dq, J = 1.5, 1.3 Hz), 4.98 (dq, J = 1.5, 0.6 Hz), 5.61 (s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$, APT): δ = 14.2 (CH_3), 14.6 (CH_2), 15.0 (C), 15.2 (CH_2), 19.0 (CH_3), 25.1 (CH_3), 40.1 (CH_2), 60.8 (CH_2), 80.5 (C), 110.8 (CH_2), 119.4 (CH), 142.4 (C), 146.6 (C), 162.9 (C); MS (70 eV, EI): *m/z* (%) = 236 (39) [M$^+$], 221 (3), 207 (8), 191 (8), 175 (9), 162 (62), 147 (55), 135 (86), 119 (73), 107 (100), 105 (40), 93 (47), 91 (53), 82 (16), 79 (25), 69 (5), 67 (21), 65 (12), 55 (13), 53 (25), 51 (7), 43 (7), 41 (27); HR-MS (ESI, MeOH/H_2O + FA): *m/z* = 237.14852, calcd. for [M + H]$^+$: 237.14907.

Ethyl 7-Ethoxy-6-oxaspiro[2.5]oct-4-ene-5-carboxylate (15)

According to GP 4A, **1j** (154 mg, 1 mmol) reacted with ethyl vinyl ether (2 mL) to afford, after column chromatography on silica gel (50 mL), eluting with hexane/*t*-BuOMe, 8:1, pure **15** as a colorless oil; yield: 179 mg (79%). IR (film): $\tilde{\nu}$ = 3080, 2979, 2929, 2873, 1729, 1640, 1480, 1468, 1461, 1445, 1390, 1371, 1332, 1310, 1260, 1232, 1201, 1171, 1160, 1125, 1090, 1050, 1037, 1004, 964, 934, 870, 860, 846, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.63–0.88 (m, 4H), 1.21 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 1.64 (ddd, J = 13.6, 4.4, 0.8 Hz, 1H), 1.95 (dd, J = 13.6, 2.6 Hz, 1H), 3.64 (dq, J = 9.8, 7.1 Hz, 1H), 3.92 (dq, J = 9.8, 7.1 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 5.22 (dd, J = 4.4, 2.6 Hz, 1H), 5.69 (d, J = 0.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 13.9 (C), 14.0 (CH_2), 14.2 (CH_3), 15.1 (CH_3), 16.1 (CH_2), 36.4 (CH_2), 60.9 (CH_2), 64.3 (CH_2), 98.2 (CH), 121.4 (CH), 140.6 (C), 162.7 (C); MS (70 eV, EI): *m/z* (%) = 226 (8) [M$^+$], 197 (17), 181 (5), 153 (30), 151 (20), 135 (3), 125 (38), 123 (36), 107 (59), 97 (32), 95 (17), 81 (41), 79 (56), 77 (19), 69 (19), 67 (54), 55 (13), 53 (47), 43 (39), 41 (100); anal. calcd. for $C_{12}H_{18}O_4$ (226.27): C 63.70, H 8.02; found: C 63.85, H 7.84.

Ethyl *cis*-4,4-Ethano-2*H*-dihydrofuro[2,3-*b*]pyran-6-ylcarboxylate (16)

According to GP 4B, **6** (235 mg, 1 mmol) reacted with 2,3-dihydrofuran (2 mL) to afford, after column chromatography on silica gel (50 mL), eluting with hexane/ethyl acetate, 5:1, pure **16** as a colorless oil; yield: 146 mg (65%). IR (film): $\tilde{\nu}$ = 3080, 2980, 2955, 2939, 2901, 1726, 1642, 1456, 1429, 1395, 1373, 1340, 1303, 1255, 1217, 1173, 1128, 1084, 1052, 1028, 1012, 970, 929, 908, 886, 864, 842, 763, 731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72–1.00 (m, 4H, 2 CH_2), 1.31 (t, J = 7.1 Hz, 3H), 1.79–2.04 (m, 3H), 3.83–3.99 (m, 1H), 4.17–4.33 (m, 3H), 5.44 (d, J = 3.2 Hz, 1H), 5.54 (d, J = 1.0 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 13.1 (CH_2), 14.4 (CH_3), 17.0 (C), 18.4 (CH_2), 27.4 (CH_2), 47.0 (CH), 61.3 (CH_2), 68.6 (CH_2), 100.2 (CH), 117.4 (CH), 141.0 (C), 162.6 (C); MS (70 eV, EI): *m/z* (%) = 224 (10) [M$^+$], 195 (18), 151 (72), 122 (9), 107 (6), 105 (27), 95 (10), 93 (8), 81 (10), 79 (13), 77 (9), 71 (100), 67 (9), 55 (8), 53 (16), 43

(22), 41 (27); anal. calcd. for $C_{12}H_{16}O_4$ (224.25): C 64.27, H 7.19; found: C 64.93, H 6.96.

Ethyl *cis*-7,7-Ethano-7,7a-dihydro-3a*H*-furo[3,2-*b*]-pyran-5-carboxylate (17)

Thus, according to GP 4A, **1j** (154 mg, 1 mmol) reacted with furan (2 mL) to afford after flash chromatography on silica gel (50 mL), eluting with hexane/ethyl acetate, 5:1 to 3:1, sufficiently pure **17** as a colorless oil; yield: 146 mg (65%). Compound **17** turned out to be sensitive to silica gel and thus could not be purified completely by column chromatography, it was characterized by NMR spectra only. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.91$–1.07 (m, 4H), 1.28 (t, $J =$ 7.1 Hz, 3H), 3.89 (ddd, $J = 6.1$, 1.5, 0.6, Hz, 1H), 4.22 (dq, $J = 9.8$, 7.1 Hz, 1H), 4.23 (dq, $J = 9.8$, 7.1 Hz, 1H), 5.13 (ddd, $J = 6.1$, 2.7, 0.5 Hz, 1H), 5.41 (dd, $J = 2.7$, 2.7 Hz, 1H), 5.64 (d, $J = 1.5$ Hz, 1H), 6.62 (ddd, $J = 2.7$, 0.6, 0.5 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): $\delta = 12.9$ (CH_2), 14.2 (CH_3), 16.6 (C), 17.6 (CH_2), 61.1 (CH_2), 78.5 (CH), 85.8 (CH), 103.4 (CH), 116.2 (CH), 144.0 (C), 151.4 (CH), 162.3 (C).

Ethyl 3-(1-Furylcycloprop-1-yl)-2-oxopropionate (18) and Ethyl (*exo, cis*)-7,7-Ethano-2-hydroxy-2,3,3a,7a-tetrahydrofuro[3,2-*b*]pyran-5-carboxylate (19)

According to GP 4A, **1j** (154 mg, 1 mmol) and furan (2 mL) gave after work-up with 5% aqueous Na_2CO_3 and subsequent column chromatography of the crude residue on silica gel (20 mL), eluting with hexane/ethyl acetate, 6:1 ($R_f = 0.3$) to 4:1, the furan derivative **18** as a colorless oil; yield: 107 mg (48%). Further elution with hexane/ethyl acetate/MeOH, 20:5:1, afforded the pure heterocyclic hemiacetal **19** as *exo*-isomer ($dr > 90$%, according to its ^{1}H NMR spectrum); yield: 30 mg (12%).

Compound 18: IR (film): $\tilde{\nu} = 3119$, 3090, 3004, 2986, 2939, 2907, 1748, 1728, 1593, 1510, 1298, 1260, 1195, 1158, 1108, 1069, 1057, 1014, 932, 913, 857, 796, 734 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.85$–0.90 (m, 2H), 1.09–1.14 (m, 2H), 1.34 (t, $J = 7.1$ Hz, 3H), 3.13 (s, 2H), 4.28 (q, $J =$ 7.1 Hz, 2H), 5.94 (dd, $J = 3.2$, 0.8 Hz, 1H), 6.23 (dd, $J = 3.2$, 1.8 Hz, 1H), 7.21 (dd, $J = 1.8$, 0.8 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): $\delta = 13.7$ (2 CH_2), 13.9 (CH_3), 15.2 (C), 45.6 (CH_2), 62.4 (CH_2), 104.2 (CH), 110.3 (CH), 140.7 (CH), 156.9 (C), 161.4 (C), 192.8 (C); MS (70 eV, EI): *m/z* (%) = 222 (25) [M$^+$], 204 (20), 193 (5), 149 (70), 131 (22), 121 (82), 107 (30), 93 (21), 91 (23), 81 (100), 77 (31), 65 (23), 53 (10), 51 (7).

Compound 19: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.82$–0.99 (m, 3H), 1.26–1.32 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H), 2.10 (ddd, $J = 14.6$, 4.3, 4.3 Hz, 1H), 2.73 (dd, $J = 14.6$, 5.8 Hz, 1H), 3.39 (d, $J = 3.2$ Hz, 1H), 3.70 (dd, $J = 1.8$, 1.5 Hz, 1H), 4.17–4.27 (m, 2H, CH_2), 4.49 (dd, $J = 4.3$, 1.8 Hz, 1H), 5.59 (d, $J = 1.5$ Hz, 1H), 5.73 (ddd, $J = 5.8$, 4.3, 3.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): $\delta = 12.7$ (CH_2), 14.2 (CH_3), 17.0 (C), 17.2 (CH_2), 42.3 (CH_2), 61.0 (CH_2), 76.9 (CH), 80.8 (CH), 97.8 (CH), 116.9 (CH), 142.5 (C), 162.3 (C); MS (70 eV, EI): *m/z* (%) = 240 (46) [M$^+$], 211 (8), 193 (30), 179 (96), 165 (19), 149 (26), 137 (33), 121 (100), 109 (40), 95 (32), 93 (60), 81 (96), 77 (42), 65 (24), 57 (64), 53 (62), 41 (26).

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