Substrate Range of the Titanium TADDOLate Catalyzed Asymmetric Fluorination of Activated Carbonyl Compounds

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The substrate range of the [$TiCl_2$(TADDOLate)] (TADDOL = $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol)-catalyzed asymmetric α-fluorination of activated β-carbonyl compounds has been investigated. Optimal conditions for catalysis are characterized by using 5 mol-% of $TiCl_2$(naphthalen-1-yl)-TADDOLate) as catalyst in a saturated (0.14 mol/l) MeCN solution of F-TEDA (1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-[tetrafluoroborate]) at room temperature. A series of α-methylated β-keto esters (3-oxobutanoates, 3-oxopentanoates) with bulky benzyl ester groups (60–90% ee) or phenyl ester (67–88% ee) have been fluorinated readily, whereas α-acyl lactones were also readily fluorinated, but gave lower inductions (13–46% ee). Double stereochemical differentiation in β-keto esters with chiral ester groups raised the stereoselectivity to a diastereomeric ratio (dr) of up to 96.5:3.5. For the first time, β-keto *S*-thioesters were asymmetrically fluorinated (62–91.5% ee) and chlorinated (83% ee). Lower inductions were observed in fluorinations of 1,3-diketones (up to 40% ee) and β-keto amides (up to 59% ee). General strategies for preparing activated β-carbonyl compounds as important model substrates for asymmetric catalytic α-functionalizations are presented (>60 examples).

1. Introduction. – The chiral *Lewis* acid-catalyzed asymmetric halogenation of β-keto esters has been introduced as a model reaction of significance for fundamental research in catalysis and for synthetic applications in 2000 (*Scheme 1*) [1–4]. Asymmetric halogenations of β-keto esters, particularly fluorinations, have since then been studied with a range of other chiral metal catalysts, including palladium(II), nickel(II), copper(II), and zinc(II) (for reviews, see [5–7]). In parallel, the substrate range of asymmetric fluorination has been extended to cyclic β-keto esters [8–10], α-chloro-β-keto esters [11–13], β-keto phosphonates [5][9][10][14][15], α-acyl-γ-lactames [16]. Besides the examples presented in our communication [1a] (*cf.* [2][3][17]) and its use in specific applications [4][11][16][18], no detailed study of the substrate range of the original titanium TADDOLate-catalyzed fluorination has been reported. Here, we describe a systematic study of the scope of the original Ti-TADDOLate (TADDOL = $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,3-dioxolane-4,5-dimethanol)-catalyzed fluorination of β-keto esters, and extensions of the substrate range to additional functional groups and substitution patterns. Important advances include the introduc-

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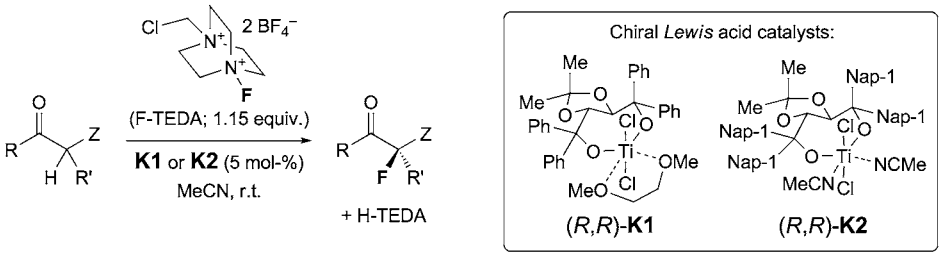
tion of phenyl β-keto esters as substrates (up to 90% ee), and the extension of the reaction to α-acyl lactones, β-keto amides, and β-diketones, and, notably, β-keto thioesters (up to 91% ee) as substrates for asymmetric catalytic fluorination reactions. The substrates **1**–**56** are investigated. In *Chapt. 3*, the syntheses of more than 60 activated carbonyl compounds, which are of general interest as substrates for asymmetric electrophilic functionalizations, are discussed.

Scheme 1. *Asymmetric Ti-Catalyzed Fluorination of Activated Carbonyl Compounds with Catalyst Complexes* **K1** *and* **K2**



2. Results and Discussion. – In a preceding article, we have detailed the development of conditions for the asymmetric Ti-TADDOLate-catalyzed fluorination (and, in part; chlorination) of β-keto esters [3]. As a result of the initial optimization, it was determined that catalytic fluorinations are best performed at a 5-mol-% level of the crystalline catalyst complexes **K1** or **K2** with a small excess of a saturated F-TEDA (=1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)) solution in MeCN as the halogenating reagent (*Scheme 1*). Some examples of the fluorination of β-keto esters had already been presented in our initial communication [1a]; they are included here for completeness, together with full experimental data. The results of the substrate screening will be presented in tabular form according to substrate type. Overall, more than 50 new halogenated products are described. The catalytic halogenations were usually characterized by complete and clean conversion to products, with reaction times ranging from a few minutes to several hours at ambient temperature. The fluorinated and some chlorinated products were isolated in analytically pure state after column chromatography in good yields.

2.1. *Catalytic Fluorination of β-Keto Esters. a*) *Catalytic Fluorination of Benzoylpropanoates.* The 2-benzoylpropanoates including the model substrate **1** for reaction development [3] have been investigated thoroughly. Results for the catalytic fluorination are collected in *Table 1*. In line with the preliminary observations [1a], the aromatic substituents of the TADDOLato ligand [1b][1c] play a key role in determining stereoselectivity. The induction obtained with catalyst **K2**, bearing naphthalen-1-yl (Nap-1) groups in the TADDOL ligand, was higher than with the Ph-bearing **K1**. All of the substrates with the open-chain 2-benzoylpropanoate substructure were fluorinated within a relatively narrow selectivity range of 60–80% ee by **K2** (*Table 1*, *Entries 1–13*). Substitutions at the benzoyl group of the substrate exert a secondary influence on the stereoselectivity, and such effects are more pronounced

in reactions with catalyst **K2**. Electronic variations of the substrates (*Entries 1* and *8*, *vs. 10*; *Entry 11 vs. 12*) had smaller effects on enantioselectivity than steric factors (*e.g.*, *Entry 1 vs. 3–5*). The bulky diphenylmethyl ester group induced high enantioselectivity in the fluorination (*Entry 5*). The crude fluorination products were often accompanied by a little chlorinated by-product [4]. A radical mechanism has been suggested to cause this side reaction, the benzoyl group favoring such a pathway [18].

b) *Catalytic Fluorination of 3-Oxobutanoates. In Tables 2* and *3*, the results obtained with 2-alkyl-3-oxobutanoates and 2-alkyl-3-oxopentanoates as substrates, respectively, are compiled. As a consequence of the greater tendency towards enolization of those substrates, due to reduced steric repulsion of the substituents at C(2) and C(3), catalytic fluorinations were faster than with the 2-benzoylpropanoates. Substrates with aliphatic chains in the ester group, *i.e.*, **15** and **16**, were fluorinated with lower enantioselectivity (*Table 2*, *Entries 1* and *2*) than benzyl esters, **17** and **18**. A fairly high ee value was observed in the fluorination of the simple phenyl ester **21** with catalyst **K2**. Additional substitutions of the phenyl group did not increase enantioselectivity (*cf.* **22**–**24**). Substrates with a 2-Me group were most successfully fluorinated, whereas other α-substituents induced lower enantioselectivity (of **25**–**27**).

c) *Catalytic Fluorination of 3-Oxopentanoates.* The 3-oxopentanoates (*Table 3*) were fluorinated with higher enantioselectivities than 2-benzoylpropanoates (*Table 1*) and 3-oxobutanoates (*Table 2*). With catalyst **K2**, inductions of over 60% ee were obtained even with the simple ethyl ester **28**, whereas the bulkier benzyl esters gave inductions of 70–90% ee (*Entries 2–4*). While steric bulk increased enantioselectivity in the benzyl ester series, it is remarkable that the simple phenyl ester **32** likewise gave fluorinated product with ee values close to 90% with catalyst **K2** (*Entry 5*). Replacing phenyl by bulkier aryl groups had no beneficial effects on reaction selectivity (*Entries 6* and *7*).

The absolute configuration of excess (+)-**1F**, (+)-**28F**, **29F**, **30F**, and **32F** (optical rotations measured in MeOH soln.) was assigned as (2*S*) by correlation experiments and comparison of the sign of optical rotation with literature data [19], as detailed in [3]. A sample of (+)-**15F** obtained by fluorination with catalyst **K2** (*Table 2*, *Entry 1*) displayed a specific rotation of $[\alpha]_D = +20.55$. By comparison with the reported optical rotation value of (+)-(*S*)-**15F**, $[\alpha]_D = +45.8$ ($c = 2.10$, MeOH) [19], the absolute configuration of the excess enantiomer in our sample could be assigned as (*S*), and the optical purity was calculated as 45%, which closely matches our GC-derived value of 45% ee. In terms of the absolute configuration, fluorinated products emerging from catalysis with (*R*,*R*)-TADDOL ligands were usually dexrotatory (positive sign of optical rotation) and had an excess-enantiomer configuration of (2*S*). This relationship was established for **1F**, **15F**, **28F**, **29F**, **30F**, and **32F**. By analogy, the reaction products in *Tables 1–3* probably all possess the (2*S*) excess-enantiomer configuration.

d) *Catalytic Fluorination of α-Acyl Lactones.* α-Acyl lactones were fluorinated with lower enantioselectivity than open-chain β-keto esters (*Table 4*). This may, in part, be a consequence of the high degree of enolization of the substrates, which favors a non-catalyzed background reaction. With the less reactive fluorinating reagents *N*-fluorobenzenesulfonimide (NFSI) or *N*-fluoropyridinium tetrafluoroborate (NFPy) rather than F-TEDA (*Fig. 1*), the enantioselectivity in the fluorination of the strongly enolized substrates **35** and **36** was increased (*Table 4*, *Entries 2*, *3*, and *5*), whereas no

Table 1. *Enantioselective Fluorination of Substituted 2-Benzoylpropanoates*[a])

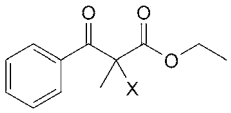
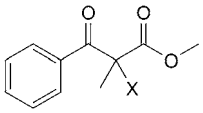
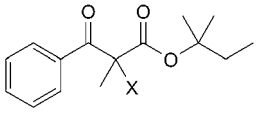
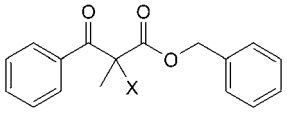
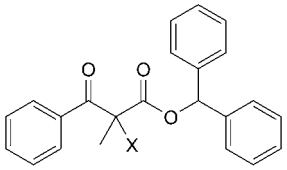
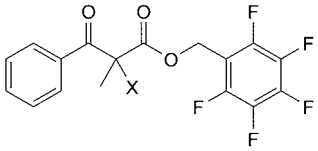
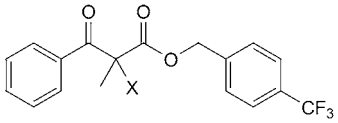
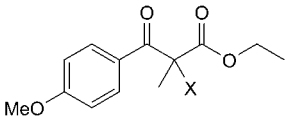
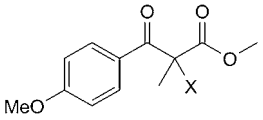
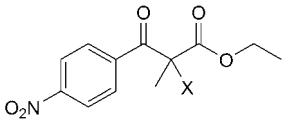
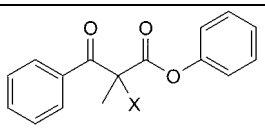
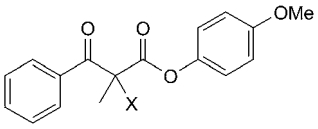
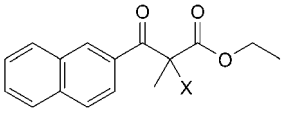
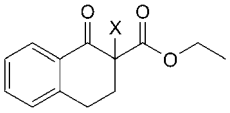
Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield [%][b])
1		**1**	**1F**	28	61.5	71
2		**2**	**2F**	35	67	76
3		**3**	**3F**	42	73	69
4		**4**	**4F**	38	70	85
5		**5**	**5F**	59	82	59
6		**6**	**6F**	57.5	62	44
7		**7**	**7F**	55	68.5	n.d.
8		**8**	**8F**	28	56	73
9		**9**	**9F**	26	61	94
10		**10**	**10F**	21	55	76

Table 1 (cont.)

Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield [%][b])
11		**11**	**11F**	n.d.	67	53
12		**12**	**12F**	17	65	34
13		**13**	**13F**	34	61	89
14		**14**	**14F**	2 – 6	20	93

[a]) For the general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. [b]) Yield of analytically pure product from a representative catalytic run.

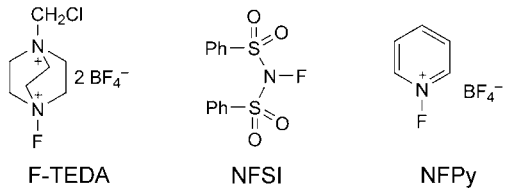


Fig. 1. *Electrophilic N–F reagents used for catalytic fluorinations*

corresponding change of ee value in dependence of the fluorinating reagent had earlier been observed for substrate **1**, for which enolization was negligible [3].

e) *Double Stereochemical Differentiation in the Catalytic Fluorination of Enantiomerically pure β-Keto Esters.* The catalytic fluorination of β-keto esters incorporating a stereogenic center in the ester alkyl group should be diastereoselective with either achiral or chiral catalysts. With enantiomerically pure catalysts of opposite absolute configurations, characteristic effects of double stereochemical differentiation can be expected, and this strategy might be used to further increase the stereoselectivity of the reaction [20]. The diastereoisomer ratio (dr) of the reaction products is conveniently measured by integration of the ^{19}F-NMR signals for the diastereoisomer fluorination products. The cholesteryl and nopyl (=2(6,6-dimethylbicyclo[3.3.1]hept-2-enyl)ethyl)

Table 2. *Enantioselective Fluorination of Substituted 3-Oxobutanoates*[a])

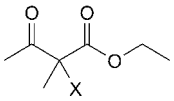
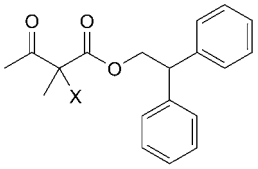
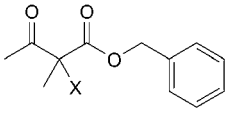
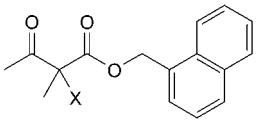
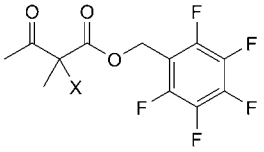
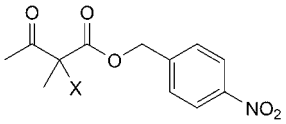
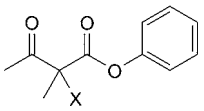
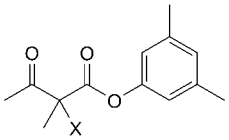
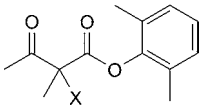
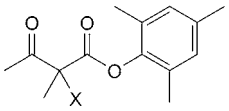
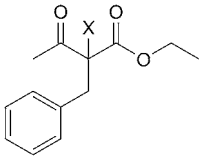
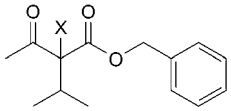
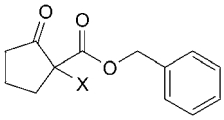
Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield[b]) [%]
1		**15**	**15F**	21	45	44[c])
2		**16**	**16F**	35 – 44	37	90
3		**17**	**17F**	30 – 37[d])	65	96
4		**18**	**18F**	51	69[e])	80
5		**19**	**19F**	55	57	88
6		**20**	**20F**	46	61	n.d.
7		**21**	**21F**	24	81	55
8		**22**	**22F**	24	74	57
9		**23**	**23F**	37	73	83
10		**24**	**24F**	48.5	67	92

Table 2 (cont.)

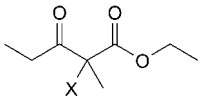
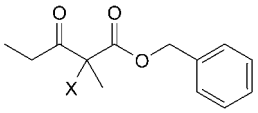
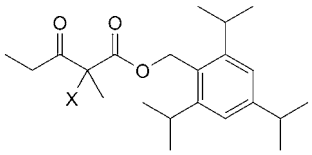
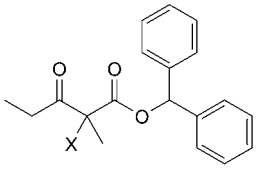
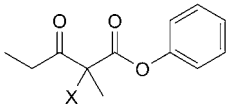
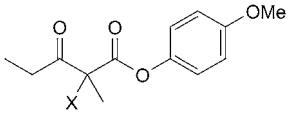
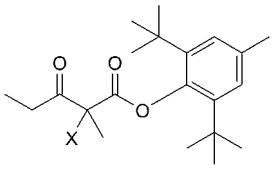
Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield[b]) [%]
11		**25**	**25F**	1	6	83
12		**26**	**26F**	1	24	40
13		**27**	**27F**	31	57	74

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. [b]) Yield of analytically pure product from a representative catalytic run involving **K2**. [c]) Losses during isolation of the volatile product. [d]) The ee range represents variability over several experiments; an ee value of 38.4% was observed at 0°. [e]) Result obtained with 3 mol-% of **K2**.

esters **40** and **41**, respectively, were fluorinated with little or no diastereoselectivity in the presence of the achiral catalyst $CpTiCl_3$ (*Table 5*, *Entries 1* and *2*), whereas the chiral catalysts **K1** and **K2** (each incorporating (*R*,*R*)-configured TADDOL ligand) induced dr values of similar magnitude than the enantiomeric ratios (er) observed in catalytic fluorinations of 2-methyl-3-oxopropanoates (*cf. Table 2*). The substrates shown in *Table 5* are enantiomerically pure only with respect to the stereogenic center of the ester group, but epimeric mixtures of keto forms by virtue of the stereogenic tertiary center at C(2). However, since the fluorination of both epimers proceeds *via* the same enolate, in which C(2) is no longer a stereogenic center, this is no complication. Menthyl esters **42** and **43** were fluorinated with moderate diastereoselectivity under $CpTiCl_3$ catalysis. There was a marked stereochemical differentiation with catalysts **K1** and **K2**. The combination of the (*R*,*R*)-TADDOL-derived catalysts with (1*S*)-menthyl ester **43** is the 'matched' combination, in which **K2** further enhances the effect of the substrate chirality. In the mismatched combination with **42**, the intrinsic diastereoisomeric induction of the substrate is neutralized by **K1**, and completely overturned by catalyst **K2**. Methyl mandelate ester **44** displayed significant double stereochemical differentiation: the 'matched' case represents the highest stereoselectivity yet observed in a Ti-TADDOLate-catalyzed fluorination (dr 96.5 : 3.5, de 93%).

f) *Steric Model of Induction in Catalytic Fluorinations of β-Keto Esters.* The absolute configurations of the diastereoisomers in the experiments of *Table 5* have been assigned, where possible, based on the known sense of induction of the catalyst **K2**, which has been shown to induce the (*S*)-configuration at the stereogenic F-carrying

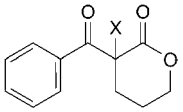
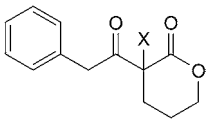
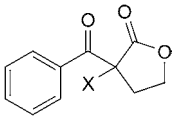
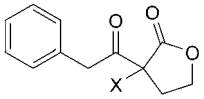
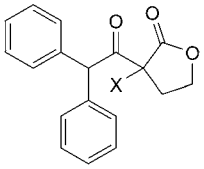
Table 3. *Enantioselective Fluorination of Substituted 3-Oxopentanoates*[a])

Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield[b]) [%]
1		**28**	**28F**	29.5	62	n.d.
2		**29**	**29F**	48	71	82
3		**30**	**30F**	53 – 55	88 – 90	89
4		**31**	**31F**	58	81	87
5		**32**	**32F**	45	87 – 88	50
6		**33**	**33F**	28	86	35
7		**34**	**34F**	15	30	55

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. The ee values show variations over several experiments. [b]) Yield of analytically pure product from a representative catalytic run.

centers [3]. A steric model of a substrate/catalyst complex has been developed in the preceding study [3], based on calculated structures of Ti-enolate intermediates [18] and the molecular structure of a dienolate complex determined by X-ray analysis [16]. According to this model, the stereoselectivity of fluorination is rationalized by assuming a trajectory of attack of the N–F reagent on the diastereotopic face of the

Table 4. *Enantioselective Fluorination of α-Acyl Lactones with Catalyst* **K2**[a])

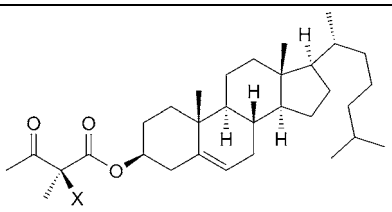
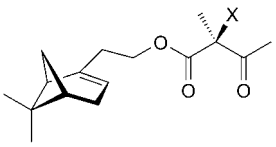
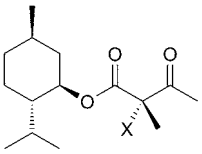
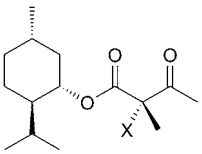
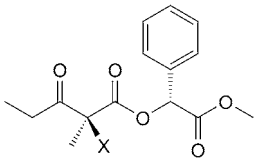
Entry	Structure	X = H	Enol[b]) [%]	X = F	ee (**K2**) [%]	Yield[c]) [%]
1		**35**	76	**35F**	16	70
2		**35**	76	**35F**	24[d])	(99)[f])
3		**35**	76	**35F**	39[e])	(75)[f])
4		**36**	45	**36F**	13	85
5		**36**	45	**36F**	46[e])	(70)[f])
6		**37**	5	**37F**	29	86
7		**38**	5	**38F**	51	63
8		**39**	2	**39F**	*ca.* 5[g])	89

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of **K2** and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. [b]) Degree of enolization of the substrate (R = H) in $CDCl_3$ soln. [c]) Yield of analytically pure product from a representative catalytic run. [d]) Reaction performed with NFSI as fluorinating agent, reaction time 24 h. [e]) NFPy-BF_4 used as fluorinating reagent, reaction time 5 d. [f]) Conversions according to NMR analysis. [g]) Value less accurate due to incomplete baseline separation in HPLC.

substrate in the energetically most favorable Ti-enolate complex that is opposite to the shielding ligand aryl group (*Fig. 2*).

This steric model is in agreement with structural information from the X-ray structure of the complex [Ti((Nap-1)-TADDOLato)$_2$(β-ketonato)$_2$] [16], incorporating the deprotonated substrate **29** twice as chelating *O*,*O*-ligand at Ti-atom. The C–H to π edge-to-face interaction in that structure (*cf. Fig. 8* in [3]) is an important element that should be present not only in benzyl, but also phenyl and thiophenyl esters, and may be responsible for the high inductions (up to 90% ee) observed with simple phenyl ester (*i.e.*, **21**, **32**, and **33**) and phenyl thioester substrates (*i.e.*, **48**), in spite of their small size. The substrate/ligand arrangement shown in *Fig. 2* can also explain the favorable result observed in the double stereochemical differentiation experiment with substrate

Table 5. *Diastereoselective Fluorination of β-Keto Esters with Chiral Ester Groups*[a])

Entry	Structure	X = H/F	dr			Yield[b]) [%]
			$CpTiCl_3$	**K1**	**K2**	
1		**40/40F**	55 : 45	60 : 40	80 : 20	56
2		**41/41F**	50 : 50	59 : 41	75 : 25	n.d.
3		**42/42F**	37 : 63[c])	51 : 49[c])	75 : 25[c])	59
4		**43/43F**	63 : 37[d])	74 : 26[d])	82 : 18[d])	n.d.
5		**44/44F**	66 : 34[e,f])	88 : 12[f])	96.5 : 3.5[f])	59

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. [b]) Yield of analytically pure product from a representative catalytic run. [c]) dr (1′*R*,2*S*)/(1′*R*,2*R*) = *ul*/*lk*. [d]) dr (1′*S*,2*S*)/(1′*S*,2*R*) = *lk*/*ul*. [e]) Ratio observed in a stoichiometric fluorination of the Na-enolate. [f]) dr (1′*R*,2*S*)/(1′*R*,2*R*) = *ul*/*lk*.

44: the latter only differs from **29** by the presence of a CO_2Me group in the benzylic position (E; representing H_{Si} of coordinated **29** in *Fig. 2*), which points away from the reaction center and tolerates more steric bulk than the constrained H_{Re} position.

2.2. *Catalytic Fluorination of β-Keto Thioesters.* Thioesters, which are more reactive than esters, are useful building blocks in synthesis. Asymmetric electrophilic α-fluorinations of thioesters have not been reported, to our knowledge. A potential side reaction, the sulfide oxidation with fluoride addition (fluoro-*Pummerer* rearrange-

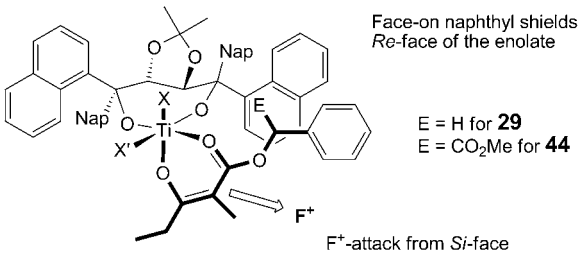
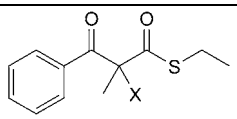
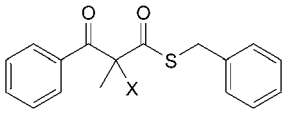
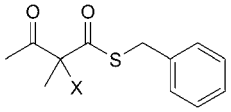
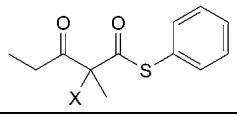


Fig. 2. *Steric model showing blockage of the* Re*-face of the deprotonated and metal-ligated substrate by the aryl group of the catalyst, directing the attack of the electrophilic NF reagent to the* Si*-face*

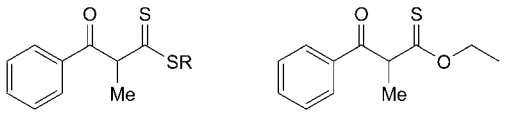
ment) of alkyl thioethers, has been realized with F-TEDA as reagent, however [21]. Nevertheless, the asymmetric Ti-catalyzed fluorination of β-keto thioesters proceeded readily and gave α-fluorinated products in up to 91.5% ee (*Table 6*; yields not optimized). Relative to their parent esters, thioesters are fluorinated with higher enantioselectivities.

Table 6. *Enantioselective Fluorination of β-Keto Thioesters*[a])

Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield [b]) [%]
1		**45**	**45F**	47	62	13
2		**46**	**46F**	50	78	39
3		**47**	**47F**	45	69	n.d.
4		**48**	**48F**	34	90–91.5	78

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. Ranges of ee values represent variations over several experiments. [b]) Yield of analytically pure product from a representative catalytic run.

Catalytic fluorination reactions of β-keto dithioesters **57** and **58**, and mixed *S*,*O*-thioester **59** (*Fig. 3*) were not successful. These substrates, bearing thiocarbonyl groups, decomposed under reaction conditions.



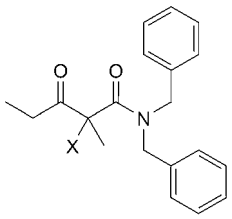
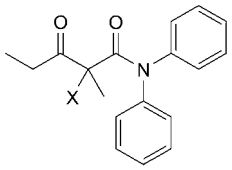
57 R = Me
58 R = Et

59

Fig. 3. *Thioester substrates, which could not be successfully fluorinated*

2.3. *Catalytic Fluorination of β-Keto Amides.* β-Keto amides were catalytically fluorinated to afford the corresponding products with moderate enantioselectivities (*Table 7*). The reaction proceeded sluggishly compared to similar esters. The enolization of secondary β-keto amides was strongly reduced by occurrence of $A^{1,3}$-strain in the enol form. In fact, none of the enols was detected by ^{1}H-NMR spectroscopy in $CDCl_3$ solutions of **49** or **50**.

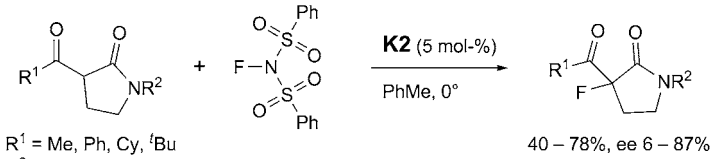
Table 7. *Fluorination of β-Keto Amides*[a])

Entry	Structure	X = H	X = F	ee (**K1**) [%]	ee (**K2**) [%]	Yield[b]) [%]
1		**49**	**49F**	21 – 27	45 – 59	n.d.[c])
2		**50**	**50F**	35.9	55.0	75

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction time < 15 h. Ranges of ee values represent variations over several experiments. [b]) Yield of analytically pure product from a representative catalytic run. [c]) Product contained inseparable chlorinated side product as impurity.

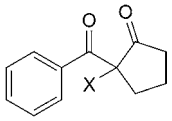
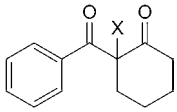
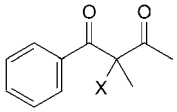
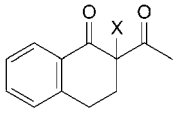
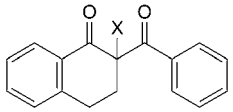
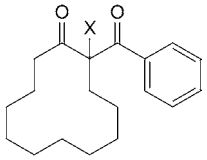
The asymmetric catalytic fluorination of a series of α-acyl γ-lactams has been realized with NFSI as fluorinating agent in toluene solution, however (*Scheme 2*); the results have already been reported [16].

Scheme 2. *Asymmetric Catalytic Fluorination of α-Acyl Lactames Reported in* [16]



2.4. *Catalytic Fluorination of 1,3-Diketones.* 1,3-Diketones should be less suitable substrates for catalytic fluorination, because they are highly enolized (danger of a background reaction), and because the electronic differentiation of the two C=O groups is less pronounced than in β-keto esters, implying that the differentiation of the enantiotopic faces of the enolized substrate is more difficult. Indeed, 1,3-diketones gave low inductions in the catalytic fluorination reaction (*Table 8*).

Table 8. *Enantioselective Fluorination of 1,3-Diketones Catalyzed by* **K2**[a])

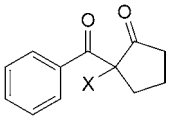
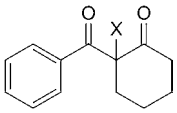
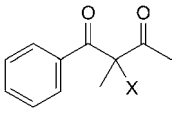
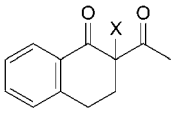
Entry	Structure	X = H	Enol[b]) [%]	X = F	ee (**K2**) [%]	Yield[c]) [%]
1		**51**	90	**51F**	0	90
2		**52**	< 1	**52F**	17	67
3		**53**	4	**53F**	27	70
4		**54**	95	**54F**	0	67
5		**55**	97	**55F**	0[d])	94
6		**56**	2	**56F**	18	82

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of **K2** and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. Reaction times range from 20 min to 5 h. [b]) Percentage of enolization in the starting material, determined by ^{1}H-NMR in $CDCl_3$ soln. of freshly dissolved samples. [c]) Yield of analytically pure product from a representative catalytic run. [d]) Value is based on a determined $[\alpha]_D$ value of 0 ($c = 0.595$, MeOH); however, the optical rotation of an enantiomerically pure sample is not known.

To clarify the influence of the non-catalyzed background fluorination of the substrate enol form, selected reactions were carried out with F-TEDA, NFSI, and NFPy (*Fig. 1*). The latter two reagents have lower fluorinating power than F-TEDA [22] and display slower background fluorinations. For the highly enolized cyclo-

pentanone **51**, enantioselectivity of fluorination was indeed higher with the less reactive reagents (*Table 9*, *Entry 1*), whereas no change of enantioselectivity was observed for fluorination of the less enolized **52** and **53** (*Table 9*, *Entries 2* and *3*). The highly enolized tetralone **54** failed to show induction with all reagents. It appears that the non-catalyzed background fluorination of highly enolized substrates is important with F-TEDA, but can sometimes be suppressed by using less reactive fluorinating reagents (compare also the results in *Table 4*). However, even in the absence of a background reaction, the levels of enantioselectivity remained low in the fluorination of 1,3-diketones, as a consequence of insufficient electronic and steric differentiation of the substrate C=O groups.

Table 9. *Variation of the Fluorinating Agent for the Diketones*[a])

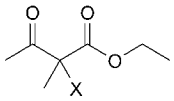
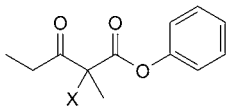
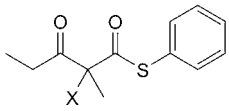
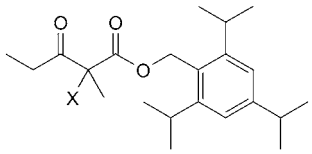
Entry	Structure	Enol[b]) [%]	X = F	ee (**K2**) [%][c])		
				F-TEDA	NFSI	NFPy-BF_4
1		90	**51F**	0	15 (1 d)	40 (2 w)
2		< 1	**52F**	17	18 (1 d)	15 (5 d)[d])
3		4	**53F**	27	26 (1 d)	23 (5 d)[d])
4		95	**54F**	0	0	n.d.

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of catalyst and 1.15 equiv. of F-TEDA in MeCN solution at ambient temperature. [b]) Enol content of a dissolved sample (^{1}H-NMR, $CDCl_3$) of substrate (X = H). [c]) Reaction time in parentheses. [d]) 50% Conversion.

2.5. *Selected Asymmetric Catalytic Chlorinations.* In connection with our work on asymmetric catalytic fluorination, we had also shown that $TiCl_2$(TADDOLato) complexes are catalysts for asymmetric chlorinations with *N*-chlorosuccinimide (NCS) [4]. Some of the new substrate types have also been submitted to the conditions of the asymmetric catalytic chlorination reaction with catalyst **K2** (*Table 10*).

3. Synthesis of Catalysis Substrates. – Over the past ten years, α-substituted β-keto esters have become popular model substrates for metal-catalyzed asymmetric electrophilic substitutions. We present here an overview of the most-efficient synthetic methods which have been used to prepare the substrates in this work. For a general review of the synthesis and reactivity of β-keto esters, see [23].

Table 10. *Asymmetric Titanium-TADDOLate Catalyzed Chlorinations*[a])

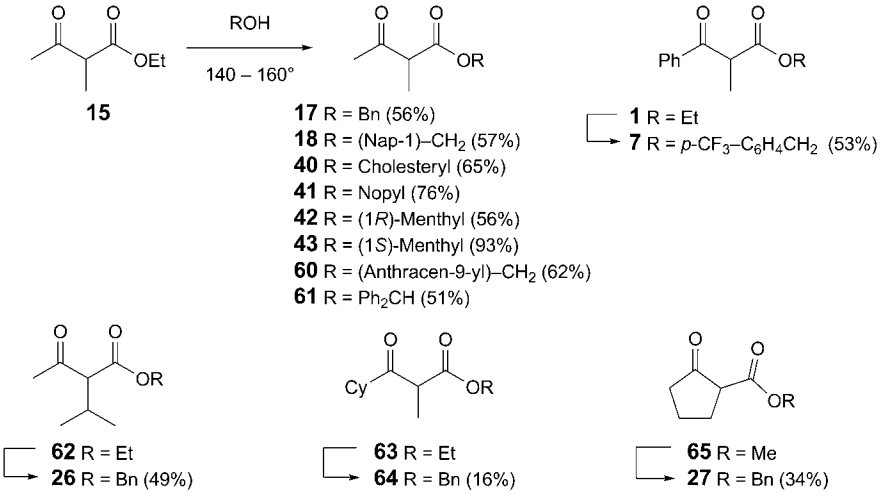
Entry	Structure	X = H	X = Cl	Time [min]	ee (**K2**) [%]	Yield [%]
1		**15**	**15Cl**	15	40	n.d.
2		**32**	**32Cl**	20	82[b])	83
3		**48**	**48Cl**	20	83	71
4		**30**	**30Cl**	30	82 ± 3[c])	82

[a]) For a general reaction scheme, see *Scheme 1*. Reactions were performed with 5 mol-% of **K2** and 1.15 equiv. of NCS in MeCN solution at ambient temperature. [b]) ee 90% at 0° in CH_2Cl_2; see also preceding report [3]. [c]) Value is less accurate due to incomplete baseline separation of HPLC peaks.

3.1. *Transesterification of β-Keto Esters.* Observations of the simplified (as opposed to regular esters) thermal exchange of alkoxy groups in β-keto esters go back to 1887 [24]. Transesterification of lower alkyl β-keto esters was studied by *Cohn* (1900) [25], *Lapworth* and *Hann* (1902) [26], and *Bader et al.* (1951) [27]. Heating an alcohol with neat ethyl acetoacetate to 140–150° is often sufficient to bring about the reaction. According to *Witzeman* and *Nottingham* [28][29], transesterifications starting from bulky alkyl acetoacetates are faster and require none of the proposed catalysts like 4-(dimethylamino)pyridine (DMAP) [30] or $Ti(O^iPr)_4$ [31], since they exchange alcohol groups *via* an elimination/addition mechanism. The ease of thermal transesterification of β-keto esters has sometimes been ignored by authors of more or less efficient catalytic protocols for that reaction (*cf.* [32] for a comment on the 'yet-another-one-catalyst' idea). We have prepared numerous substituted acetoacetates starting from ethyl 2-methylacetoacetate (**15**) or other lower alkyl β-keto esters in fair-to-good yield (*Scheme 3*). The reactants were sometimes refluxed in toluene with addition of catalytic DMAP [30], though the latter may not always be necessary. Since the reaction is reversible, either one reactant should be used in excess, or the lower alcohol component should be removed, which is most easily achieved by evaporation (for MeOH and EtOH), if the reaction is performed in a vessel open to air.

3.2. *Esterification* via *Acyl Activation of β-Keto Carboxylic Acids.* Even though β-keto carboxylic acids are not thermally stable at elevated temperatures, they can be esterified *via* acyl-activation protocols, or *O*-alkylation by dialkyl sulfates or *Meerwein* salt [23]. Acyl activation of 2-methyl-3-oxobutanoic acid (**66**), in particular, with the

Scheme 3. *Transesterifications*

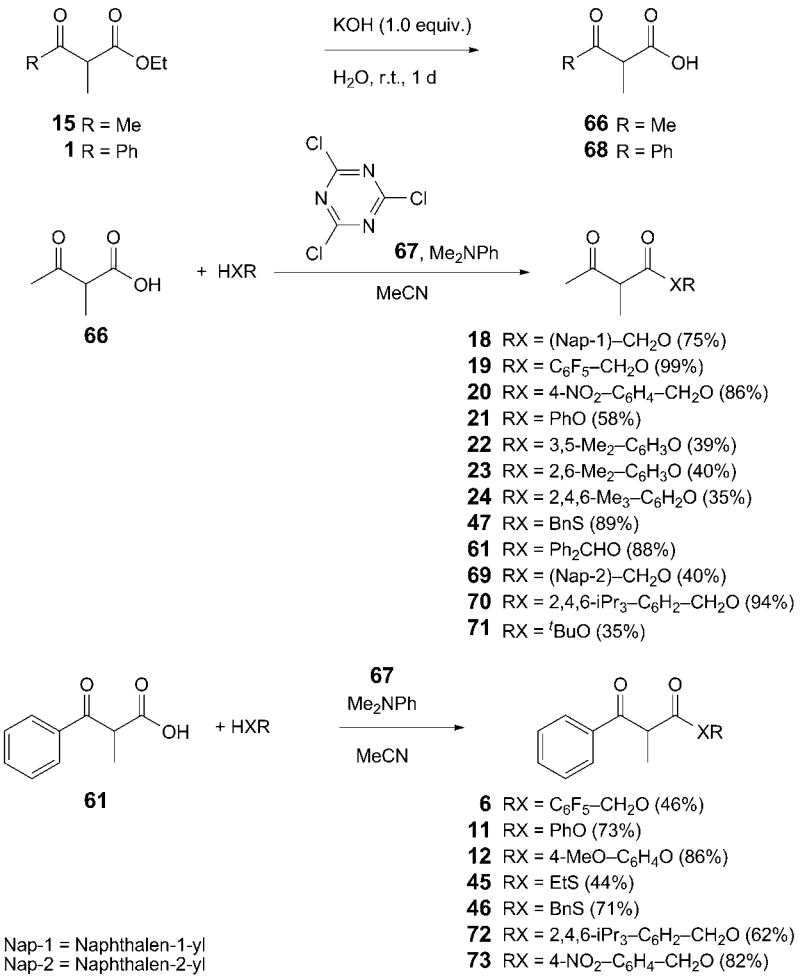


Appel reagent (PPh_3/CCl_4) [33] has been reported [34]. We have successfully used cyanuric chloride (=2,4,6-trichloro-1,3,5-triazine; **67**) as an acyl activating reagent [35] for the coupling of carboxylic acids **66** and **68** with several benzylic alcohols, phenols, or thiols in the presence of *N*,*N*-dimethylaniline as mild base (*Scheme 4*). The moderately stable acid **66** [36] was either freshly synthesized prior to use, or stored at $-78°$, whereas the crystalline acid **68** was stable under ambient conditions.

An alternative acyl activation protocol for the free β-keto carboxylic acids *via* an azolide is described further below.

3.3. *Alcoholysis of Diketenes.* In an attempt to prepare 1,1-dimethylpropyl propanoate (**74**) from propanoyl chloride and 2-methylbutan-2-ol in the presence of Et_3N, oxetanone **75** was obtained instead (*Scheme 5*). This β-lactone is more directly formed from Et_3N and propanoyl chloride *via* elimination to a ketene and dimerization [37][38]. This side reaction does not take place in the presence of the weaker base *N*,*N*-dimethylaniline, and the desired ester **74** is obtained (*Scheme 5*). Still, the generation of the ketene dimer was welcome, since the nucleophilic ring opening of **75** with alcohols provided a straightforward route to 2-methyl-3-oxopropanoates as suitable model substrates for our studies. We have already reported a simplified synthesis of **75** (56% yield, 97% purity; remainder: propionic anhydride) that profits from an aqueous workup [4]. The reaction, which had originally been performed on large scale, gave lower yields when repeated on smaller scale. On large-scale, the heat of reaction was sufficient to bring the mixture to the boiling point, but, on small scale, at ambient temperature, the reaction was slow and gave lower yield, unless external heating was applied. β-Lactone **75** is a lachrymatory liquid with limited shelf-life, which polymerizes slowly at ambient temperature. It reacts with Ph_2CHOH to ester **31** in a pyrrolidinopyridine (PPy)-catalyzed [39] reaction (*Scheme 5*, *b*). For more-hindered alcohols as nucleophiles, the polymerization of **75**, which is presumably also catalyzed by the pyridine, accompanies esterification. Such problems were circumvented by an initial

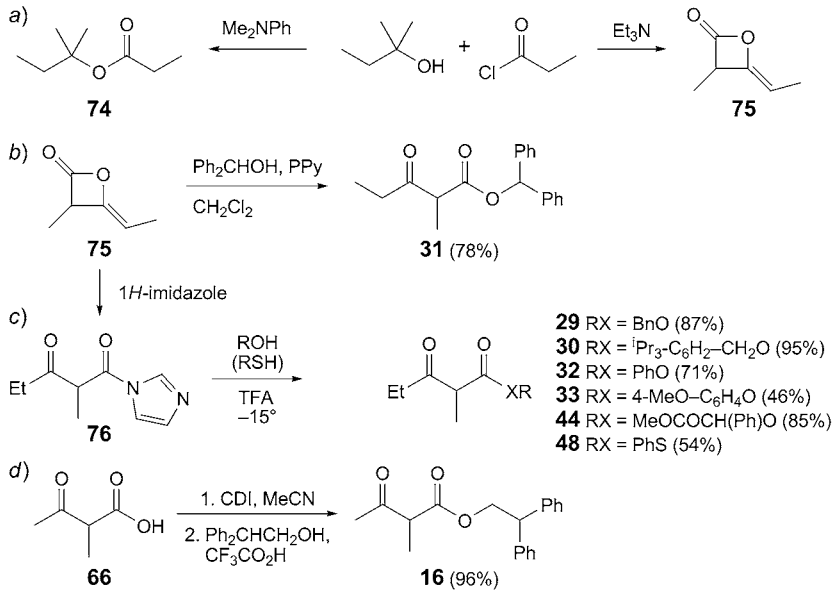
Scheme 4. *Esterification* via *Acyl Activation of β-Keto Carboxylic Acids*



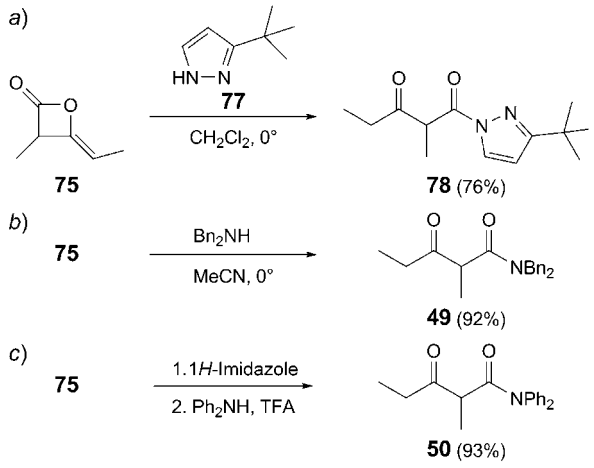
ring opening of **75** with 1*H*-imidazole to the 1-acyl-1*H*-imidazolide **76** [40]. Reaction of the latter with alcohols proceeded readily in the presence of CF_3COOH (TFA) [4], rather than the more common base catalysis used in esterifications with azolides [41]. Several alcohols, phenols, and thiophenol were transformed to 2-methyl-3-oxopentanoates by this method (*Scheme 5*, *c*); the reaction was not successful with 4-nitrophenol.

The activated 1-acyl-1*H*-imidazole can also be prepared directly from *β*-keto carboxylic acids and carbonyldiimidazole (CDI). For example, ester **16** was prepared from acid **66** by one-pot 1-acyl-1*H*-imidazole generation and esterification under acidic conditions (*Scheme 5*, *d*). Lactone **75** undergoes non-catalyzed ring opening also with other azoles, such as 3-(*tert*-butyl)-1*H*-pyrazole (**77**) to give pyrazolide **78**, or with Bn_2NH to give amide **49** (*Scheme 6*, *a* and *b*). For the weak nucleophile Ph_2NH, the 1*H*-imidazole/TFA activation strategy was used with success (*Scheme 6*, *c*).

Scheme 5. *Synthesis of β-Keto Esters* via *Diketenes and Acylimidazolides:* a) *Expected and Unexpected Product from the Reaction of* tert-*Amyl Alcohol, Propanoyl Chloride, and Different Amine Bases;* b) *Nucleophilic Ring Opening of a Diketene;* c) *Diketene Ring Opening with Azoles to Acyl Azolides, Followed by Esterification under Acid Activation*; d) *Esterification* via *Imidazolides Generated from a β-Keto Acid*

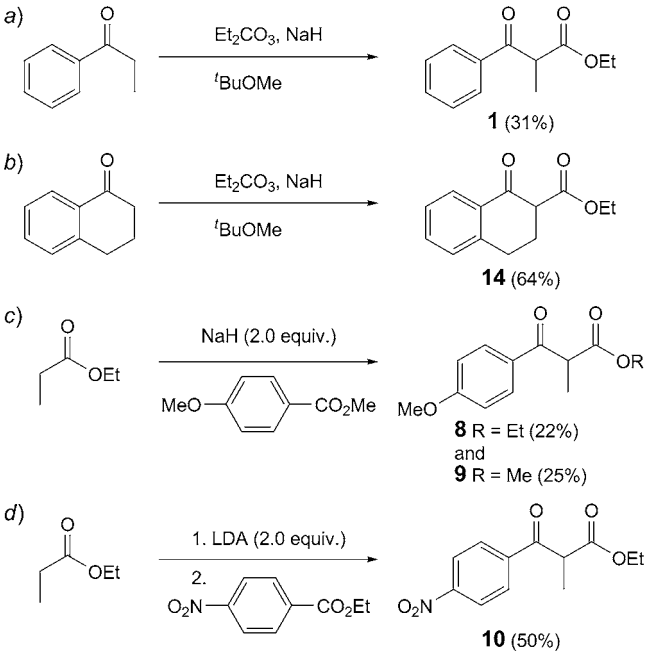


Scheme 6. *Ring-Opening Reactions of Diketene* **75** *with N-Containing Nucleophiles*



3.4. *Synthesis of β-Keto Esters by* Claisen *Condensation*. *Claisen* condensation of ketones with Et_2CO_3 in the presence of 2 equiv. of NaH gave **1** and **14** (*Scheme 7*, *a* and *b*) [42]. The procedure was straightforward, but the products required additional

Scheme 7. *Synthesis of β-Keto Esters by* Claisen *Condensation*



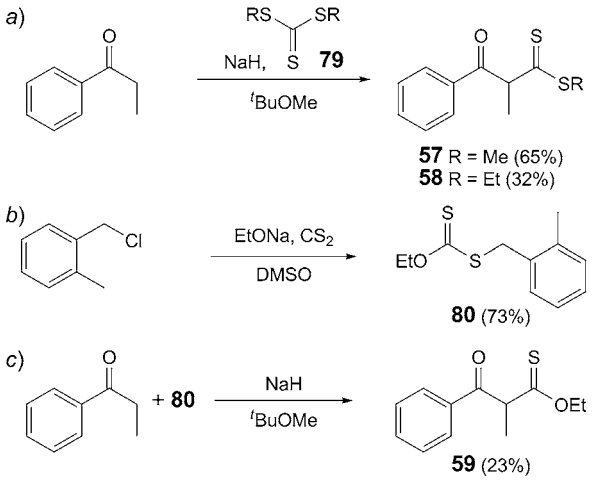
purification by chromatography for use as catalysis substrates. In case a solid Na-enolate was obtained from the *Claisen*-reaction mixture, the latter could be purified by filtration and washing with inert solvent, before the ester was released by acidification. Aroyl propanoates were alternatively obtained *via Claisen* condensation of propanoates with alkyl benzoates (*Scheme 7*, *c* and *d*).

Claisen condensations with alkyl trithiocarbonates **79** gave β-keto dithioesters **57** and **58** (*Scheme 8*, *a*), or, using the mixed *O*-ethyl-*S*-(α-xylyl) dithiocarbonate **80** as electrophile (*Scheme 8*, *b*), the *O*-ethyl 2-benzoylthiopropanoate (**59**; *Scheme 8*, *c*). Reagent **80** was used, because an initial *Claisen* condensation of the propanoylphenone enolate with *O*,*S*-diethyl dithiocarbonate had produced inseparable mixtures of dithioester **58** and thioester **59**. The analogous product mixture generated from **80** was readily separated by chromatography.

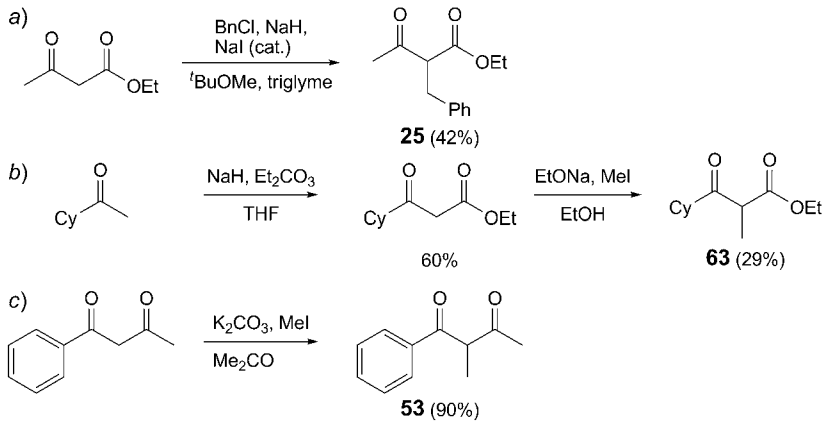
3.5. *α-Alkylation of Enolates.* Classical acetoacetate alkylation was applied in some cases, but the selectivity of mono- *vs.* dialkylation was low. Examples are shown in *Scheme 9*. The low yields of **25** and **63** reflect losses during the separation of mono- and dialkylation products by chromatography. However, benzoylacetone was methylated in high yield to diketone **53** (*Scheme 9*, *c*).

3.6. *Synthesis of β-Keto Esters* via *Aldol Addition and Oxidation*. A general access to α-methylated β-keto esters involves the addition of a propanoate to an aldehyde, followed by oxidation of the hydroxy ester. *Scheme 10*, *a*, shows applications of this strategy for the synthesis of **3**–**5** and **69**. Oxidation of the aldol adducts was carried out with pyridinium chlorochromate (PCC) or *Jones* reagent.

Scheme 8. *Synthesis of Thioester Derivatives*



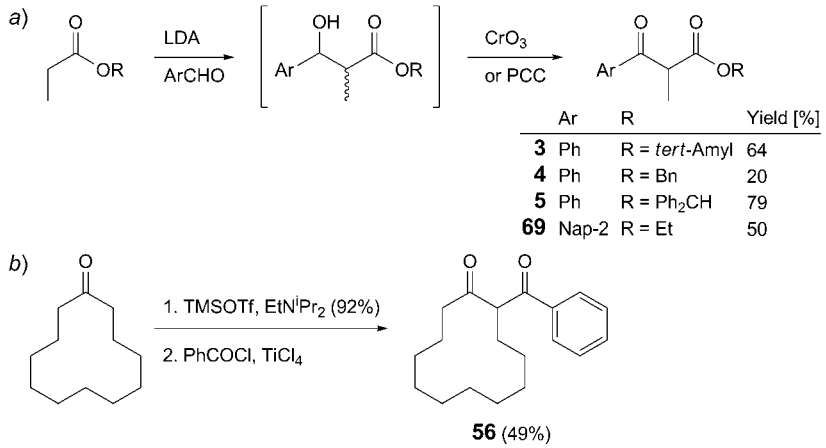
Scheme 9. *Synthesis of α-Substituted β-Dicarbonyl Compounds by Alkylation*



3.7. *Synthesis of 1,3-Diketones and α-Acyl Lactones.* α-Acyl lactones **35**–**39** and 1,3-diketones **51**–**55** were prepared by *Claisen* condensation [43]. A *Mukaiyama*-type *Claisen* reaction [44] was used in the preparation of 2-benzoylcyclododecanone (**56**) (*Scheme 10*, *b*).

4. Conclusions. – The substrate range of the Ti-TADDOLate *Lewis* acid-catalyzed electrophilic fluorination of activated dicarbonyl compounds has been studied. The original β-keto ester substrates have been structurally varied in the ester moiety, at C(2) and C(3). Variations at C(3) were readily tolerated, but variations at C(2) were not. Increasing the size of the benzyl ester group in β-keto esters led to higher enantioselectivities (up to 90% ee) in the catalytic fluorination. However, an equally

Scheme 10. a) *Synthesis of β-Keto Esters by Oxidation of Hydroxy Esters Obtained from Aldol Additions.* b) *Synthesis of a 1,3-Diketone by* Mukaiyama *Acylation.*



	Ar	R	Yield [%]
3	Ph	R = *tert*-Amyl	64
4	Ph	R = Bn	20
5	Ph	R = Ph_2CH	79
69	Nap-2	R = Et	50

56 (49%)

high enantioselectivity was obtained with simple phenyl ester substrates. The reaction has also been extended to other activated carbonyl derivatives, including β-keto thioesters, β-keto amides, and β-diketones. β-Keto thioesters have been fluorinated with up to 90% ee and showed no sign of oxidative degradation. On the other hand, thioesters and dithioesters were no suitable substrates. For highly enolized β-diketones, it was established that a non-catalyzed background fluorination takes place; this background reaction is partially suppressed by using less reactive fluorinating reagents such as NFSI or *N*-fluoropyridinium tetrafluoroborate. The steric course of the fluorination has been interpreted in terms of a model which correctly predicts the absolute sense of induction.

Experimental Part

General. Reactions were carried out under Ar. Substrate **15** was purchased from *Acros* or *Avocado.* F-TEDA ('*Selectfluor*'; the BF_4 salt was used on all occasions) and NCS were obtained from *Aldrich.* Column chromatography (CC): silica gel *60* (SiO_2; 40–63 μm; *Fluka*). NMR Spectra: in $CDCl_3$ at ambient temp. (20–25°), chemical shifts (δ [ppm]) relative to internal Me_4Si, unless otherwise noted; ^{13}C-NMR shifts relative to solvent peaks; ^{19}F-NMR spectra referenced against internal $CFCl_3$.

2. *Abbreviations.* CDI, 1,1′-Carbonyldiimidazole; Cy, cyclohexyl; DMAP, 4-(dimethylamino)pyridine; F-TEDA, 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate); LDA, lithium diisopropylamide, ^{i}Pr$_2$NLi; NCS, *N*-chlorocuccinimide; NFPy, 1-fluoropyridinium tetrafluoroborate; NFSI, *N*-fluorobenzenesulfonimide; Nopyl, 2-(6,6-dimethylbicyclo[3.1.1]hept-2-enyl)ethyl; PCC, pyridinium chlorochromate; TFA, CF_3COOH; ψ, pseudo.

3. *Enantiomer Excesses* (ee) *Determinations.* The ee-values were determined by HPLC or GC analyses; HPLC analyses were conducted on normal phase *Daicel Chiralcel* anal. columns (4.6 × 250 mm) of the *OJ*, *OD*, or *OB* type with hexane/^{i}PrOH as mobile phase. GC analyses were performed on *Supelco β-* or *γ-DEX 120* (30 m) columns; carrier gas, He flow rate, 1.4 ml min^{-1}; split injector, 42 ml min^{-1}, 200°; FID detector, air/H_2 350/35 ml min^{-1}, 250°.

4. *General Procedures for Catalytic Halogenations.* a) *Preparation of a Sat. Soln. of F-TEDA.* In a 100-ml brown glass bottle, MeCN (anal. reagent grade) was added to finely powdered F-TEDA (BF_4

salt; '*Selectfluor*'; 6.0 g) and granular molecular sieves (3 Å, 10 g) up to the 100-ml mark. The contents were stirred magnetically for 1 h. The bottle was set aside for sedimentation of suspended particles. The supernatant, a sat. soln. of the F-TEDA, had a concentration of *ca.* 0.145M (iodometric titration) [45], and was used for catalytic reactions. *Note:* The soln. had a shelf-life of at least two weeks. Occasionally, the soln. became turbid (opalescent), and this was accompanied by unsatisfactory performances in catalysis.

b) *General Procedure for Catalytic Fluorinations* (*GP 1*). To the substrate (0.25 mmol) in MeCN (1 ml), the catalyst was added (0.0125 mmol, 5 mol-%), and the mixture was stirred until a clear soln. had formed. Optionally, molecular sieves or other additives were added at this point. The reaction was started by addition of a sat. F-TEDA soln. (0.145M in MeCN; 2.0 ml, 0.29 mmol). The mixture was stirred at r.t. to complete conversion (TLC check) or until no further change could be observed. *Workup:* 1) *Aqueous Workup:* The mixture was flushed into a separatory funnel using ^{t}BuOMe (30–50 ml) and H_2O (50–100 ml). The aq. phase was discarded, and the org. phase was filtered over a small plug of neutral/deactivated Al_2O_3 on cotton. The filtrate was evaporated, and the residue was analyzed by chiral HPLC or GC. Yields and additional analytical data were obtained after further purification by CC on SiO_2.

2) *Nonaqueous Workup:* Alternatively, the mixture was diluted with ^{t}BuOMe (30–50 ml) and directly filtered over Al_2O_3 as described above.

c) *General Procedure for Catalytic Halogenations* (Fluorination and Chlorination) *with Non-Ionic Reagents* (*GP 2*). Given the good solubility of the respective reagents, catalytic fluorination with NFSI or chlorination with NCS was readily carried out in a range of solvents: to a soln. of the substrate (0.25 mmol) in the solvent (1 ml; MeCN unless otherwise mentioned) was added catalyst, and the mixture was stirred until all was dissolved. The solid halogenation reagent (0.275–0.325 mmol; 1.1–1.3 equiv.) was added, and the mixture was stirred at r.t.; see *GP 1* for workup and purification.

5. *Catalysis Products.* The halogenated compounds were prepared according to *GP 1* (chlorinations: *GP 2*) and purified by CC with an appropriate solvent mixture (^{t}BuOMe/hexane). Optical rotations refer to product samples obtained by catalysis with (*R*,*R*)-configured TADDOL-ligands, unless otherwise mentioned.

6. *Catalytic Fluorination of β-Keto Esters.* a) *Catalytic Fluorination of 2-Benzoylpropanoates.* Products were prepared according to *GP 1*; typical reaction times: 4–16 h. Yields and ee values are compiled in *Table 1*.

Ethyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**1F**). The product was dried in a rotary evaporator to prevent evaporation losses. HPLC (*Chiralcel OB-H*; hexane/^{i}PrOH 96:4; 0.5 ml min^{-1}): t_R(minor) 13.5, t_R(major) 16.0 min. R_f (^{t}BuOMe/hexane 1:5) 0.45. $[\alpha]_D = +16.5$ ($c = 0.595$, MeOH; 21% ee by HPLC); $[\alpha]_D = +53.8$ ($c = 0.545$, MeOH; 61.7% ee). ^{1}H-NMR (300 MHz): 1.20 (*t*, *J* = 7.1, 3 H); 1.87 (*d*, *J*(F,H) = 22.5, 3 H); 4.25 (*CD* of A_3CD; *ψ-qd*, *J* = 7.1, 2.3, 2 H); 7.42–7.51 (*m*, 2 H); 7.56–7.63 (*m*, 1 H); 8.00–8.10 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 13.8 (Me); 20.9 (*d*, *J*(F,C) = 23, Me); 62.5 (CH_2); 97.0 (*d*, *J*(F,C) = 195, C); 128.6 (CH); 129.7 (*d*, *J*(F,C) = 5, CH); 133.4 (*d*, *J*(F,C) = 3, C); 133.9 (CH); 168.4 (*d*, *J*(F,C) = 25, CO); 191.7 (*d*, *J*(F,C) = 25, CO). ^{19}F-NMR (282 MHz): −152.3 (*qt*, *J*(F,H) = 22.5, 1.5). EI-MS: 225 (0.4, $[M+H]^+$), 105 (100). Anal. calc. for $C_{12}H_{13}FO_3$ (224.23): C 64.28, H 5.84; found: C 64.14, H 5.68. Known compound [19][46]: the literature value for an enantiomerically pure sample with (*S*)-configuration: $[\alpha]_D = +85.4$ ($c = 1.97$, MeOH) [19].

Methyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**2F**). GC: (*β-DEX*, 100°): t_R(minor) 101.4, t_R(major) 103.8 min. R_f (^{t}BuOMe/hexane 1:10) 0.19. ^{1}H-NMR (250 MHz): 1.88 (*d*, *J*(F,H) = 22.5, 3 H); 3.80 (*s*, MeO); 7.42–7.51 (*m*, 2 H); 7.56–7.64 (*m*, 1 H); 8.02–.07 (*m*, 2 H). ^{13}C-NMR (62.9 MHz): 21.3 (*d*, *J*(F,C) = 24.7, Me); 53.5 (Me); 97.3 (*d*, *J*(F,C) = 195.0, C); 128.8 (*d*, *J*(F,C) = 0.8, CH); 129.9 (*d*, *J*(F,C) = 5.5, CH); 133.4 (*d*, *J*(F,C) = 3.7, C); 134.1 (CH); 169.0 (*d*, *J*(F,C) = 25.6, CO); 191.9 (*d*, *J*(F,C) = 25.0, CO). ^{19}F-NMR (282 MHz): −152.2 (*q*, *J*(F,H) = 22.6). EI-MS: 210 (< 1, M^+), 105 (100). Known compound, CAS No. 144462-33-9 (*R*).

1,1-Dimethylpropyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**3F**). HPLC (*Chiralcel OB-H;* hexane/^{i}PrOH 99.7:0.3; 0.5 ml min^{-1}): t_R(minor) 14.7, t_R(major) 18.9 min. R_f (^{t}BuOMe/hexane 1:10) 0.51. $[\alpha]_D = +25.2 \pm 0.7$ ($c = 1.825$, MeOH; 32.9% ee). ^{1}H-NMR (300 MHz): 0.72 (*t*, *J* = 7.5, 3 H); 1.31 (*s*, 3 H); 1.38 (*s*, 3 H); 1.60–1.76 (*AB* of ABC_3, 2 H); 1.83 (*d*, *J*(F,C) = 22.4, 3 H); 7.42–7.50 (*m*, 2 H); 7.55–7.62 (*m*, 1 H); 8.02–8.08 (*m*, 2 H). ^{13}C-NMR (62.9 MHz): 7.8, 20.7 (*d*, *J*(F,C) = 24); 24.9; 25.1; 33.5; 86.5;

91.6 (*d*, *J*(F,C) = 193); 128.5 (*d*, *J*(F,C) = 1); 129.6 (*d*, *J*(F,C) = 5); 133.6 (*d*, *J*(F,C) = 3); 133.7; 167.4 (*d*, *J*(F,C) = 26, CO); 191.6 (*d*, *J*(F,C) = 25, CO). ^{19}F-NMR (282 MHz): −151.2 (*qq*, *J*(F,H) = 22.4, 1.6). FAB-MS: 289 (8, $[M+Na]^+$), 267 (20, $[M+H]^+$), 197 (100). Anal. calc. for $C_{15}H_{19}FO_3$ (266.31): C 67.65, H 7.19; found: C 67.63, H 7.15.

Benzyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**4F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 95 : 5; 1.0 ml min^{-1}): t_R(minor) 17.1, t_R(major) 20.6 min. R_f (^{t}BuOMe/hexane 1 : 5) 0.51. $[\alpha]_D = +37.2$ (*c* = 1.0, MeOH; 70.0% ee). ^{1}H-NMR (200 MHz): 1.87 (*d*, *J*(F,H) = 22.5, 3 H); 5.17 (*d*, *J* = 12.1, 1 H); 5.24 (*d*, *J* = 12.1, 1 H); 7.14–7.31 (*m*, 5 H); 7.32–7.45 (*m*, 2 H); 7.49–7.61 (*m*, 1 H); 7.93–8.04 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 20.9 (*d*, *J*(F,C) = 23, Me); 67.9 (CH_2); 96.9 (*d*, *J*(F,C) = 196, CF); 128.2 (CH); 128.5 (CH); 128.6 (CH); 128.6 (CH); 129.7 (*d*, *J*(F,C) = 5, CH); 133.3 (*d*, *J*(F,C) = 4, C); 133.8 (CH); 134.4 (C); 168.3 (*d*, *J*(F,C) = 26, CO); 191.4 (*d*, *J*(F,C) = 25, CO). ^{19}F-NMR (188.3 MHz): −152.1 (*qt*, *J*(F,H) = 22.5, 1.5). ESI-MS: 304.3 (100, $[M+NH_4]^+$). Anal. calc. for $C_{17}H_{15}FO_3$ (286.30): C 71.32, H 5.28; found: C 71.42, H 5.21.

Diphenylmethyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**5F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 95 : 5; 1.0 ml min^{-1}): t_R(major) 14.1, t_R(minor) 18.9 min. R_f (^{t}BuOMe/hexane 1 : 5) 0.50. $[\alpha]_D = +19.0 \pm 0.2$ (*c* = 1.83, MeOH; 56% ee). ^{1}H-NMR (300 MHz): 1.89 (*d*, *J*(F,H) = 22.5, 3 H); 6.91 (*s*, 1 H); 7.01–7.07 (*m*, 2 H); 7.10–7.21 (*m*, 3 H); 7.22–7.37 (*m*, 7 H); 7.48–7.55 (*m*, 1 H); 7.90–7.97 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 20.8 (*d*, *J*(F,C) = 23.5, Me); 78.9 (CH); 81.7 (*d*, *J*(F,C) = 195.5, C); 126.7 (CH); 127.1 (CH); 128.0 (CH); 128.3 (CH); 128.4 (CH); 128.5 (CH); 128.6 (CH); 129.6 (CH); 129.7 (CH); 133.3 (*d*, *J*(F,C) = 3, C); 133.8 (CH); 138.5 (C); 138.7 (C); 167.5 (*d*, *J*(F,C) = 26, CO); 191.2 (*d*, *J*(F,C) = 25, CO). ^{19}F-NMR (282 MHz): −152.5 (*qt*, *J*(F,H) = 22.4, 1.5). HR-MALDI-MS: 385.121 ($[M+Na]^+$; calc. 385.121). Anal. calc. for $C_{23}H_{19}FO_3$ (362.40): C 76.23, H 5.28; found: C 76.28, H 5.49.

2,3,4,5,6-Pentafluorobenzyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**6F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 95 : 5; 0.5 ml min^{-1}): t_R(major) 17.1, t_R(minor) 19.3 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.22. ^{1}H-NMR (300 MHz): 1.88 (*d*, *J*(F,H) = 22.6, 3 H); 5.23 (*dt*, *J* = 12.2, *J*(F,H) = 1.4, 1 H); 5.34 (*dt*, *J* = 12.2, *J*(F,H) = 1.4, 1 H); 7.38–7.47 (*m*, 2 H); 7.54–7.63 (*m*, 1 H); 7.94–8.01 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 20.9 (*d*, *J*(F,C) = 23.2, Me); 55.0 (CH_2); 96.9 (*d*, *J*(F,C) = 196.5, CF); 108.0 (*m*, C); 128.8 (CH); 129.7 (*d*, *J*(F,C) = 5.5, CH); 133.2 (C); 134.2 (CH); 135.6–147.8 (*m*, 5 CF[2]); 168.0 (*d*, *J*(F,C) = 26.2, CO); 190.8 (*d*, *J*(F,C) = 24.4, CO). ^{19}F-NMR (282 MHz): −161.5 (*m*, 2 F–C_{Ar}); −152.5 (*q*, *J*(F,H) = 22.6, 1 F–C(2)); −151.9 (*tt*, *J*(F,F) = 20.9, 2.7, 1 F–C_{Ar}); −141.8 (*m*, 2 F–C_{Ar}). EI-MS: 376 (M^+), 105 (100). Anal. calc. for $C_{17}H_{10}O_3F_6$ (376.25): C 54.27, H 2.68; found: C 54.56, H 2.99.

4-(Trifluoromethyl)benzyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**7F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 98 : 2; 0.5 ml min^{-1}): t_R(major) 34.4, t_R(minor) 41.3 min. ^{1}H-NMR (250 MHz): 1.89 (*d*, *J*(F,H) = 22.5, 3 H); 5.21 (*d*, *J* = 12.5, 1 H); 5.29 (*d*, *J* = 12.5, 1 H); 7.28 (*d*, *J* = 8.0, 2 H); 7.35–7.43 (*m*, 2 H); 7.50 (*d*, *J* = 8.0, 2 H); 7.53–7.61 (*m*, 1 H); 7.93–8.00 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 21.1 (*d*, *J*(F,C) = 23.2, Me); 67.0 (CH_2); 97.1 (*d*, *J*(F,C) = 194.9, CF); 124.0 (*q*, *J*(F,C) = 272.3, C); 125.7 (*q*, *J*(F,C) = 3.7, CH); 128.4 (CH); 128.8 (CH); 129.8 (*d*, *J*(F,C) = 5.5, CH); 130.9 (*q*, *J*(F,C) = 32.4, C); 133.3 (*d*, *J*(F,C) = 3.7, C); 134.2 (CH); 138.4 (*d*, *J*(F,C) = 1, C); 168.3 (*d*, *J*(F,C) = 25.9, CO); 191.4 (*d*, *J*(F,C) = 24.7, CO). ^{19}F-NMR (282 MHz): −152.3 (*qt*, *J*(F,H) = 22.5, 1.5, 1 F); −63.2 (3 F). EI-MS: 354 ($2.4 \cdot 10^{-5}$, M^+), 105 (100). Anal. calc. for $C_{18}H_{14}F_4O_3$ (354.30): C 61.02, H 3.98; found: C 60.87, H 4.14.

Ethyl 2-Fluoro-3-(4-methoxyphenyl)-2-methyl-3-oxopropanoate (**8F**). GC (*β-DEX*, 138°): t_R(minor) 116.5, t_R(major) 119.0 min. R_f (^{t}BuOMe/hexane 1 : 5) 0.27. $[\alpha]_D = +18.7$ (*c* = 0.58, MeOH; 56.3% ee). ^{1}H-NMR (300 MHz): 1.20 (*t*, *J* = 7.1, 3 H); 1.86 (*d*, *J*(F,H) = 22.6, 3 H); 3.88 (*s*, 3 H); 4.25 (*m*, 2 H); 6.90–6.96 (*m*, 2 H); 8.02–8.09 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 14.1 (Me); 21.2 (*d*, *J*(F,C) = 23.5, Me); 55.7 (Me); 62.6 (CH_2); 97.3 (*d*, *J*(F,C) = 194.9, CF); 114.0 (*d*, *J*(F,C) = 1, CH); 126.4 (*d*, *J*(F,C) = 3.7, C); 132.4 (*d*, *J*(F,C) = 5.8, CH); 164.3 (C); 168.9 (*d*, *J*(F,C) = 25.6, CO); 190.1 (*d*, *J*(F,C) = 24.7, CO). ^{19}F-NMR (282 MHz): −151.5 (*qt*, *J*(F,H) = 22.6, 1.5). EI-MS: 254 (1.2, M^+), 135 (100). Anal. calc. for $C_{13}H_{15}O_4F$ (254.26): C 61.41, H 5.95; found: C 61.44, H 5.95.

Methyl 2-Fluoro-3-(4-methoxyphenyl)-2-methyl-3-oxopropanoate (**9F**). GC (*β-DEX*, 134°): t_R(minor) 118.6, t_R(major) 121.2 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.16. $[\alpha]_D = +26.7 \pm 0.1$ (*c* = 1.025, MeOH;

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[2]) Quaternary C(–F)-nuclei (higher-order spin system) gave rise to 5 *m* signals centered at 135.8, 139.2, 140.5, 144.0, and 147.4.

61.7% ee). ^{1}H-NMR (300 MHz): 1.87 (*d*, *J*(F,H) = 22.6, 3 H); 3.78 (*s*, 3 H); 3.88 (*s*, 3 H); 6.88–6.97 (*m*, 2 H); 8.02–8.09 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 21.3 (*d*, *J*(F,C) = 23.5, Me); 53.4 (Me); 55.7 (Me); 97.4 (*d*, *J*(F,C) = 194.9, CF); 114.1 (*d*, *J*(F,C) = 1, CH); 126.4 (*d*, *J*(F,C) = 3.5, C); 132.5 (*d*, *J*(F,C) = 5.8, CH); 164.4 (C); 169.3 (*d*, *J*(F,C) = 25.8, CO); 190.2 (*d*, *J*(F,C) = 24.7, CO). ^{19}F-NMR (282 MHz): −151.5 (*qt*, *J*(F,H) = 22.6, 1.5). EI-MS: 240 (1.5, M^+), 135 (100). Anal. calc. for $C_{12}H_{13}FO_4$ (240.23): C 60.00, H 5.45; found: C 59.96, H 5.52.

Ethyl 2-Fluoro-2-methyl-3-(4-nitrophenyl)-3-oxopropanoate (**10F**). GC (*β*-dex, 150°): t_R(minor) 84.1, t_R(major) 86.1 min. R_f (^{t}BuOMe/hexane 1:5) 0.44. ^{1}H-NMR (300 MHz): 1.23 (*t*, *J* = 7.1, 3 H); 1.90 (*d*, *J*(F,H) = 22.6, 3 H); 4.28 (*m*, 2 H); 8.19–8.24 (*m*, 2 H); 8.28–8.33 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 14.0 (Me); 20.9 (*d*, *J*(F,C) = 23.2, Me); 63.1 (CH_2); 97.3 (*d*, *J*(F,C) = 194.3, CF); 123.9 (*d*, *J*(F,C) = 1, CH); 130.9 (*d*, *J*(F,C) = 5.8, CH); 138.1 (*d*, *J*(F,C) = 3.4, C); 150.7 (C); 167.8 (*d*, *J*(F,C) = 25.6, CO); 190.9 (*d*, *J*(F,C) = 26.2, CO). ^{19}F-NMR (282 MHz): −152.9 (*qt*, *J*(F,H) = 22.6, 1.3). EI-MS: 269 (0.3, M^+), 150 (100). Anal. calc. for $C_{12}H_{12}FNO_5$ (269.23): C 53.54, H 4.49, N 5.20; found: C 53.51, H 4.60, N 5.21.

Phenyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**11F**). HPLC (*Chiralcel OD-H*; hexane/^{i}PrOH 99.5:0.5; 0.5 ml min^{-1}): t_R(major) 21.6, t_R(minor) 23.3 min. R_f (^{t}BuOMe/hexane 1:10) 0.33. ^{1}H-NMR (300 MHz): 2.04 (*d*, *J*(F,H) = 22.5, 3 H); 6.95–6.99 (*m*, 2 H); 7.21–7.26 (*m*, 1 H); 7.31–7.39 (*m*, 2 H); 7.47–7.55 (*m*, 2 H); 7.61–7.68 (*m*, 1 H); 8.12–8.17 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 21.1 (*d*, *J*(F,C) = 23.1, Me); 97.1 (*d*, *J*(F,C) = 196.1, CF); 121.0 (CH); 126.7 (CH); 129.0 (CH); 129.7 (CH); 129.9 (*d*, *J*(F,C) = 5.2, CH); 133.5 (*d*, *J*(F,C) = 3.4, C); 134.3 (CH); 150.0 (C); 167.3 (*d*, *J*(F,C) = 26.3, CO); 191.4 (*d*, *J*(F,C) = 25.7, CO). ^{19}F-NMR (282 MHz): −152.3 (*qt*, *J*(F,H) = 22.5, 1.5). EI-MS: 272 (0.7, M^+), 105 (100). Anal. calc. for $C_{16}H_{13}FO_3$ (272.28): C 70.58, H 4.81; found: C 70.74, H 4.98.

4-Methoxyphenyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**12F**). HPLC (*Chiralcel OD-H*; hexane/^{i}PrOH 99.5:0.5; 0.5 ml min^{-1}): t_R(minor) 40.1, t_R(major) 44.3 min. R_f (^{t}BuOMe/hexane 1:5) 0.37. ^{1}H-NMR (250 MHz): 2.03 (*d*, *J*(F,H) = 22.6, 3 H); 3.77 (*s*, 3 H); 6.81–6.91 (*m*, 4 H); 7.47–7.56 (*m*, 2 H); 7.60–7.68 (*m*, 1 H); 8.12–8.16 (*m*, 2 H). ^{13}C-NMR (62.9 MHz): 21.1 (*d*, *J*(F,C) = 23.3, Me); 55.7 (Me); 97.1 (*d*, *J*(F,C) = 196.3, CF); 114.7 (CH); 121.8 (CH); 129.0 (CH); 129.9 (CH); 133.5 (C); 134.3 (CH); 143.5 (C); 157.9 (C); 167.6 (*d*, *J*(F,C) = 26.2, CO); 191.4 (*d*, *J*(F,C) = 24.7, CO). ^{19}F-NMR (282 MHz): −152.2 (*q*, *J*(F,H) = 22.6). EI-MS: 302 (19, M^+), 105 (100). Anal. calc. for $C_{17}H_{15}FO_4$ (302.30): C 67.54, H 5.00; found: C 67.60, H 5.15.

Ethyl 2-Fluoro-2-methyl-3-(naphthalen-2-yl)-3-oxopropanoate (**13F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 90:10; 0.6 ml min^{-1}): t_R(minor) 14.5, t_R(major) 17.1 min. R_f (^{t}BuOMe/hexane 1:5) 0.60. $[\alpha]_D$ = −13.0 (*c* = 1.065, MeOH; 60.6% ee). ^{1}H-NMR (300 MHz): 1.19 (*t*, *J* = 7.1, 3 H); 1.93 (*d*, *J*(F,H) = 22.6, 3 H); 4.17–4.35 (*m*, 2 H); 7.52–7.65 (*m*, 2 H); 7.84–7.91 (*m*, 2 H); 7.95–8.00 (*m*, 1 H); 8.04–8.08 (*m*, 1 H); 8.66 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 13.9 (Me); 21.0 (*d*, *J*(F,C) = 23, Me); 62.6 (CH_2); 97.2 (*d*, *J*(F,C) = 195, CF); 124.7 (*d*, *J*(F,C) = 3, CH); 126.8 (CH); 127.7 (CH); 128.4 (CH); 129.0 (CH); 130.0 (CH); 130.6 (*d*, *J*(F,C) = 4, C); 132.1 (*d*, *J*(F,C) = 8, CH); 132.3 (*d*, *J*(F,C) = 1, C); 135.8 (C); 168.6 (*d*, *J*(F,C) = 26, CO); 191.5 (*d*, *J*(F,C) = 25, CO). ^{19}F-NMR (188.3 MHz): −151.3 (*qdd*, *J*(F,H) = 22.6, 1.7, 1.3). EI-MS: 274 (8, M^+), 155 (100). Anal. calc. for $C_{16}H_{15}FO_3$ (274.29): C 70.06, H 5.51; found: C 70.21, H 5.59.

Ethyl 2-Fluoro-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (**14F**). HPLC (*Chiralcel OB-H*; hexane/^{i}PrOH 85:15; 0.5 ml min^{-1}): t_R(minor) 27.6, t_R(major) 33.7 min. R_f (^{t}BuOMe/hexane 1:5) 0.23. $[\alpha]_D$ = +0.2 (*c* = 1.25, MeOH; 19.8% ee). ^{1}H-NMR (250 MHz): 1.28 (*t*, *J* = 7.2, 3 H); 2.55 (*dddd*, *J*(F,H) = 22.5, *J* = 14.0, 7.3, 5.2, 1 H–C(3)); 2.73 (*dddd*, *J*(F,H) = 11.4, *J* = 14.0, 7.5, 5.4, 1 H–C(3)); 3.08 (*ddd*, *J* = 17.2, 7.5, 5.1, 1 H of CH_2(4)); 3.20 (*ddd*, *J* ≈ 17, 7, 6, 1 H of CH_2(4)); 4.30 (*q*, *J* = 7.1, 2 H); 7.26–7.41 (*m*, 2 H); 7.56 (*td*, *J* = 7.5, 1.5, 1 H); 8.08 (*dd*, *J* = 7.9, 1.4, H–C(8)). ^{13}C-NMR (62.9 MHz): 14.0 (Me); 24.8 (*d*, *J*(F,C) = 7, CH_2); 31.8 (*d*, *J*(F,C) = 22, CH_2); 62.4 (CH_2); 93.1 (*d*, *J*(F,C) = 194, CF); 127.2 (CH); 128.4 (*d*, *J*(F,C) = 1, CH); 128.7 (CH); 130.5 (C); 134.5 (CH); 143.1 (C); 167.3 (*d*, *J*(F,C) = 26, CO); 188.6 (*d*, *J*(F,C) = 19, CO). ^{19}F-NMR (188.3 MHz): −164.7 (*ddd*, *J*(F,H) = 22.4, 11.4, 1.1). ESI-MS: 254.16 (100, $[M + NH_4]^+$). Anal. calc. for $C_{13}H_{13}FO_3$ (236.24): C 66.09, H 5.55; found: C 65.82, H 5.55.

b) *Catalytic Fluorination of 3-Oxobutanoates.* Products were obtained according to *GP 1*; yields and ee values are compiled in *Table 2*. The reaction times for this set of substrates were usually < 1 h.

Ethyl 2-Fluoro-2-methyl-3-oxobutanoate (**15F**). GC (*β-DEX,* 70°): t_R(minor) 15.7, t_R(major) 16.5 min. R_f (Et_2O/hexane 1:5) 0.64. $[\alpha]_D = +20.55 \pm 0.08$ (*c* = 1.00, MeOH; 45.3% ee). ^{1}H-NMR

(250 MHz): 1.31 (*t*, *J* = 7.1, 3 H); 1.69 (*d*, *J*(F,H) = 22.1, 3 H); 2.33 (*d*, *J*(F,H) = 4.6, 3 H); 4.27 (*q*, *J* = 7.1, 2 H). ^{13}C-NMR (62.9 MHz): 14.1 (Me); 19.9 (*d*, *J*(F,C) = 22.8, Me); 25.1 (Me); 62.7 (CH_2); 97.8 (*d*, *J*(F,C) = 193.7, CF); 167.0 (*d*, *J*(F,C) = 25.3, CO); 202.5 (*d*, *J*(F,C) = 28.6, CO). ^{19}F-NMR (282 MHz): – 157.6 (*qq*, *J*(F,H) = 22.1, 4.6). Known compound, CAS No. 122795-13-5.

2,2-Diphenylethyl 2-Fluoro-2-methyl-3-oxobutanoate (**16F**). HPLC (*Chiralcel OD-H*; hexane/^{i}PrOH 98 : 2; 0.4 ml min^{-1}): t_R(minor) 26.6, t_R(major) 28.5 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.37. $[\alpha]_D$ = + 12.8 (*c* = 0.39, MeOH; 35.2% ee). ^{1}H-NMR (300 MHz): 1.50 (*d*, *J*(F,H) = 22.1, 3 H); 2.00 (*d*, *J*(F,H) = 4.5, 3 H); 4.41 (*t*, *J* = 7.7, 1 H); 4.69 – 4.82 (*m*, 2 H); 7.18 – 7.36 (*m*, 10 H). ^{13}C-NMR (75.5 MHz): 19.5 (*d*, *J*(F,C) = 23, Me); 24.6 (Me); 49.6 (CH); 68.2 (CH_2); 97.4 (*d*, *J*(F,C) = 194, CF); 127.0 (CH); 128.1 (CH); 128.1 (CH); 128.7 (CH); 140.1 (C); 140.1 (C); 166.6 (*d*, *J*(F,C) = 26, CO); 201.6 (*d*, *J*(F,C) = 28, CO). ^{19}F-NMR (188.3 MHz): – 157.5 (*qq*, *J*(F,H) = 22.1, 4.5). ESI-MS: 332.3 (100, $[M + NH_4]^+$). Anal. calc. for $C_{19}H_{19}FO_3$ (314.36): C 72.60, H 6.09; found: C 72.44, H 6.18.

Benzyl 2-Fluoro-2-methyl-3-oxobutanoate (**17F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 96 : 4; 0.5 ml min^{-1}): t_R(minor) 34.5, t_R(major) 42.1 min. R_f (^{t}BuOMe/ hexane 1 : 5) 0.45. $[\alpha]_D$ = + 17.8 (*c* = 1.13, MeOH; 50.4% ee). ^{1}H-NMR (300 MHz): 1.69 (*d*, *J*(F,H) = 22.1, 3 H); 2.28 (*d*, *J*(F,H) = 4.6, 3 H); 5.24 (*s*, 2 H); 7.30 – 7.41 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 19.7 (*d*, *J*(F,C) = 23); 24.9; 68.0; 97.6 (*d*, *J*(F,C) = 194); 128.1; 128.6; 128.7; 134.6; 166.7 (*d*, *J*(F,C) = 26, CO); 202.1 (*d*, *J*(F,C) = 29, CO). ^{19}F-NMR (282 MHz): – 157.5 (*qqq*, *J*(F,H) = 22.1, 4.5, 0.4). EI-MS: 224 (0.1, M^+), 91 (100). Anal. calc. for $C_{12}H_{13}FO_3$ (224.23): C 64.28, H 5.84; found: C 64.25, H 5.78.

(Naphthalen-1-yl)methyl 2-Fluoro-2-methyl-3-oxobutanoate (**18F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 96 : 4; 1.0 ml min^{-1}): t_R(minor) 24.0, t_R(major) 27.7 min. R_f (^{t}BuOMe/hexane 1 : 5) 0.49. $[\alpha]_D$ = + 19.6 (*c* = 1.14, MeOH; 68.8% ee). ^{1}H-NMR (300 MHz): 1.67 (*d*, *J*(F,H) = 22.1, 3 H); 2.22 (*d*, *J*(F,H) = 4.5, 3 H); 5.63 – 5.73 (*m*, *AB*-system, 2 H); 7.40 – 7.60 (*m*, 4 H); 7.79 – 7.96 (*m*, 3 H). ^{13}C-NMR (75.5 MHz): 19.7 (*d*, *J*(F,C) = 23, Me); 24.9 (Me); 66.5 (CH_2); 97.6 (*d*, *J*(F,C) = 194, C); 123.2 (CH); 125.2 (CH); 126.1 (CH); 126.8 (CH); 127.8 (CH); 129.8 (CH); 130.0 (C); 131.4 (C); 133.7 (C); 166.7 (*d*, *J*(F,C) = 26, CO); 202.1 (*d*, *J*(F,C) = 28, CO). ^{19}F-NMR (282 MHz): – 157.4 (*qq*, *J*(F,H) = 22.1, 4.5). EI-MS: 274 (11, M^+), 141 (100). Anal. calc. for $C_{16}H_{15}FO_3$ (274.29): C 70.06, H 5.51; found: C 70.04, H 5.66.

2,3,4,5,6-Pentafluorobenzyl 2-Fluoro-2-methyl-3-oxobutanoate (**19F**). GC (*β-DEX*, 95°): t_R(minor) 92.1, t_R(major) 93.8 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.22. ^{1}H-NMR (300 MHz): 1.69 (*d*, *J*(F,H) = 22.2, 3 H); 2.31 (*d*, *J*(F,H) = 4.5, 3 H); 5.32 (*s*, 2 H). ^{13}C-NMR (75.5 MHz): 20.0 (*d*, *J*(F,C) = 22.8, Me); 25.0 (Me); 55.2 (CH_2); 96.7 (*d*, *J*(F,C) = 195.2, CF); 108.4 (*m*, CF); 136.1 – 147.4 (*m*, CF [3])); 166.4 (*d*, *J*(F,C) = 25.9, CO); 201.9 (*d*, *J*(F,C) = 28.6, CO). ^{19}F-NMR (282 MHz): – 161.4 (*m*, 2 F); – 157.8 (*qq*, *J*(F,H) = 22.2, 4.5, 1 F); – 151.7 (*tt*, *J*(F,F) = 20.8, 2.5, F); – 142.1 (*m*, 2 F). EI-MS: 314 (0.5, M^+), 181 (100). Anal. calc. for $C_{12}H_8F_6O_3$ (314.18): C 45.88, H 2.57; found: C 45.84, H 2.77.

4-Nitrobenzyl 2-Fluoro-2-methyl-3-oxobutanoate (**20F**). HPLC (*Chiralcel OB-H*; hexane/^{i}PrOH 75 : 25; 0.4 ml min^{-1}): t_R(major) 20.9, t_R(minor) 22.2 min. R_f (^{t}BuOMe/hexane 1 : 2) 0.31. ^{1}H-NMR (300 MHz): 1.73 (*d*, *J*(F,H) = 22.2, 3 H); 2.33 (*d*, *J*(F,H) = 4.7, 3 H); 5.33 (*s*, 2 H); 7.51 (*d*, *J* = 8.5, 2 H); 8.24 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR (75.5 MHz): 20.1 (*d*, *J*(F,C) = 22.8, Me); 25.1 (Me); 66.4 (CH_2); 97.8 (*d*, *J*(F,C) = 194.9, CF); 124.1 (CH); 128.5 (CH); 141.9 (C); 148.1 (C); 166.6 (*d*, *J*(F,C) = 25.6, CO); 202.6 (*d*, *J*(F,C) = 28.6, CO). ^{19}F-NMR (282 MHz, $CDCl_3$): – 157.6 (*qq*, *J*(F,H) = 22.2, 4.7). Anal. calc. for $C_{12}H_{12}FNO_5$ (269.23): C 53.54, H 4.49, N 5.20; found: C 54.02, H 5.04, N 5.16.

Phenyl 2-Fluoro-2-methyl-3-oxobutanoate (**21F**). GC (*β-DEX*, 105°): t_R(minor) 57.9, t_R(major) 59.1 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.28. ^{1}H-NMR (300 MHz): 1.83 (*d*, *J*(F,H) = 22.1, 3 H); 2.44 (*d*, *J*(F,H) = 4.6, 3 H); 7.09 – 7.13 (*m*, 2 H); 7.24 – 7.31 (*m*, 1 H); 7.37 – 7.43 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 20.0 (*d*, *J*(F,C) = 22.5, Me); 25.2 (Me); 97.8 (*d*, *J*(F,C) = 195.2, C); 121.1 (CH); 126.7 (CH); 129.8 (CH); 150.2 (C); 165.6 (*d*, *J*(F,C) = 25.6, CO); 202.3 (*d*, *J*(F,C) = 28.5, CO). ^{19}F-NMR (282 MHz): – 157.4 (*qq*, *J*(F,H) = 22.1, 4.6). EI-MS: 210 (4, M^+), 121 (100). Anal. calc. for $C_{11}H_{11}FO_3$ (210.20): C 62.85, H 5.27; found: C 62.13, H 5.44.

3,5-Dimethylphenyl 2-Fluoro-2-methyl-3-oxobutanoate (**22F**). GC (*β-DEX*, 84°): t_R(minor) 621, t_R(major) 632 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.38. $[\alpha]_D$ = + 7.3 ± 0.4 (*c* = 1.09, MeOH; 73.7% ee).

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[3]) Quaternary C(–F)-nuclei (higher order spin system) gave rise to 5 *m* signals centered at: 136.1, 139.4, 140.6, 144.1, and 147.4.

^{1}H-NMR (300 MHz): 1.81 (*d*, *J*(F,H) = 22.1, 3 H); 2.31 (*s*, 6 H); 2.43 (*d*, *J*(F,H) = 4.5, 3 H); 6.71 (*s*, 2 H); 6.90 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 20.0 (*d*, *J*(F,C) = 22.5, Me); 21.3 (Me); 25.2 (Me); 97.8 (*d*, *J*(F,C) = 195.5, C); 118.6 (C); 128.4 (C); 139.7 (C); 150.0 (C); 165.7 (*d*, *J*(F,C) = 25.6, CO); 202.3 (*d*, *J*(F,C) = 28.3, CO). ^{19}F-NMR (282 MHz): −157.3 (*qq*, *J*(F,H) = 22.2, 4.6). EI-MS: 238.1 (32, M^+), 122 (100). Anal. calc. for $C_{13}H_{15}FO_3$ (238.26): C 65.54, H 6.35; found: C 65.48, H 6.19.

2,6-Dimethylphenyl 2-Fluoro-2-methyl-3-oxobutanoate (**23F**). GC (*β-DEX*, 102°): t_R(minor) 139, t_R(major) 142 min. R_f (^{t}BuOMe/hexane 1:10) 0.39. $[\alpha]_D = +12.30 \pm 0.06$ (*c* = 1.11, MeOH; 72.7% ee). ^{1}H-NMR (300 MHz): 1.86 (*d*, *J*(F,H) = 22.2, 3 H); 2.12 (*s*, 6 H); 2.46 (*d*, *J*(F,H) = 4.9, 3 H); 7.07 (*s*, 3 H). ^{13}C-NMR (75.5 MHz): 16.2 (Me); 20.2 (*d*, *J*(F,C) = 12.8, Me); 25.3 (Me); 98.1 (*d*, *J*(F,C) = 195.0, CF); 126.7 (CH); 129.0 (CH); 130.0 (C); 147.5 (C); 164.7 (*d*, *J*(F,C) = 25.8, CO); 202.8 (*d*, *J*(F,C) = 28.8, CO). ^{19}F-NMR (282 MHz): −156.5 (*qq*, *J*(F,H) = 22.2, 4.9). EI-MS: 238 (30, M^+), 122 (100). Anal. calc. for $C_{13}H_{15}FO_3$ (238.26): C 65.54, H 6.35; found: C 65.34, H 6.25.

2,4,6-Trimethylphenyl 2-Fluoro-2-methyl-3-oxobutanoate (**24F**). GC (*β-DEX*, 113°): t_R(minor) 137, t_R(major) 140 min. R_f (^{t}BuOMe/hexane 1:10) 0.40. ^{1}H-NMR (300 MHz): 1.85 (*d*, *J*(F,H) = 22.1, 3 H); 2.07 (*s*, 6 H); 2.26 (*s*, 3 H); 2.46 (*d*, *J*(F,H) = 4.8, 3 H); 6.87 (*s*, 2 H). ^{13}C-NMR (75.5 MHz): 16.1 (Me); 20.2 (*d*, *J*(F,C) = 22.5, Me); 20.9 (Me); 25.3 (Me); 98.0 (*d*, *J*(F,C) = 194.3, CF); 129.6 (C); 129.6 (CH); 136.2 (C); 145.2 (C); 164.9 (*d*, *J*(F,C) = 25.6, C); 202.8 (*d*, *J*(F,C) = 28.9, C). ^{19}F-NMR (282 MHz): −156.5 (*qq*, *J*(F,H) = 22.1, 4.8). EI-MS: 252 (37, M^+), 136 (100). Anal. calc. for $C_{14}H_{17}FO_3$ (252.28): C 66.65, H 6.79; found: C 66.75, H 6.93.

Ethyl 2-Benzyl-2-fluoro-3-oxobutanoate (**25F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 95:5; 1.0 ml min^{-1}): t_R(major) 16.4, t_R(minor) 25.7 min. R_f (^{t}BuOMe/hexane 1:5) 0.39. $[\alpha]_D = +1.6$ (*c* = 1.535, MeOH; 6.2% ee). ^{1}H-NMR (300 MHz): 1.24 (*t*, *J* = 7.1, 3 H); 2.13 (*d*, *J*(F,H) = 5.1, 3 H); 3.37 (*dd*, *J*(F,H) = 26.5, *J* = 14.7, 1 H) 3.43 (*dd*, *J*(F,H) = 25.1, *J* = 14.7, 1 H); 4.22 (*q*, *J* = 7.1, 2 H); 7.18–7.32 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 13.9 (Me); 26.2 (Me); 39.7 (*d*, *J*(F,C) = 20, CH_2); 62.6 (CH_2); 99.9 (*d*, *J*(F,C) = 200, C); 127.4 (CH); 128.4 (CH); 130.3 (*d*, *J*(F,C) = 1, CH); 133.0 (C); 165.6 (*d*, *J*(F,C) = 25, CO); 202.3 (*d*, *J*(F,C) = 30, CO). ^{19}F-NMR (282 MHz): −165.1 (*tq*, *J*(F,H) = 25.5, 5.2). EI-MS: 238 (8, M^+), 218 (98, $[M-HF]^+$), 196 (100). Anal. calc. for $C_{13}H_{15}FO_3$ (238.26): C 65.54, H 6.35; found: C 65.25, H 6.14.

Benzyl 2-Acetyl-2-fluoro-3-methylbutanoate (**26F**). HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 98.5:1.5; 1.0 ml min^{-1}): t_R(major) 20.6, t_R(minor) 26.0 min. R_f (^{t}BuOMe/hexane 1:5) 0.44. $[\alpha]_D = +8.4$ (*c* = 0.835, MeOH; 23.8% ee). ^{1}H-NMR (250 MHz): 0.91 (*d*, *J* = 6.9, 3 H); 0.91 (*d*, *J* = 6.9, 3 H); 2.27 (*d*, *J*(F,H) = 5.3, 3 H); 2.73 (*dsept.*, *J*(F,H) = 30.4, *J* = 6.9, 1 H); 5.20, 5.26 (*AB*, *J* = 12.2, 2 H); 7.28–7.42 (*m*, 5 H). ^{13}C-NMR (62.9 MHz): 15.8 (*d*, *J*(F,C) = 3, Me); 16.1 (*d*, *J*(F,C) = 3, Me); 26.8 (*d*, *J*(F,C) = 1, Me); 33.4 (*d*, *J*(F,C) = 21, CH); 67.9 (CH_2); 128.3 (CH); 128.6 (CH); 128.6 (CH); 134.7 (C); 165.9 (*d*, *J*(F,C) = 27, CO); 202.4 (*d*, *J*(F,C) = 29, CO). ^{19}F-NMR (188.3 MHz): −182.2 (*dq*, *J*(F,H) = 30.4, 5.3). ESI-MS: 270.3 (100, $[M+NH_4]^+$). Anal. calc. for $C_{14}H_{17}FO_3$ (252.28): C 66.65, H 6.79; found: C 66.59, H 6.85.

Benzyl 1-Fluoro-2-oxocyclopentanecarboxylate (**27F**). HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 85:15; 0.8 ml min^{-1}): t_R(major) 27.1, t_R(minor) 34.9 min. R_f (^{t}BuOMe/hexane 1:5) 0.19. $[\alpha]_D = -33.2$ (*c* = 1.285, MeOH; 56.8% ee). ^{1}H-NMR (250 MHz): 2.03–2.16 (*m*, 2 H); 2.21–2.42 (*m*, 1 H); 2.42–2.51 (*m*, 3 H); 2.4 (*ddd*, *J*(F,H) = 19.9, *J* = 14.4, 7.3, 1 H); 5.21, 5.27 (*AB*, *J* = 12.2, 2 H); 7.28–7.41 (*m*, 5 H). ^{13}C-NMR (62.9 MHz): 18.0 (*d*, *J*(F,C) = 3, CH_2); 33.8 (*d*, *J*(F,C) = 21, CH_2); 35.6 (CH_2); 67.7 (CH_2); 94.7 (*d*, *J*(F,C) = 200, CF); 128.1 (CH); 128.6 (CH); 128.6 (CH); 134.6 (C); 167.2 (*d*, *J*(F,C) = 28, CO); 207.3 (*d*, *J*(F,C) = 17, CO). ^{19}F-NMR (188.3 MHz): −164.4 (*dd*, *J*(F,H) = 21.2, 20.2). ESI-MS: 254.3 (100, $[M+NH_4]^+$). Anal. calc. for $C_{13}H_{13}FO_3$ (236.24): C 66.09, H 5.55; found: C 65.93, H 5.53.

c) *Catalytic Fluorination of 3-Oxopentanoates.* Products were obtained according to *GP 1*; yields and ee values are compiled in *Table 3*. Reaction times for this type of substrates were typically < 1 h.

Ethyl 2-Fluoro-2-methyl-3-oxopentanoate (**28F**). GC (*β-DEX*, 82°): t_R(minor) 15.1, t_R(major) 16.3 min. ^{1}H-NMR (300 MHz): 1.08 (*t*, *J* = 7.2, 3 H); 1.29 (*t*, *J* = 7.2, 3 H); 1.68 (*d*, *J*(F,H) = 22.3, 3 H); 2.59–2.76 (*m*, 2 H); 4.25 (*q*, *J* = 7.2, 2 H). ^{19}F-NMR (282 MHz): −159.7 (*qt*, *J*(F,H) = 22.3, 3.0). Known compound, CAS No. 106815-14-9 (*S*), 106815-09-2 (*R*).

Benzyl 2-Fluoro-2-methyl-3-oxopentanoate (**29F**). HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 96:4; 1.0 ml min^{-1}): t_R(minor) 11.7, t_R(major) 15.3 min. R_f (^{t}BuOMe/hexane 1:10) 0.30. $[\alpha]_D = +32.5$ (*c* = 0.905, MeOH; 70.8% ee). ^{1}H-NMR (300 MHz): 1.04 (*t*, *J* = 7.2, 3 H); 1.70 (*d*, *J*(F,H) = 22.2, 3 H); 2.53–2.79 (*CD* of A_3CDX, 2 H); 5.23 (*s*, 2 H); 7.27–7.45 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 7.0 (*d*, *J*(F,C) = 2, Me);

20.1 (*d*, *J*(F,C) = 23, Me); 30.6 (CH_2); 67.8 (CH_2); 97.8 (*d*, *J*(F,C) = 194, CF); 128.1 (CH); 128.6 (CH); 128.6 (CH); 134.7 (C); 166.8 (*d*, *J*(F,C) = 26, CO); 204.9 (*d*, *J*(F,C) = 27, CO). ^{19}F-NMR (188.3 MHz): − 159.5 (*qt*, *J*(F,H) = 22.2, 3.1). EI-MS: 238 (0.02, M^+), 91 (100). Anal. calc. for $C_{13}H_{15}FO_3$ (238.26): C 65.54, H 6.35; found: C 65.28, H 6.30.

2,4,6-Tris(1-methylethyl)benzyl 2-Fluoro-2-methyl-3-oxopentanoate (**30F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 99.8 : 0.2; 0.3 ml min^{-1}): t_R(major) 27.8, t_R(minor) 29.8 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.48. $[\alpha]_D = +14.8$ (*c* = 0.77, MeOH; 52.5% ee); +24.1 (*c* = 1.11, MeOH; 85.6% ee). ^{1}H-NMR (300 MHz): 1.03 (*t*, *J* = 7.2, 3 H); 1.22 (*d*, *J* = 6.9, 6 H); 1.23 (*d*, *J* = 6.9, 6 H); 1.26 (*d*, *J* = 6.9, 6 H); 1.67 (*d*, *J*(F,H) = 22.2, 3 H); 2.61 (*ddq*, *J* = 19.1, 7.1, *J*(F,H) = 2.6, 1 H); 2.72 (*ddq*, *J* = 19.2, 7.1, *J*(F,H) = 3.5, 1 H); 2.89 (*sept.*, *J* = 7.0, 1 H); 3.13 (*sept.*, *J* = 6.9, 2 H); 5.33 (*s*, 2 H); 7.04 (*s*, 2 H). ^{13}C-NMR (75.5 MHz): 6.9 (*d*, *J*(F,C) = 2); 20.1 (*d*, *J*(F,C) = 23); 23.9; 24.3; 29.5; 30.5; 34.3; 61.4; 97.8 (*d*, *J*(F,C) = 194); 121.2; 125.1; 149.0; 150.1; 167.2 (*d*, *J*(F,C) = 25, CO); 204.9 (*d*, *J*(F,C) = 27, CO). ^{19}F-NMR (188.3 MHz): − 159.2 (*qt*, *J*(F,H) = 22.3, 2.9). EI-MS: 365 (0.3, M^+), 217 (100). Anal. calc. for $C_{22}H_{33}FO_3$ (364.50): C 72.49, H 9.13; found: C 72.36, H 9.07.

Diphenylmethyl 2-Fluoro-2-methyl-3-oxopentanoate (**31F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 70 : 30; 0.25 ml min^{-1}): t_R(major) 36.1, t_R(minor) 39.4 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.37. $[\alpha]_D = +38.2$ (*c* = 1.02, MeOH; 81.2% ee). ^{1}H-NMR (300 MHz): 1.00 (*t*, *J* = 7.2, 3 H); 1.71 (*d*, *J*(F,C) = 22.1, 3 H); 2.53 (*ddq*, *J* = 19.0, 7.1, *J*(F,H) = 2.5, 1 H); 2.68 (*ddq*, *J* = 19.0, 7.2, *J*(F,H) = 3.7, 1 H); 6.91 (*s*, 1 H); 7.24 – 7.38 (*m*, 10 H). ^{13}C-NMR (75.5 MHz): 6.9 (*d*, *J*(F,C) = 2); 20.0 (*d*, *J*(F,C) = 23); 30.7; 78.8; 97.8 (*d*, *J*(F,C) = 194); 126.8; 126.9; 128.2; 128.3; 128.6; 128.6; 139.0; 166.0 (*d*, *J*(F,C) = 26, CO); 204.6 (*d*, *J*(F,C) = 27, CO). ^{19}F-NMR (188.3 MHz): − 159.5 (*qdd*, *J*(F,H) = 22.1, 3.4, 2.6). ESI-MS: 332.3 (100, $[M + NH_4]^+$). HR-MALDI-MS: 337.121 ($[M + Na]^+$; calc. 337.121). Anal. calc. for $C_{19}H_{19}FO_3$ (314.35): C 72.60, H 6.09; found: C 72.58, H 6.28.

After standing for 1 d in $CDCl_3$ soln., the hydro-dealkyloxycarbonylation product, 2-fluoropentan-3-one (probably formed by reaction with traces of HCl from the solvent), could be detected in an NMR sample: ^{19}F-NMR: − 184.6 (*dq*, *J*(F,H) = 46.9, 23.5).

Phenyl 2-Fluoro-2-methyl-3-oxopentanoate (**32F**). GC (*β-DEX*, 132°): t_R(minor) 23.8, t_R(major) 24.4 min. R_f (^{t}BuOMe /hexane 1 : 10) 0.35. $[\alpha]_D = +17.8 \pm 0.1$ (*c* = 0.64, MeOH; 88.2% ee). ^{1}H-NMR (300 MHz): 1.16 (A_3 of A_3CD, *ψ-t*, *J* = 7.2, 3 H); 1.84 (*d*, *J*(F,H) = 22.3, 3 H); 2.83 (*CD* of A_3CD, *ψ-qd*, *J* = 7.2, 2.5, 2 H); 7.07 – 7.13 (*m*, 2 H); 7.23 – 7.30 (*m*, 1 H); 7.36 – 7.43 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 7.2 (Me); 20.3 (*d*, *J*(F,C) = 22.8, Me); 30.8 (CH_2); 97.8 (*d*, *J*(F,C) = 195.4, C); 121.1 (CH); 126.7 (CH); 129.8 (CH); 150.2 (C); 165.7 (*d*, *J*(F,C) = 25.9, CO); 205.2 (*d*, *J*(F,C) = 27.2, CO). ^{19}F-NMR (282 MHz): − 159.6 (*qt*, *J*(F,H) = 22.3, 3.0). EI-MS: 224 (11, M^+), 57 (100). Anal. calc. for $C_{12}H_{13}FO_3$ (224.23): C 64.28, H 5.84; found: C 64.37, H 5.82.

4-Methoxyphenyl 2-Fluoro-2-methyl-3-oxopentanoate (**33F**). GC (*β-DEX*, 140°): t_R(minor) 58.2, t_R(major) 59.2 min. R_f (^{t}BuOMe/hexane 1 : 5) 0.28. ^{1}H-NMR (250 MHz): 1.16 (A_3 of A_3CD, *ψ-t*, *J* = 7.1, 3 H); 1.82 (*d*, *J*(F,H) = 22.3, 3 H); 2.82 (*CD* of A_3CD, *ψ-qd*, *J* = 7.1, 2.5, 2 H); 3.80 (*s*, 3 H); 6.87 – 6.91 (*m*, 2 H); 7.01 – 7.04 (*m*, 2 H). ^{13}C-NMR (62.9 MHz): 7.2 (Me); 20.3 (*d*, *J*(F,C) = 22.2, Me); 30.8 (CH_2); 55.7 (Me); 97.9 (*d*, *J*(F,C) = 194.8, CF); 114.7 (CH); 121.9 (CH); 143.7 (C); 157.9 (C); 166.0 (*d*, *J*(F,C) = 25.7, CO); 205.2 (*d*, *J*(F,C) = 27.2, CO). ^{19}F-NMR (282 MHz): − 159.5 (*q*, *J*(F,H) = 22.6). EI-MS: 254 (50, M^+), 57 (100). Anal. calc. for $C_{13}H_{15}FO_3$ (254.26): C 61.41, H 5.95; found: C 61.36, H 5.89.

*2,6-Di-(*tert*-butyl)-4-methylphenyl 2-Fluoro-2-methyl-3-oxopentanoate* (**34F**). The product used for analysis was exceptionally obtained using a catalyst derived from (*S*,*S*)-configured (nap-1)-TADDOL. HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 99.5 : 0.5; 0.8 ml min^{-1}): t_R(minor) 20.6, t_R(major) 35.2 min. R_f (^{t}BuOMe/hexane 1 : 10) 0.55. $[\alpha]_D = +3.9$ (*c* = 0.79, MeOH; 45.4% ee). ^{1}H-NMR (300 MHz): 1.11 (*t*, *J* = 7.1, 3 H); 1.24 (*s*, 9 H); 1.31 (*s*, 9 H); 1.85 (*d*, *J*(F,H) = 22.2, 3 H); 2.30 (*t*, *J* = 0.6, 3 H); 2.77 – 3.05 (*m*, 2 H); 7.11 (*q*, *J* = 0.6, 2 H). ^{13}C-NMR (75.5 MHz): 6.8 (*d*, *J*(F,C) = 2, Me); 21.6 (*d*, *J*(F,C) = 23, Me); 31.2 (Me); 31.2 (Me); 31.2 (Me); 31.6 (CH_2); 35.2 (C); 35.2 (C); 98.9 (*d*, *J*(F,C) = 198, CF); 127.2 (CH); 127.2 (CH); 135.2 (C); 141.9 (C); 141.9 (C); 146.0 (C); 166.5 (*d*, *J*(F,C) = 24, CO); 205.5 (*d*, *J*(F,C) = 28, CO). ^{19}F-NMR (188.3 MHz): − 158.5 (*qdd*, *J*(F,H) = 22.2, 3.1, 3.0). ESI-MS: 368.35 ($[M + NH_4]^+$). Anal. calc. for $C_{21}H_{31}FO_3$ (350.47): C 71.97, H 8.92; found: C 72.14, H 8.79.

d) *Catalytic Fluorination of α-Acyl Lactones.* Products were obtained according to *GP 1*; yields and ee values are collected in *Table 4*.

*3-Benzoyl-3-fluoro-3,4,5,6-tetrahydro-2*H*-pyran-2-one* (**35F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 90:10; 0.5 ml min^{-1}): t_R(major) 20.7, t_R(minor) 23.3 min. ^{1}H-NMR (300 MHz): 2.10–2.19 (*m*, 2 H); 2.33–2.45 (*m*, 1 H); 2.76–2.92 (*m*, 1 H); 4.52 (*t*, *J* = 6, 2 H); 7.61–7.66 (*m*, 1 H); 7.47–7.52 (*m*, 2 H); 8.11–8.14 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 19.8 (*d*, *J*(F,C) = 5.3, CH_2); 30.3 (*d*, *J*(F,C) = 23.4, CH_2); 69.5 (CH_2); 95.7 (*d*, *J*(F,C) = 196.2, CF); 128.0 (CH); 130.0 (*d*, *J*(F,C) = 7.5, CH) 133.0 (*d*, *J*(F,C) = 7.5, C); 133.9 (CH); 165.3 (*d*, *J*(F,C) = 23.1, CO); 194.5 (*d*, *J*(F,C) = 26.5, CO). ^{19}F-NMR (282 MHz): −146.18 (*dd*, *J*(F,H) = 22.5, 16.9). EI-MS: 222 (0.3, M^+), 105 (100). Anal. calc. for $C_{12}H_{11}FO_3$ (222.21): C 64.86, H 4.99; found: C 64.98, H 5.08.

*3-Fluoro-3,4,5,6-tetrahydro-3-(2-phenylacetyl)-2*H*-pyran-2-one* (**36F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 95:5; 0.5 ml min^{-1}): t_R(major) 37.5, t_R(minor) 46.3 min. ^{1}H-NMR (300 MHz): 1.93–2.01 (*m*, 1 H); 2.54–2.64 (*m*, 3 H); 2.75–2.82 (*m*, 2 H); 3.02–3.08 (*m*, 2 H); 7.21–7.26 (*m*, 3 H); 7.92–7.98 (*m*, 1 H); 7.99–8.03 (*m*, 1 H). ^{13}C-NMR (62.9 MHz): 19.8 (*d*, *J*(F,C) = 3.3, CH_2) 29.8 (*d*, *J*(F,C) = 22.5, CH_2); 44.5 (CH_2); 70.3 (CH_2); 95.6 (*d*, *J*(F,C) = 195.2, CF); 127.3 (CH); 128.6 (CH); 131.4 (CH); 133.1 (*d*, *J*(F,C) = 1.8, C); 164.6 (*d*, *J*(F,C) = 23.4, CO); 203.7 (*d*, *J*(F,C) = 29.2, CO). ^{19}F-NMR (282 MHz): −151.68 to −151.52 (*m*). Anal. calc. for $C_{13}H_{13}FO_3$ (236.24): C 66.09, H 5.55; found: C 66.34, H 5.80.

*3-Benzoyl-3-fluoro-4,5-dihydrofuran-2(3*H*)-one* (**37F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 99.5:0.5; 0.5 ml min^{-1}): t_R(minor) 57.5, t_R(major) 60.5 min. ^{1}H-NMR (300 MHz): 2.68–2.83 (*m*, 1 H); 3.06–3.16 (*m*, 1 H); 4.49–4.60 (*m*, 2 H) 7.50–7.56 (*m*, 2 H); 7.63–7.69 (*m*, 1 H); 8.17–8.22 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 33.5 (*d*, *J*(F,C) = 22, CH_2); 65.5 (*d*, *J*(F,C) = 5.4, CH_2); 96.7 (*d*, *J*(F,C) = 208.4, CF); 128.3 (CH); 130.0 (*d*, *J*(F,C) = 7.5, CH); 134.2 (C); 136.3 (CH); 169.4 (*d*, *J*(F,C) = 19.3, CO); 193.5 (*d*, *J*(F,C) = 30.1, CO). ^{19}F-NMR (282 MHz): −157.38 (*dd*, *J*(F,H) = 22.6, 8.5). EI-MS: 208 (1.5, M^+), 105 (100). Anal. calc. for $C_{11}H_9FO_3$ (208.19): C 63.46, H 4.36; found: C 63.39, H 4.46.

*3-Fluoro-4,5-dihydro-3-(2-phenylacetyl)furan-2(3*H*)-one* (**38F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 90:10; 0.5 ml min^{-1}): t_R(minor) 23.9, t_R(major) 28.0 min. ^{1}H-NMR (300 MHz): 2.57–2.63 (*m*, 1 H) 2.75–2.82 (*m*, 1 H); 4.09–4.14 (*m*, 2 H); 4.37–4.51 (*m*, 2 H); 7.19–7.38 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 32.6 (*d*, *J*(F,C) = 20.9, CH_2); 44.8 (CH_2); 65.7 (*d*, *J*(F,C) = 4.5, CH_2); 96.5 (*d*, *J*(F,C) = 205.4, CF); 127.5 (CH); 128.7 (CH); 129.8 (CH); 131.6 (*d*, *J*(F,C) = 1.5, C); 169.0 (*d*, *J*(F,C) = 25.3, CO); 202.7 (*d*, *J*(F,C) = 30, CO). ^{19}F-NMR (282 MHz): −164.43 to −164.58 (*m*). EI-MS: 222 (25, M^+), 91 (100). Anal. calc. for $C_{12}H_{11}FO_3$ (222.21): C 64.86; H 4.99; found: C 64.67, H 5.20.

*3-(2,2-Diphenylacetyl)-3-fluoro-4,5-dihydrofuran-2(3*H*)-one* (**39F**). HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 95:5; 0.5 ml min^{-1}): t_R 45.5/46.9 min; incomplete separation. ^{1}H-NMR (300 MHz): 2.47–2.63 (*m*, 1 H); 2.75–2.82 (*m*, 1 H); 4.14 (*d*, *J* = 3.8, 1 H); 4.37–4.51 (*m*, 2 H); 7.19–7.48 (*m*, 10 H). ^{13}C-NMR (62.9 MHz): 33.4 (*d*, *J*(F,C) = 20.7, CH_2); 58.9 (CH); 65.6 (*d*, *J*(F,C) = 4.4, CH_2); 96.6 (*d*, *J*(F,C) = 207.5, CF); 127.5 (CH); 127.9 (CH); 128.5 (CH); 128.9 (CH); 129.1 (CH); 129.2 (CH); 135.6 (C); 136.9 (C); 164.6 (CO); 203.5 (*d*, *J*(F,C) = 29.5, CO). ^{19}F-NMR (282 MHz): −164.43 to −164.58 (*m*). EI-MS: 298 (3, M^+), 167 (100). Anal. calc. for $C_{18}H_{15}FO_3$ (298.10): C 72.47, H 5.07; found: C 71.97, H 5.06.

7. *Double Stereochemical Differentiation Studies with Enantiomerically Pure β-Keto Esters.* Products were obtained according to *GP 1*; yields and de values (determined by ^{19}F-NMR) are given in *Table 5*.

(3β)-Cholest-5-en-3-yl 2-Fluoro-2-methyl-3-oxobutanoate (**40F**). Prepared according to *GP1*. Colorless crystalline solid. The reactions were performed with added CH_2Cl_2 (2 ml) to enhance the solubility of the substrate. The F-TEDA is only partially dissolved under these conditions (suspension). R_f (^{t}BuOMe/hexane 1:10) 0.45. M.p. 151.5–152.5°. ^{1}H-NMR (300 MHz): 0.67 (*s*, 3 H); 0.86 (*d*, *J* = 6.6, 3 H); 0.87 (*d*, *J* = 6.7, 3 H); 0.91 (*d*, *J* = 6.6, 3 H); 0.95–1.67 (*m*, 21 H); 1.02 (*s*, 3 H); 1.67 (*d*, *J*(F,H) = 22.2, 3 H); 1.76–2.07 (*m*, 5 H); 2.32 (*d*, *J*(F,H) = 4.5, 3 H); 2.29–2.39 (*m*, 2 H); 4.64–4.78 (*m*, 1 H); 5.38 (*d*, *J ca.* 5, 1 H). ^{13}C-NMR (75.5 MHz): 11.8 (Me); 18.7 (Me); 19.3 (Me); 19.7 (*d*, *J*(F,C) = 23, *Me*CF); 21.0 (CH_2); 22.5 (Me); 22.8 (Me); 23.8 (CH_2); 24.3 (CH_2); 24.9 (CH); 27.4 (CH_2); 28.0 (Me); 28.2 (CH_2); 31.8 (CH); 31.9 (CH_2); 35.8 (CH); 36.2 (CH_2); 36.5 (C); 36.8 (CH_2); 37.6 (CH_2); 39.5 (CH_2); 39.7 (CH_2); 42.3 (C); 49.9 (CH); 56.1 (CH); 56.6 (CH); 76.5 (CH); 97.6 (*d*, *J*(F,C) = 193, CF); 123.2 (CH); 138.9 (C); 166.3 (*d*, *J*(F,C) = 25, CO); 202.2 (*d*, *J*(F,C) = 28, CO). ^{19}F-NMR (188.3 MHz): −157.3 (*qq*, *J*(F,H) = 22.1, 4.4); ^{19}F{^{1}H}-NMR (188.3 MHz): −157.202 (*s*, 80%); −157.211 (*s*, 20%). HR-MALDI-MS: 525.372 ([*M* + Na]$^+$; calc. 525.371). Anal. calc. for $C_{32}H_{51}FO_3$ (502.74): C 76.45, H 10.22; found: C 76.41, H 10.21.

Nopyl 2-Fluoro-2-methyl-3-oxo-butanoate (=*2-[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]ethyl 2-fluoro-3-oxobutanoate*; **41F**). The product was not isolated. Spectral data (^{19}F-NMR) was

obtained from crude mixtures after aqueous workup. $^{19}F\{^1H\}$-NMR (188.3 MHz): −157.08 (*s*, 75%), −157.10 (*s*, 25%).

*(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-Fluoro-2-methyl-3-oxobutanoate* (**42F**). R_f (^{t}BuOMe/hexane 1:5) 0.65. ^{1}H-NMR (300 MHz): (major diastereoisomer): 0.75 (*d*, *J* = 7.0, 3 H); 0.80–0.96 (*m*, 1 H); 0.89 (*d*, *J* = 6.9, 3 H); 0.91 (*d*, *J ca.* 6, 3 H); 0.96–1.14 (*m*, 2 H); 1.39–1.59 (*m*, 2 H); 1.67 (*d*, *J*(F,H) = 22.0, 3 H); 1.61–1.74 (*m*, 2 H); 1.73–1.86 (*m*, 1 H); 1.92–2.02 (*m*, 1 H); 2.31 (*d*, *J* = 4.4, 3 H); 4.71–4.62 (*m*, 1 H); (minor diastereoisomer; selected signals): 0.74 (*d*, *J* = 7.0, 3 H); 1.67 (*d*, *J*(F,H) = 22.0, 3 H). ^{13}C-NMR (75.5 MHz): (major diastereoisomer): 15.9 (Me); 19.6 (*d*, *J*(F,C) = 23, Me); 20.7 (Me); 21.9 (Me); 23.2 (CH_2); 24.9 (CH); 26.2 (CH); 31.3 (Me); 34.0 (CH_2); 40.2 (CH_2); 46.7 (CH); 76.9 (CH); 97.5 (*d*, *J*(F,C) = 193, CF); 166.5 (*d*, *J*(F,C) = 26, CO); 202.0 (*d*, *J*(F,C) = 28, CO); (minor diastereoisomer; selected signals): 16.0 (Me); 19.6 (*d*, *J*(F,C) = 23, Me); 20.6 (Me); 23.2 (CH_2); 24.9 (CH); 26.1 (Me); 34.0 (CH_2); 40.3 (CH_2); 77.0 (CH); 97.7 (*d*, *J*(F,C) = 193, CF). $^{19}F\{^1H\}$-NMR (188.3 MHz): −156.94 (*s*, major); −157.08 (*s*, minor). ESI-MS: 290.3 ($[M+NH_4]^+$). Anal. calc. for $C_{15}H_{25}FO_3$ (272.356): C 66.15, H 9.25; found: C 66.02, H 9.20.

*(1*S*,2*R*,5*S*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-Fluoro-2-methyl-3-oxobutanoate* (**43F**). Enantiomeric to **42F**, product not isolated; spectra recorded after aqueous workup of the crude mixture. $^{19}F\{^1H\}$-NMR (188.3 MHz): −156.94 (*s*, minor); −157.08 (*s*, major).

*(1*R*)-2-Methoxy-2-oxo-1-phenylethyl 2-Fluoro-2-methyl-3-oxopentanoate* (**44F**). a) *According to* GP 1 *from* **44** *with* **K1**. After CC, a colorless oil (53 mg, 59%) with a dr of 13:87 was obtained.

b) *By Fluorination of the Na-Enolate.* To compound **44** (278.3 mg, 1 mmol) in sat. F-TEDA (7.5 ml in MeCN, 1.1 mmol) were added NaH (27 mg, 1.1 mmol) and *tert*-amyl alcohol (0.2 ml). Bubbles developed, and the suspension went slowly into soln. After 1 h, the reaction was not yet finished, thus two additional portions of NaH (total 20 mg) and finally some additional F-TEDA soln. (2.5 ml) were added. TLC indicated almost complete conversion and the generation of a side product. After workup with H_2O/^{t}BuOMe, the org. phase was filtered over little Al_2O_3 and evaporated. CC (^{t}BuOMe/hexane 1:10) gave 178 mg (*ca.* 60%) of a colorless oil, which consisted, according to ^{1}H-NMR, of a mixture of the diastereoisomers of **44F**, and, in addition, cleavage products ((1*R*)-2-methoxy-2-oxo-1-phenylethyl 2-fluoropropanoate) in a ratio of 6.2:1 (^{19}F-NMR). According to HPLC and ^{19}F-NMR, the product diastereoisomers were present in a dr of 66:34, and the cleavage products in a dr of 56:44. R_f (^{t}BuOMe/hexane 1:5) 0.27. ^{1}H-NMR (200 MHz): (major diastereoisomer): 1.09 (*t*, *J* = 7.2, 3 H); 1.79 (*d*, *J*(F,H) = 22.1, 3 H); 2.59–2.93 (*m*, 2 H); 3.72 (*s*, 3 H); 6.00 (*s*, 1 H); 7.34–7.51 (*m*, 5 H); (minor diastereoisomer): 1.12 (*t*, *J* = 7.2, 3 H); 1.74 (*d*, *J*(F,H) = 22.1, 3 H); 2.59–2.93 (*m*, 2 H); 3.72 (*s*, 3 H); 5.96 (*s*, 1 H); 7.34–7.51 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): (major diastereoisomer) 7.0 (*d*, *J*(F,C) = 2); 20.1 (*d*, *J*(F,C) = 22); 30.6; 52.8; 75.4; 97.7 (*d*, *J*(F,C) = 196); 127.4; 128.9; 129.5; 132.6; 166.4 (*d*, *J*(F,C) = 26); 168.1; 203.9 (*d*, *J*(F,C) = 27). ^{19}F-NMR (188.3 MHz): −160.1 (*qt*, *J*(F,H) = 22.1, 3.2, minor); −160.4 (*qt*, *J*(F,H) = 22.1, 2.9, major). $^{19}F\{^1H\}$-NMR (188.3 MHz): −160.1 (*s*, minor); −160.4 (*s*, major). ESI-MS: 314.3 (100, $[M+NH_4]^+$), 297.2 (8, $[M+H]^+$). Anal. calc. for $C_{15}H_{17}FO_5$ (296.29): C 60.81, H 5.78; found: C 60.95, H 5.70.

*Data of (1*R*)-2-Methoxy-2-oxo-1-phenylethyl 2-Fluoropropanoate:* ^{1}H-NMR (200 MHz): (2 diastereoisomers): 1.61 (*dd*, *J* = 15.3, 6.9, MeCF); 1.73 (*dd*, *J* = 15.4, 6.9, MeCF); 3.74 (*s*, MeO); 5.13 (*dq*, *J* = 48.4, 6.9, CHF); 5.17 (*dq*, *J* = 48.4, 6.9, CHF); 6.03 (*s*, CHPh); 7.34–7.51 (*m*, 5 arom. H). $^{19}F\{^1H\}$-NMR (188.3 MHz): −185.5 (*s*, 56%); −185.6 (*s*, 44%).

8. *Catalytic Fluorination of β-Keto Thioesters.* Products were obtained according to *GP 1*; yields and ee values are compiled in *Table 6*.

S-*Ethyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanethioate* (**45F**). GC (*γ-DEX*, 100°): t_R(minor) 404, t_R(major) 411 min. R_f (^{t}BuOMe/hexane 1:10) 0.37. ^{1}H-NMR (300 MHz): 1.28 (*t*, *J* = 7.4, 3 H); 1.86 (*d*, *J*(F,H) = 22.8, 3 H); 2.96 (*q*, *J* = 7.4, 2 H); 7.42–7.49 (*m*, 2 H); 7.56–7.60 (*m*, 1 H); 8.03–8.08 (*d*, *J* = 8.3, 2 H). ^{13}C-NMR (75.5 MHz): 14.4 (Me); 22.4 (*d*, *J*(F,C) = 23.1, Me); 29.8 (CH_2); 103.6 (*d*, *J*(F,C) = 199.5, C); 128.7 (CH); 130.1 (*d*, *J*(F,C) = 5.9, CH); 133.7 (*d*, *J*(F,C) = 3.6, C); 134.0 (CH); 192.0 (*d*, *J*(F,C) = 25.3, CO); 197.3 (*d*, *J*(F,C) = 29.5, CO). ^{19}F-NMR (282 MHz): −150.1 (*qt*, *J*(F,H) = 22.6, 1.6). EI-MS: 240 (1.8, M^+), 105 (100). Anal. calc. for $C_{12}H_{13}FO_2S$ (240.30): C 59.98, H 5.45; found: C 61.31, H 5.34.

An unidentified impurity could not be removed by CC.

S-*Benzyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanethioate* (**46F**). HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 84:16; 0.4 ml min^{-1}): t_R(major) 40.1, t_R(minor) 43.4 min. R_f (^{t}BuOMe/hexane 1:10) 0.41. ^{1}H-NMR (300 MHz): 1.87 (*d*, *J*(F,H) = 22.8, 3 H); 4.15 (*d*, *J* = 13.9, 1 H); 4.22 (*d*, *J* = 13.9, 1 H); 7.26 (*m*, 5 H); 7.39–7.46 (*m*, 2 H); 7.54–7.61 (*m*, 1 H); 7.99–8.04 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 22.3 (*d*, *J*(F,C) = 23.2, Me); 33.1 (*d*, *J*(F,C) = 3.8, CH_2); 103.5 (*d*, *J*(F,C) = 199.5, CF); 127.8 (CH); 128.7 (*d*, *J*(F,C) = 0.8, CH); 128.9 (CH); 129.0 (CH); 130.0 (*d*, *J*(F,C) = 5.3, CH); 133.6 (*d*, *J*(F,C) = 3.7, C); 134.0 (CH); 136.5 (C, 10); 191.8 (*d*, *J*(F,C) = 25.0, CO); 196.8 (*d*, *J*(F,C) = 29.9, CO). ^{19}F-NMR (282 MHz): −150.1 (*qt*, *J*(F,H) = 22.8, 1.7). EI-MS: 302 (7, M^+), 105 (100). Anal. calc. for $C_{17}H_{15}FO_2S$ (302.37): C 67.53, H 5.00; found: C 67.59, H 5.15.

S-*Benzyl 2-Fluoro-2-methyl-3-oxobutanethioate* (**47F**). HPLC (*Chiralcel OJ;* hexane/^{i}PrOH = 85:15; 0.5 ml min^{-1}): t_R(minor) 27.6, t_R(major) 29.9 min. R_f (^{t}BuOMe/hexane 1:10) 0.31. ^{1}H-NMR (300 MHz): 1.69 (*d*, *J*(F,H) = 22.1, 3 H); 2.29 (*d*, *J*(F,H) = 4.4, 3 H); 4.15 (*s*, 2 H); 7.26–7.32 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 20.9 (*d*, *J*(F,C) = 22.2, Me); 25.3 (Me); 33.3 (*d*, *J*(F,C) = 4.4, CH_2); 103.9 (*d*, *J*(F,C) = 198.0, C); 127.8 (CH); 128.9 (CH); 129.0 (CH); 136.4 (C); 195.5 (*d*, *J*(F,C) = 31.3, CO); 200.5 (*d*, *J*(F,C) = 27.7, CO). ^{19}F-NMR (282 MHz): −156.1 (*qq*, *J*(F,H) = 22.1, 4.4). EI-MS: 240 (4, M^+), 91 (100). Anal. calc. for $C_{12}H_{13}FO_2S$ (240.30): C 59.98, H 5.45; found: C 59.85, H 5.32.

S-*Phenyl 2-Fluoro-2-methyl-3-oxopentanethioate* (**48F**). GC (*β-DEX*, 140°): t_R(minor) 49.2, t_R(major) 50.3 min. R_f (^{t}BuOMe/hexane 1:10) 0.39. ^{1}H-NMR (300 MHz): 1.11 (*t*, *J* = 7.3, 3 H); 1.74 (*d*, *J*(F,H) = 22.4, 3 H); 2.63–2.90 (*m*, 2 H); 7.38–7.46 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 7.3 (Me); 21.2 (*d*, *J*(F,C) = 22.2, Me); 31.1 (CH_2); 104.3 (*d*, *J*(F,C) = 198.4, C); 125.7 (*d*, *J*(F,C) = 6.4, C); 129.6 (CH); 130.1 (CH); 134.9 (CH); 194.5 (*d*, *J*(F,C) = 31.4, CO); 202.9 (*d*, *J*(F,C) = 25.8, CO). ^{19}F-NMR (282 MHz): −157.9 (*qt*, *J*(F,H) = 22.4, 3.1). EI-MS: 240 (17, M^+), 184 (100). Anal. calc. for $C_{12}H_{13}FO_2S$ (240.30): C 59.98, H 5.45; found: C 59.91, H 5.47.

9. *Catalytic Fluorination of β-Keto Amides.* Products obtained according to *GP 1*; for yields and ee values, see *Table 7*.

N,N-*Dibenzyl-2-fluoro-2-methyl-3-oxopentanamide* (**49F**). Prepared according to *GP 1* from **49** with **K2**, reaction time < 4 h. The product contained a minor impurity, presumably 2-Cl product. HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 80:20; 0.7 ml min^{-1}): t_R(major) 12.0, t_R(minor) 18.7 min. R_f (^{t}BuOMe/hexane 1:2) 0.55. ^{1}H-NMR (200 MHz): 1.07 (*t*, *J* = 7.2, 3 H); 1.82 (*d*, *J*(F,H) = 23.0, 3 H); 2.66 (*ψ-qd*, *J* = 7.2, 2.0, 2 H); 4.27 (*d*, *J* = 14.7, 1 H); 4.32 (*d*, *J* = 16.2, 1 H); 4.51 (*d*, *J* = 16.2, 1 H); 4.69 (*d*, *J* = 14.7, 1 H); 7.09–7.46 (*m*, 10 H). ^{13}C-NMR (75.5 MHz): 7.3 (Me); 21.4 (*d*, *J*(F,C) = 24, Me); 29.9 (CH_2); 48.1 (CH_2); 49.6 (*d*, *J*(F,C) = 10, CH_2); 100.0 (*d*, *J*(F,C) = 197, C); 127.2–128.8 (several CH); 135.6 (C); 136.2 (C); 167.2 (*d*, *J*(F,C) = 21, CO); 204.8 (*d*, *J*(F,C) = 23, CO). ^{19}F-NMR (188 MHz): −152.1 (*q*, *J*(F,H) = 23.0).

2-Fluoro-2-methyl-3-oxo-N,N-*diphenylpentanamide* (**50F**). Prepared according to *GP 1* from **50** with **K2**; reaction time < 4 h. CC (^{t}BuOMe/hexane 1:10) gave 56 mg (75%) of colorless oil. HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 70:30; 1.0 ml min^{-1}): t_R(major) 14.6, t_R(minor) 26.4 min. R_f (^{t}BuOMe/hexane 1:2) 0.44. ^{1}H-NMR (200 MHz): 0.83 (*t*, *J* = 7.1, 3 H); 1.68 (*d*, *J*(F,H) = 23.0, 3 H); 2.24 (*dqd*, *J* = 19.7, 7.1, *J*(F,H) = 2.0, 1 H); 2.38 (*dqd*, *J* = 19.7, 7.2, *J*(F,H) = 3.8, 1 H); 7.20–7.44 (br. *m*, 10 H). ^{13}C-NMR (75.5 MHz): 6.7 (*d*, *J*(F,C) = 2, Me); 22.4 (*d*, *J*(F,C) = 24, Me); 29.3 (CH_2); 99.7 (*d*, *J*(F,C) = 198, CF); 125.8–132.6 (br. *m*, CH); 129.1 (CH); 166.4 (*d*, *J*(F,C) = 21, CO); 208.3 (*d*, *J*(F,C) = 26, CO). ^{19}F-NMR (188.3 MHz): −149.1 (br. *q*, *J*(F,H) = 23.1). FAB-MS: 300 (100, $[M+H]^+$), 196 (21). Anal. calc. for $C_{18}H_{18}FNO_2$ (299.34): C 72.22, H 6.06, N 4.68; found: C 72.13, H 5.91, N 4.68.

10. *Catalytic Fluorination of 1,3-Diketones.* Products were obtained according to *GP 1*; for yields and ee values, see *Tables 8* and *9*.

2-Benzoyl-2-fluorocyclopentanone (**51F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 99.2:0.8; 0.5 ml min^{-1}): t_R20.5, 22.2 min. ^{1}H-NMR (300 MHz): 2.12–2.21 (*m*, 2 H); 2.25–2.42 (*m*, 1 H); 2.48–2.56 (*m*, 2 H); 2.74–2.87 (*m*, 1 H); 7.44–7.50 (*m*, 2 H); 7.56–7.62 (*m*, 1 H); 8.05–8.10 (*m*, 2 H). ^{13}C-NMR (62.9 MHz): 17.4 (CH_2); 34.3 (*d*, *J*(F,C) = 4.6, CH_2); 37.5 (CH_2); 102.0 (*d*, *J*(F,C) = 186.4, CF); 128.3 (CH); 129.1 (*d*, *J*(F,C) = 6.5, CH); 130.0 (CH); 134.3 (*d*, *J*(F,C) = 4.7, C); 168.2 (*d*, *J*(F,C) = 18.7, CO); 210.4 (*d*, *J*(F,C) = 29.1). ^{19}F-NMR (282 MHz): −157.03 (*dd*, *J*(F,H) = 22.6, 14.1). EI-MS: 206 (2, M^+), 105 (100).

2-Benzoyl-2-fluorocyclohexanone (**52F**). HPLC (*Chiralcel OD-H*; hexane/^{i}PrOH 99.2:0.8; 0.5 ml min^{-1}): t_R(major) 17.6, t_R(minor) 20.1 min. ^{1}H-NMR (250 MHz): 1.94–2.21 (*m*, 5 H); 3.79–3.88 (*m*,

1 H); 2.60–2.71 (*m*, 2 H); 7.3–7.4 (*m*, 2 H); 7.5–7.6 (*m*, 1 H); 7.9–8.2 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 21.6 (*d*, *J*(F,C) = 7.5, CH_2); 26.9 (CH_2); 37.0 (*d*, *J*(F,C) = 21.9, CH_2); 40.1 (CH_2); 103.8 (*d*, *J*(F,C) = 199.2, CF); 128.2 (CH); 129.7 (*d*, *J*(F,C) = 7.9, CH); 133.5 (CH); 133.9 (*d*, *J*(F,C) = 3.6, C); 194.5 (*d*, *J*(F,C) = 25.3, CO); 203.9 (*d*, *J*(F,C) = 18.9, CO). ^{19}F-NMR (282 MHz): −151.42 (*t*, *J*(F,H) = 12.5). EI-MS: 220 (1.4, M^+), 105 (100), 77 (29). Anal. calc. for $C_{13}H_{13}FO_2$ (220.09): C 70.90, H 5.95; found: C 70.99, H 5.93.

2-Fluoro-2-methyl-1-phenylbutane-1,3-dione (**53F**). HPLC (*Chiralcel OJ;* hexane/^{i}PrOH 96 : 4; 0.5 ml min^{-1}): t_R(major) 24.7, t_R(minor) 25.4 min. ^{1}H-NMR (250 MHz): 1.81 (*d*, *J* = 7.0, 3 H); 2.34 (*d*, *J*(F,H) = 3.2, 3 H); 7.43–7.49 (*m*, 2 H); 7.57–7.59 (*m*, 1 H); 7.95–8.01 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 20.4 (*d*, *J*(F,C) = 22.4, Me); 24.6 (Me); 102.5 (*d*, *J*(F,C) = 194.0, CF); 128.4 (CH); 129.3 (*d*, *J*(F,C) = 5.7, CH); 133.3 (*d*, *J*(F,C) = 4.2, CH); 133.7 (CH); 193.5 (*d*, *J*(F,C) = 25.0); 202.1 (*d*, *J*(F,C) = 23.0, CO). ^{19}F-NMR (282 MHz): −152.30 (*q*, *J*(F,H) = 22.5). EI-MS: 194 (0.02, M^+), 105 (100). Anal. calc. for $C_{11}H_{11}FO_2$ (194.07): C 68.03, H 5.71; found: C 68.07, H 5.88.

*2-Acetyl-2-fluoro-3,4-dihydronaphthalen-1(2*H*)-one* (**54F**). HPLC (*Chiralcel OD-H;* hexane/^{i}PrOH 98 : 2; 0.5 ml min^{-1}): t_R 15.3, 16.3 min. ^{1}H-NMR (300 MHz): 2.42 (*d*, *J*(F,H) = 9, 3 H); 2.41–2.48 (*m*, 1 H); 2.58–2.66 (*m*, 1 H); 3.13–3.22 (*m*, 2 H); 7.26 (*d*, *J* = 8.0, 1 H); 7.36 (*t*, *J* = 7.5, 1 H); 7.55 (*t*, *J* = 7.5, 1 H); 8.04 (*d*, *J* = 8.0, 1 H). ^{13}C-NMR (75.5 MHz): 24.6 (*d*, *J*(F,C) = 8.3, CH_2); 26.2 (CH_2); 30.5 (*d*, *J*(F,C) = 21.9, CH_2); 97.5 (*d*, *J*(F,C) = 193.1, CF); 126.9 (CH); 128.5 (CH); 127.9 (CH); 130.5 (C); 134.3 (CH); 143.3 (C); 190.0 (*d*, *J*(F,C) = 7.6, CO); 205.3 (*d*, *J*(F,C) = 27.0, CO). ^{19}F-NMR (282 MHz): −160.86 (*t*, *J*(F,H) = 14.1). EI-MS: 206 (M^+). Anal. calc. for $C_{12}H_{11}FO_2$ (206.21): C 69.89, H 5.38; found: C 70.03, H 5.53.

*2-Benzoyl-2-fluoro-3,4-dihydronaphthalen-1(2*H*)-one* (**55F**). ^{1}H-NMR (300 MHz): 2.61–2.72 (*m*, 1 H); 2.89–2.99 (*m*, 1 H); 3.19–3.55 (*m*, 2 H); 7.28–8.13 (*m*, 9 H). ^{13}C-NMR (75.5 MHz): 25.1 (*d*, *J*(F,C) = 15.1, CH_2); 32.4 (*d*, *J*(F,C) = 22.6, CH_2); 98.5 (*d*, *J*(F,C) = 196.4, CF); 126.9 (CH); 128.0 (CH); 128.2 (CH); 128.5 (CH); 129.7 (*d*, *J*(F,C) = 7.5, CH); 130.8 (C); 133.5 (CH); 134.0 (C); 134.2 (CH); 142.8 (C); 190.7 (*d*, *J*(F,C) = 17.3, CO); 196.2 (*d*, *J*(F,C) = 27.1, CO). ^{19}F-NMR (282 MHz): −157.53 (*dd*, *J*(F,H) = 16.9, 11.3). EI-MS: 268 (1, M^+), 105 (100). Anal. calc. for $C_{17}H_{13}FO_2$ (268.28): C 76.11, H 4.88; found: C 75.96, H 5.02.

2-Benzoyl-2-fluorocyclododecanone (**56F**). Colorless solid. HPLC (*Chiralcel OJ*; hexane/^{i}PrOH 96 : 4; 1.0 ml min^{-1}): t_R(minor) 6.4, t_R(major) 8.6 min. R_f (^{t}BuOMe/hexane 1 : 5) 0.60. M.p. 86.5–87.5° (2% ee); 79.4–88.3° (18% ee). $[\alpha]_D$ = −40.3 (*c* = 1.07, CH_2Cl_2; 18.3% ee). ^{1}H-NMR (300 MHz): 1.10–1.63 (*m*, 15 H); 1.97–2.16 (*m*, 3 H); 2.63 (*dddd*, *J* = 37.9, 15.1, 12.1, 2.8, 1 H); 2.96–3.10 (*m*, 1 H); 7.38–7.47 (*m*, 2 H); 7.53–7.60 (*m*, 1 H); 7.91–7.98 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 18.4 (CH_2); 18.4 (CH_2); 21.1 (*d*, *J*(F,C) = 1, CH_2); 22.2 (CH_2); 22.3 (CH_2); 22.6 (CH_2); 23.6 (CH_2); 26.2 (CH_2); 32.3 (*d*, *J*(F,C) = 22, CH_2); 34.3 (CH_2); 106.6 (*d*, *J*(F,C) = 200, C); 128.6 (CH); 129.7 (*d*, *J*(F,C) = 6, CH); 133.9 (CH); 194.3 (*d*, *J*(F,C) = 26, CO); 203.8 (*d*, *J*(F,C) = 19, CO); C_{ipso} not detected. ^{19}F-NMR (282 MHz): −162.8 (br. *d*, *J*(F,H) = 38). EI-MS: 304 (1, M^+), 105 (100). Anal. calc. for $C_{19}H_{25}FO_2$ (304.40): C 74.97, H 8.28; found: C 74.85, H 8.45.

11. *Selected Asymmetric Catalytic Chlorinations.* Products were obtained according to *GP 2*; for yields and ee values, see *Table 10*.

Ethyl 2-Chloro-2-methyl-3-oxobutanoate (**15Cl**). Prepared according to *GP 2* from **K2** (9.0 mg, 10 μmol), ethyl 2-methyl-3-oxobutanoate (30 μl, 0.21 mmol), and NCS (31.5 mg, 0.24 mmol). Reaction time to complete conversion: 15 min, ee 40%. The product was not isolated, but the mixture was directly analyzed by chiral GC (*β-DEX*, 56°): t_R(minor) 109.4, t_R(major) 111.4 min. Known compound, CAS-RN 37935-39-0.

Phenyl 2-Chloro-2-methyl-3-oxopentanoate (**32Cl**). Prepared according to *GP 2* from **K2** (19 mg, 6.1 μmol), **32** (97 mg, 0.47 mmol), and NCS (70 mg, 0.52 mmol). Reaction time: 25 min. CC (^{t}BuOMe/hexanes 1 : 15) gave 94 mg (83%) of **32Cl**. Colorless liquid. GC (*β-DEX*, 125°): t_R(minor) 70.7, t_R(major) 72.6 min. R_f (^{t}BuOMe/hexanes 1 : 10) 0.48. $[\alpha]_D$ = +15.00 ± 0.05 (*c* = 1.05, MeOH; 83.4% ee). ^{1}H-NMR (300 MHz): 1.18 (*t*, *J* = 7.2, CH_2*Me*); 1.98 (*s*, CClMe); 2.84–2.95 (*m*, C*H*$_2$Me); 7.09–7.15 (*m*, 2 arom. *ortho*-H); 7.24–7.31 (*m*, 1 arom. H); 7.37–7.45 (*m*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 8.5 (Me); 24.8 (Me); 31.2 (CH_2); 70.8 (C); 121.0 (CH); 126.7 (CH); 129.8 (CH); 150.5 (C); 167.0 (C); 202.5 (C). EI-MS: 240 (0.5, M^+), 65 (100). Anal. calc. for $C_{12}H_{13}ClO_3$ (240.69): C 59.88, H 5.44; found: C 59.91, H 5.37.

S-*Phenyl 2-Chloro-2-methyl-3-oxopentanethioate* (**48Cl**). Prepared according to *GP 2* from **K2** (13 mg, 15 μmol), **48** (67.3 mg, 0.30 mmol), and NCS (46 mg, 0.34 mmol). Reaction time: 20 min. After CC (*t*BuOMe/hexane 1:15), **48Cl** (55.2 mg, 71%) was obtained. Colorless liquid. GC (*β-DEX*, 164°): t_R(minor) 32.3, t_R(major) 33.2 min. R_f (*t*BuOMe/hexane 1:10) 0.33. ^{1}H-NMR (300 MHz): 1.13 (*q*, *J* = 7.2, *Me*CH_2); 1.91 (*s*, MeCCl); 2.60 (*dq*, *J* = 18.1, 7.2, 1 H of MeCH_2); 2.90 (*dq*, *J* = 18.1, 7.2, 1 H of MeCH_2); 7.39–7.48 (*m*, 5 arom. H). ^{13}C-NMR (75.5 MHz): 8.5 (Me); 25.3 (Me); 31.2 (CH_2); 127.0 (C); 129.6 (CH); 130.2 (CH); 134.8 (CH); 196.5 (C); 200.5 (C). EI-MS: 256 (3, M^+), 109 (100). Anal. calc. (%) for $C_{12}H_{13}ClO_2S$ (256.75): C 56.14, H 5.10; found: C 55.97, H 5.34.

2,4,6-Tris(1-methylethyl)benzyl 2-Chloro-2-methyl-3-oxopentanoate (**30Cl**). Prepared according to *GP 2* from **K2** (9.0 mg, 11 μmol), **30** (74.0 mg, 0.214 mmol), and NCS (36.1 mg, 0.270 mmol). Reaction time: 30 min. CC (*t*BuOMe/hexane 1:10) gave **30Cl** (67.0 mg, 82%). Colorless oil; ee 82 ± 3% (value less accurate due to incomplete HPLC baseline separation). HPLC (*Chiralcel OD-H*; hexane/*i*PrOH 99.9:0.1; 0.3 ml min^{-1}): t_R(major) 26.1, t_R(minor) 27.9 min; not baseline-separated. ^{1}H-NMR (300 MHz): 0.97 (*t*, *J* = 7.2, *Me*CH_2); 1.16 (*d*, *J* = 6.9, *Me*$_2$CH); 1.16 (*d*, *J* = 6.9, *Me*$_2$CH); 1.18 (*d*, *J* = 6.9, *Me*$_2$CH); 1.75 (*s*, Me–C(2)); 2.56 (*dq*, *J* = 18.3, 7.2, 1 H of CH_2(4)); 2.71 (*dq*, *J* = 18.3, 7.2, 1 H of CH_2(4)); 2.82 (*sept.*, *J* = 6.9, Me$_2$C*H*); 3.06 (*sept.*, *J* = 6.9, 2 Me$_2$C*H*); 5.24 (*d*, *J* = 12.4, 1 H of OCH_2Ar); 5.29 (*d*, *J* = 12.4, 1 H of OCH_2Ar); 6.91 (*s*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 8.3 (Me, C(5)); 24.1 (Me of ^{i}Pr); 24.5, 24.5 (2 Me of 2 ^{i}Pr); 24.8 (*Me*–C(2)); 29.6 (CH, of ^{i}Pr); 31.1 (CH_2(4)); 34.5 (CH of ^{i}Pr); 62.0 (OCH_2Ar); 70.9 (C(2)); 121.4 (C_{Ar}H); 125.2 (C_{Ar}); 149.2 (C_{Ar}); 150.3 (C_{Ar}); 168.6 (C(1)=O); 202.3 (C(3)=O). EI-MS: 380 (0.06, M^+), 216 (100). Anal. calc. for $C_{22}H_{33}ClO_3$ (380.95): C 69.36, H 8.73; found: C 69.30, H 8.92.

12. *Synthesis of Catalysis Substrates.* For enolized substrates, the enol content was determined by ^{1}H-NMR spectroscopy, and the % content of enol is given in brackets. These values are not necessarily equilibrium values, as complete keto ⇌ enol equilibration may take several days. Selected NMR signals are given for the enols.

a) *Precursors: 2-Methyl-3-oxobutanoic Acid* (**66**). Obtained by saponification of the ethyl ester [34], followed by acidification and extraction with *t*BuOMe. The substance slowly decomposed by decarboxylation, either at r.t. or 0°, and was stored at −78°. Partially decomposed samples can be purified as follows: dissolution of the sample in $NaHCO_3$ (aq.) followed by extraction with *t*BuOMe twice. The org. phases were discarded. After cooling to 5°, the aq. phase was acidified with diluted HCl (aq.) at 5° and extracted with *t*BuOMe (3×). The org. phase was dried (Na_2SO_4) and evaporated in a rotatory evaporator.

(4Z)-4-Ethylidene-3-methyloxetan-2-one (**75**). This compound was synthesized as described in [4]. Care has to be taken to allow the mixture to reach reflux temp. during the addition of propanoyl chloride. In small-scale reactions, external heating is necessary in the addition step, or the reported yields cannot be obtained.

b) *Catalysis Substrates* **1**–**56**. *Ethyl 2-Methyl-3-oxo-3-phenylpropanoate* (**1**). Synthesized by slow addition of propiophenone (40 ml, 0.30 mol) to a refluxing suspension of pure NaH (9.0 g, 0.375 mol) in *t*BuOMe (300 ml) and ET_2CO_3 (60 ml, 0.49 mol). On refluxing overnight and cooling, the Na-enolate was isolated by filtration and washing with *t*BuOMe and pentane. Acidification with AcOH in H_2O, followed by extraction (*t*BuOMe), drying (Na_2SO_4), and evaporation, yielded the raw product, which was purified by CC (*t*BuOMe/hexane 1:20) to give **1** (19.11 g, 31%). Almost colorless oil (yellow aspect). R_f (*t*BuOMe/hexane 1:5) 0.30. ^{1}H-NMR (300 MHz): 1.16 (*t*, *J* = 7.2, 3 H); 1.49 (*d*, *J* = 7.1, 3 H); 4.14 (*q*, *J* = 7.2, 2 H); 4.39 (*q*, *J* = 7.1, 1 H); 7.43–7.51 (*m*, 2 H); 7.54–7.61 (*m*, 1 H); 7.95–8.01 (*m*, 2 H); (enol, 1.8%): 1.35 (*t*, *J* = 7.1, 3 H); 1.84 (*s*, MeC=C); 4.29 (*q*, *J* = 7.2, OCH_2Me); 12.99 (*s*, OH). ^{13}C-NMR (75.5 MHz): 13.6 (Me); 13.8 (Me); 48.1 (CH); 61.1 (CH_2); 128.4 (CH); 128.5 (CH); 133.3 (CH); 135.7 (C); 170.7 (CO); 195.7 (CO). Known compound.

Methyl 2-Methyl-3-oxo-3-phenylpropanoate (**2**). To a suspension of NaH (60% in oil, 2.432 g, 56 mmol) and Me_2CO_3 (5 ml, 59.4 mmol) in *t*BuOMe (40 ml) propiophenone (4.9 ml, 37.1 mmol) were added at 0° within 45 min. After stirring at r.t. (3 d) and cooling at 0°, H_2O was added, and the mixture was acidified to pH 2 with 1M HCl. Workup with Et_2O, washing of the org. phase with H_2O and sat. NaCl, drying ($MgSO_4$), evaporation of solvents, and CC (AcOEt/hexane 1:10–4:10) gave **2** (894 mg, 13%). Oil. R_f (*t*BuOMe/hexane 1:5) 0.14. ^{1}H-NMR (250 MHz): 1.49 (*d*, *J* = 7.2, 3 H); 3.68 (*s*, 3 H); 4.40 (*q*, *J* = 7.2, 1 H); 7.43–7.51 (*m*, 2 H); 7.54–7.62 (*m*, 1 H); 7.94–8.00 (*m*, 2 H); (enol, 0.3%) 12.87 (*s*, OH).

^{13}C-NMR (62.9 MHz): 13.9 (Me); 48.1 (Me); 52.6 (CH); 128.7 (CH); 128.9 (CH); 133.6 (CH); 135.8 (C); 171.4 (CO); 195.9 (CO). Known compound, CAS No. 29540-54-3.

2-Methylbutan-2-yl 2-Methyl-3-oxo-3-phenylpropanoate (**3**). *tert*-Amyl propanoate (4.326 g, 30 mmol; obtained from *tert*-amyl alcohol, propanoyl chloride, and *N*,*N*-dimethylaniline in ^{t}BuOMe) was slowly added to a soln. of LDA (from 4.4 ml ^{i}Pr$_2$NH (31 mmol), THF (20 ml), and BuLi (15.5 ml, 2M in pentane, 31 mmol)) at $-78°$. After 1 h, PhCHO (3.29 g, 31 mmol) was added, and the mixture was stirred for 3 h. Quenching the reaction with sat. NH_4Cl (10 ml) was followed by the usual workup (^{t}BuOMe/H_2O). Oxidation of the raw product (40 ml of CH_2Cl_2, 9.70 g PCC (45 mmol), 5.0 g of finely ground molecular sieves (4 Å), and 1.0 g of finely ground AcONa), followed by filtration through Al_2O_3 and CC (^{t}BuOMe/hexane 1:15), gave **3** (4.80 g, 64%) Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.40. ^{1}H-NMR (300 MHz): 0.72 (*t*, *J* = 7.5, 3 H); 1.30 (*s*, 3 H); 1.32 (*s*, 3 H); 1.46 (*d*, *J* = 7.1, 1 H); 1.65 (ψ-*qd*, *J* = 7.6, 1.8, 2 H); 4.27 (*q*, *J* = 7.0, 1 H); 7.43–7.50 (*m*, 2 H); 7.53–7.61 (*m*, 1 H); 7.94–8.01 (*m*, 2 H); (enol. 1.5%, selected signals) 13.10 (*s*, OH). ^{13}C-NMR (75.5 MHz): 7.9; 13.5; 25.1; 33.4; 49.5; 84.2; 128.5; 128.6; 133.2; 136.3; 170.0; 196.0. EI-MS: 248 (0.5, M^+), 105 (100). Anal. calc. for $C_{15}H_{20}O_3$ (248.32): C 72.55, H 8.12; found: C 72.51, H 8.24.

Benzyl 2-Methyl-3-oxo-3-phenylpropanoate (**4**). Freshly distilled PhCHO (2.33 g, 22 mmol) was added dropwise at $-70°$ to the enolate prepared ($-78°$) from benzyl propanoate (20 mmol) and LDA (20 mmol). Usual workup (NH_4Cl sat./^{t}BuOMe) gave 4.942 g of yellow oil that was dissolved in acetone (30 ml) and oxidized with *Jones* reagent (7.0 ml, 1.9 M CrO_3, 2.8M H_2SO_4 in H_2O) at $-10°$ for 2 h (excess reagent was destroyed with ^{i}PrOH). Workup (H_2O/^{t}BuOMe) gave an oil (4.80 g), which was separated by CC (^{t}BuOMe/hexane 1:10) to give product fractions *A* (590 mg) and *B* (1.179 g). *Fr. A* contained 19 mol% of **29** as impurity. *Fr. B* was pure product (by ^{1}H-NMR). An anal. sample was prepared by bulb-to-bulb distillation of *Fr. B* (200°/0.006 mbar). R_f (^{t}BuOMe/hexane 1:5) 0.38. ^{1}H-NMR (300 MHz): 1.51 (*d*, *J* = 7.1, 3 H); 4.41 (*q*, *J* = 7.1, 1 H); 5.11 (*s*, 2 H); 7.15–7.34 (*m*, 5 H); 7.38–7.46 (*m*, 2 H); 7.51–7.59 (*m*, 1 H); 7.91–7.96 (*m*, 2 H); (enol, 2.6%, selected signals): 1.73 (*s*, 3 H); 5.27 (*s*, 2 H); 12.89 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 13.7 (Me); 48.2 (CH); 66.9 (CH_2); 127.9 (CH); 128.1 (CH); 128.4 (CH); 128.5 (CH); 128.6 (CH); 133.4 (CH); 135.3 (C); 135.7 (C); 170.6 (CO); 195.5 (CO). EI-MS: 269 (6, M^+), 105 (100). Anal. calc. for $C_{17}H_{16}O_3$ (268.31): C 76.10, H 6.01; found: C 76.01, H 6.04.

Diphenylmethyl 2-Methyl-3-oxo-3-phenylpropanoate (**5**). To a soln. of LDA (6.8 mmol in 15 ml THF), diphenylmethyl propanoate (1.44 g, 6.0 mmol) was added dropwise at $-78°$ over 1 h. After stirring for 2 h, PhCHO (0.70 ml, 6.9 mmol) was added, and the mixture was allowed to warm to r.t. over 2 h. Quenching the reaction with NH_4Cl sat. (15 ml) and workup (^{t}BuOMe/H_2O) of the mixture gave 2.304 g of a yellow oil, which was oxidized (20 ml of acetone, 0°, dropwise addn. of 4 ml of *Jones* reagent (1.9M CrO_3, 2.75M H_2SO_4). After stirring for 3 h, the excess reagent was destroyed (2 ml ^{i}PrOH). Workup (^{t}BuOMe/H_2O), followed by CC (^{t}BuOMe/hexane 1:15), gave **5** (1.629 g, 79%) Colorless oil. R_f (^{t}BuOMe/hexane 1:5) 0.50. ^{1}H-NMR (300 MHz): 1.53 (*d*, *J* = 7.1, 3 H); 4.44 (*q*, *J* = 7.1, 1 H); 6.84 (*s*, 1 H); 7.09–7.34 (*m*, 10 H); 7.36–7.44 (*m*, 2 H); 7.51–7.58 (*m*, 1 H); 7.90–7.96 (*m*, 2 H); (enol, 1.5%, selected signals): 12.79 (*s*, OH). ^{13}C-NMR (75.5 MHz): 13.5 (Me); 48.6 (CH); 77.8 (CH); 126.9 (CH); 127.0 (CH); 127.9 (CH); 128.4 (CH); 128.4 (CH); 128.6 (CH); 128.7 (CH); 133.4 (CH); 135.9 (C); 139.5 (C); 139.5 (C); 169.8 (CO); 195.3 (CO). EI-MS: 326 (0.1, $[M - H_2O]^+$), 167 (100). Anal. calc. for $C_{23}H_{20}O_3$ (344.41): C 80.21, H 5.85; found: C 80.27, H 5.95.

2,3,4,5,6-Pentafluorobenzyl 2-Methyl-3-oxo-3-phenylpropanoate (**6**). Obtained from 2,3,4,5,6-pentafluorobenzyl alcohol (0.593 g, 2.99 mmol), 2-methyl-3-oxo-3-phenylpropanoic acid (0.800 g, 4.49 mmol), and *cyanuric chloride* (= *2,4,6-trichloro-1,3,5-triazine*; **67**; 0.277 g, 1.50 mmol) in 2.5 ml of MeCN at 0° by slow addition of *N*,*N*-dimethylaniline (0.453 g, 3.7 mmol), stirring for 2 h, warming up to r.t., and stirring overnight. Workup was performed with H_2O/^{t}BuOMe. The org. phase was washed 2 × with aq. HCl (0.5 m) and 1 × with H_2O. Evaporation and CC (^{t}BuOMe/hexane 1:20) yielded **6** (0.488 g, 46%). White microcrystalline powder. R_f (^{t}BuOMe/hexane 1:10) 0.27. M.p. 58°. ^{1}H-NMR (250 MHz): 1.51 (*d*, *J* = 7.1, 3 H); 4.39 (*q*, *J* = 7.1, 3 H); 5.20 (*dt*, *J* = 5.5, 1.5, 1 H); 5.21 (*dt*, *J* = 5.5, 1.5, 1 H); 7.40–7.49 (*m*, 2 H); 7.55–7.58 (*m*, 1 H); 7.87–7.93 (*m*, 2 H). ^{13}C-NMR (62.9 MHz): 13.8 (Me); 48.3 (CH); 54.2 (CH_2); 128.6 (CH); 128.8 (C); 128.9 (CH); 133.7 (CH); 135.6 (C); 137.4 (*d*, *J*(F,C) = 258, CF); 141.6 (*d*, *J*(F,C) = 258, CF); 145.7 (*d*, *J*(F,C) = 258, CF); 170.2 (CO); 195.1 (CO). EI-MS: 358.1 (21, M^+), 105 (100), 77 (29). Anal. calc. for $C_{17}H_{11}F_5O_3$ (358.26): C 56.99, H 3.09; found: C 56.81, H 3.34.

4-(Trifluoromethyl)benzyl 2-Methyl-3-oxo-3-phenylpropanoate (**7**). Obtained by heating ethyl **1** (1.00 g, 4.85 mmol) and [4-(trifluoromethyl)phenyl]methanol (0.854 g, 4.85 mmol) at 160° for 1 d (allowing for release of EtOH vapors). CC (AcOEt/hexane 1:25–1:10) afforded **7** (871 mg, 53%). Slightly yellow oil. R_f (^{t}BuOMe/hexane 1:10) 0.17. ^{1}H-NMR (300 MHz): 1.53 (*d*, *J* = 7.1, 3 H); 4.45 (*q*, *J* = 7.1, 1 H); 5.18 (*s*, 2 H); 7.29 (*d*, *J* = 8.0, 2 H); 7.44 (*t*, *J* = 7.7, 2 H); 7.52 (*d*, *J* = 8.0, 2 H); 7.58 (*t*, *J* = 7.6, 1 H); 7.94 (*d*, *J* = 7.7, 2 H). ^{13}C-NMR (75.5 MHz): 13.9 (Me); 48.5 (CH); 66.1 (CH_2); 124.1 (*q*, *J*(F,C) = 272.1, CF_3); 125.6 (*q*, *J*(F,C) = 3.8, CH); 128.2 (CH); 128.7 (CH); 128.9 (CH); 130.5 (*q*, *J*(F,C) = 32.5, C); 133.8 (CH); 135.9 (C); 139.5 (C); 170.7 (CO); 195.7 (CO). EI-MS: 335 (0.4, M^+), 105 (100). Anal. calc. for $C_{18}H_{15}F_3O_3$ (336.29): C 64.29, H 4.50; found: C 64.28, H 4.65.

Ethyl 3-(4-Methoxyphenyl)-2-methyl-3-oxopropanoate (**8**). To methyl 4-methoxybenzoate (8.00 g, 48.1 mmol) and NaH (2.43 g, 101 mmol) in refluxing THF (100 ml), ethyl propanoate (5.5 ml, 48 mmol) was added over 1 h. The suspension was heated under reflux for 18 h, cooled to r.t., and worked up by addition of AcOH (10 ml) and H_2O (10 ml, 0°), followed by AcOH (10 ml) and H_2O (40 ml, 0°). The org. layer was collected, and the aq. layer was extracted three times with ^{t}BuOMe. Washing the combined org. layers (3 × sat. $NaHCO_3$, 1 × H_2O), drying (Na_2SO_4), and evaporation of the solvents gave crude product (10.50 g), which was purified by CC (^{t}BuOMe/hexane 1:6–1:2) to give **8** (2.52 g; 22%) and **9** (2.62 g, 25%), the latter formed by ester alkoxide exchange.

Data of **8**: R_f (^{t}BuOMe/hexane 1:2) 0.39. ^{1}H-NMR (250 MHz): 1.18 (*t*, *J* = 7.2, 3 H); 1.48 (*d*, *J* = 7.1, 3 H); 3.88 (*s*, 3 H); 4.15 (*q*, *J* = 7.2, 2 H); 4.33 (*q*, *J* = 7.1, 1 H); 6.91–6.98 (*m*, *AA′* of *AA′CC′*, 2 H); 7.93–8.00 (*m*, *CC′* of *AA′CC′*, 2 H). ^{13}C-NMR (62.9 MHz): 14.0 (Me); 14.1 (Me); 48.2 (CH); 55.6 (Me); 61.4 (CH_2); 114.0 (CH); 129.0 (C); 131.1 (CH); 163.9 (C); 171.2 (CO); 194.5 (CO). EI-MS: 236 (6.8, M^+), 135 (100). Anal. calc. for $C_{13}H_{16}O_4$ (236.27): C 66.09, H 6.83; found: C 66.18, H 6.85. Known compound, CAS No. 1575-08-2.

Methyl 3-(4-Methoxyphenyl)-2-methyl-3-oxopropanoate (**9**). Obtained as side product in the synthesis of **8**, see above. R_f (^{t}BuOMe/hexane 1:2) 0.34. ^{1}H-NMR (250 MHz): 1.49 (*d*, *J* = 7.0, 3 H); 3.69 (*s*, 3 H); 3.88 (*s*, 3 H); 6.92–6.99 (*m*, *AA′* of *AA′CC′*, 2 H); 7.94–8.00 (*m*, *CC′* of *AA′CC′*, 2 H). ^{13}C-NMR (62.9 MHz): 14.1 (Me); 47.9 (CH); 52.6 (Me); 55.7 (Me); 114.1 (CH); 128.8 (C); 131.1 (CH); 164.0 (C); 171.7 (CO); 194.4 (CO). EI-MS: 222 (17, M^+), 135 (100). Anal. calc. for $C_{12}H_{14}O_4$ (222.24): C 64.85, H 6.35; found: C 64.71, H 6.44. Known compound, CAS No. 86109-34-4.

Ethyl 2-Methyl-3-(4-nitrophenyl)-3-oxopropanoate (**10**). To a soln. of LDA (40 mmol) in THF (50 ml) at −78°, a soln. of ethyl propanoate (2.3 ml, 20 mmol) in THF (20 ml) was added during 15 min. After 30 min, a soln. of methyl 4-nitrobenzoate (3.62 g, 20.0 mmol) in THF (30 ml) was added to the mixture. The brown soln. was slowly warmed to r.t. with stirring overnight. After cooling to −78°, glacial AcOH (10 ml) was added to quench the reaction. After workup with ^{t}BuOMe/H_2O, the org. layer was washed with H_2O and sat. $NaHCO_3$, dried ($MgSO_4$), and evaporated to dryness. CC (^{t}BuOMe/hexane 1:4) gave **10** (2.506 g, 50%) Red liquid. R_f (^{t}BuOMe/hexane 1:5) 0.19. ^{1}H-NMR (300 MHz): 1.18 (*t*, *J* = 7.1, 3 H); 1.53 (*d*, *J* = 7.0, 3 H); 4.16 (*q*, *J* = 7.1, 2 H); 4.37 (*q*, *J* = 7.0, 1 H); 8.11–8.16 (*m*, 2 H); 8.31–8.36 (*m*, 2 H); (enol, 12%; 8% after 3–4 d): 1.37 (*t*, *J* = 7.2, 3 H); 1.84 (*s*, 3 H); 4.32 (*q*, *J* = 7.2, 2 H); 7.67–7.71 (*m*, 2 H); 8.26–8.30 (*m*, 2 H). ^{13}C-NMR (75.5 MHz): 13.5 (Me); 14.1 (Me); 49.1 (CH); 61.9 (CH_2); 124.1 (CH); 129.7 (CH); 140.6 (C); 150.6 (C); 170.2 (CO); 194.4 (CO); (enol) 12.9 (Me); 14.4 (Me); 61.4 (CH_2); 98.4 (C); 123.5 (CH); 129.8 (CH); 141.5 (C); 166.8 (C); 173.9 (C). Known compound, CAS No. 13051-16-6.

Phenyl 2-Methyl-3-oxo-3-phenylpropanoate (**11**). Prepared from PhOH (0.117 g, 1.24 mmol), 2-methyl-3-oxo-3-phenylpropanoic acid (0.303 g, 1.70 mmol), and **67** (0.222 g, 1.20 mmol) in MeCN (1.2 ml) at 0° by slow addition of *N*,*N*-dimethylaniline (0.20 ml, 1.6 mmol) with stirring and slow warming of the mixture to r.t., and stirring for 20 h. Workup with H_2O/^{t}BuOMe, washing the org. phase (2 × 0.5M aq. HCl, 1 × H_2O), drying (Na_2SO_4), and evaporation gave the crude, which was purified by CC (^{t}BuOMe/hexane 1:20) to give **11** (0.23 g, 73%). R_f (^{t}BuOMe/hexane 1:10) 0.21. ^{1}H-NMR (300 MHz): 1.63 (*d*, *J* = 7.2, 3 H); 4.61 (*q*, *J* = 7.2, 1 H); 6.97–7.01 (*m*, 2 H); 7.17–7.23 (*m*, 1 H); 7.30–7.36 (*m*, 2 H); 7.49–7.55 (*m*, 2 H); 7.63 (*tt*, *J* = 7.3, 1.2, 1 H); 8.03–8.08 (*m*, 2 H); (enol, 1.3%): 12.69 (*s*, OH). ^{13}C-NMR (62.9 MHz): 14.0 (Me); 48.7 (CH); 121.4 (CH); 126.2 (CH); 128.8 (CH); 129.1 (CH); 129.6 (CH); 133.9 (CH); 135.8 (C); 169.7 (CO); 195.8 (CO). EI-MS: 254 (0.25, M^+), 161 (51.6), 105 (100). Anal. calc. for $C_{16}H_{14}O_3$ (254.29): C 75.58, H 5.55; found: C 75.29, H 5.72.

4-Methoxyphenyl 2-Methyl-3-oxo-3-phenylpropanoate (**12**). Prepared from 4-methoxyphenol (0.152 g, 1.22 mmol), 2-methyl-3-oxo-3-phenylpropanoic acid (0.300 g, 1.68 mmol), and **67** (0.224 g, 1.21 mmol) in MeCN (1.2 ml) by slow addition of *N,N*-dimethylaniline (0.20 ml, 1.6 mmol) at 0°. The mixture was slowly warmed to r.t. and stirred for 20 h. After workup with H_2O/^{t}BuOMe, the org. phase was washed (2×0.5 M aq. HCl, $1 \times H_2O$), dried (Na_2SO_4), and evaporated. The residue was purified by CC (^{t}BuOMe/hexane 1:10–1:5) to give **12** (0.300 g, 86%). R_f (^{t}BuOMe/hexane 1:5) 0.15. ^{1}H-NMR (250 MHz): 1.62 (*d*, *J* = 7.5, 3 H); 3.77 (*s*, 3 H); 4.59 (*q*, *J* = 7.5, 1 H); 6.84 (*d*, *J* = 9.4, 2 H); 6.90 (*d*, *J* = 9.4, 2 H); 7.48–7.57 (*m*, 2 H); 7.59–7.67 (*m*, 1 H); 8.03–8.09 (*m*, 2 H); (enol, 1.1%): 12.71 (*s*, OH). ^{13}C-NMR (75.5 MHz): 14.0 (Me); 48.6 (CH); 55.7 (Me); 114.6 (CH); 122.2 (CH); 128.8 (CH); 129.0 (CH); 133.8 (CH); 135.9 (C); 144.2 (C); 157.6 (C); 170.1 (CO); 195.8 (CO). EI-MS: 284 (1.1, M^+), 105 (100). Anal. calc. for $C_{17}H_{16}O_4$ (284.31): C 71.82, H 5.67; found: C 71.73, H 5.32.

Ethyl 2-Methyl-3-(naphthalen-2-yl)-3-oxopropanoate (**13**). Prepared as described in [4].

Ethyl 1,2,3,4-Tetrahydro-1-oxonaphthalene-2-carboxylate (**14**). Synthesized according to a general procedure in [42]. Distillation of the raw material (109–117°/0.04 mbar) gave 64% of a slightly yellow liquid. Purification by CC (^{t}BuOMe/hexane 1:20) gave colorless, pure **14**. R_f (^{t}BuOMe/hexane 1:5) 0.5–0.7. ^{1}H-NMR (300 MHz): (enol form, 50%): 1.28 (*t*, *J* = 7.1, 3 H); 2.52–2.59 (*m*, CH_2(3)); 2.75–2.82 (*m*, CH_2(4)); 4.27 (*q*, *J* = 7.1, 2 H); 7.12–7.17 (*m*, 1 H); 7.20–7.34 (*m*, 2 H); 7.78 (*dd*, *J* = 7.2, 2.0, 1 H); 12.51 (*s*, 1 H); (keto form, 50%): 1.33 (*t*, *J* = 7.1, 3 H); 2.34 (*ddt*, *J* = 13.5, 5.7, 4.8, H_{eq}–C(3)); 2.47 (*dddd*, *J* = 13.5, 10.4, 9.1, 5.2, H_{ax}–C(3)); 2.96 (*ddd*, *J* = 16.9, 9.0, 4.8, H_{ax}–C(4)); 3.04 (*ddd*, *J* = 16.9, 5.7, 5.2, H_{eq}–C(4)); 3.58 (*dd*, *J* = 10.4, 4.8, H–C(2)); 4.21 (*dq*, *J* = 10.8, 7.1, 1 H; *A* of *ABM*$_3$); 4.24 (*dq*, *J* = 10.8, 7.1, 1 H; *B* of *ABM*$_3$); 7.20–7.34 (*m*, 2 H); 7.47 (*td*, *J* = 7.5, 1.5, 1 H); 8.03 (*dd*, *J* = 7.8, 1.4, 1 H). ^{13}C-NMR (75.5 MHz): (enol form): 14.2 (Me); 20.4 (CH_2); 27.6 (CH_2); 60.4 (CH_2); 96.9 (C); 124.1 (CH); 126.4 (CH); 127.2 (CH); 129.9 (C); 130.3 (CH); 139.2 (C); 164.8 (C); 172.6 (C); (keto form); 14.0 (Me); 26.2 (CH_2); 27.5 (CH_2); 54.4 (CH); 61.1 (CH_2); 126.7 (CH); 127.5 (CH); 128.7 (CH); 131.6 (C); 133.7 (CH); 143.5 (C); 170.1 (CO); 193.1 (CO). Known compound, see, *e.g.*, [47].

Ethyl 2-Methyl-3-oxobutanoate (**15**). Commercially available.

2,2-Diphenylethyl 2-Methyl-3-oxobutanoate (**16**). Freshly extracted *2-methyl-3-oxobutanoic acid* (**66**; see *Sect. 12*, *a*, for synthesis; 2.33 g, 20 mmol) dissolved in MeCN (7 ml) was combined with CDI (3.23 g, 19.9 mmol) in portions. After stirring for 2 h at r.t., Ph_2CHCH_2OH (3.37 g, 17.0 mmol; from $Ph_2CHCO_2H + LiAlH_4$) was added, and the mixture was stirred until a homogeneous soln. had formed. To this, TFA (3.05 ml, 39.8 mmol) was added dropwise with cooling (r.t., water bath). After stirring for 1 d at r.t., workup with ^{t}BuOMe/H_2O, washing the org. phase ($2 \times H_2O$), and evaporation gave a residue, which was purified by CC (^{t}BuOMe/hexane 1:10) to give **16** (4.829 g, 96%). Colorless liquid. R_f (^{t}BuOMe/hexane 1:5) 0.30. ^{1}H-NMR (300 MHz): 1.21 (*d*, *J* = 7.1, 3 H); 1.91 (*s*, 3 H); 3.38 (*q*, *J* = 7.1, 1 H); 4.39 (*t*, *J* = 7.7, 1 H); 4.63–4.76 (*m*, 2 H); 7.18–7.34 (*m*, 10 H); (enol, 12%): 1.57 (*q*, *J* = 0.7, 3 H); 1.95 (*quint*, *J* = 0.7, 3 H); 4.40 (*t*, *J* = 7.6, 1 H); 4.70 (*d*, *J* = 7.6, 2 H); 12.54 (*q*, *J* = 0.7, 1 H). ^{13}C-NMR (75.5 MHz): 12.5 (Me); 28.1 (Me); 49.8 (CH); 53.4 (CH); 67.4 (CH_2); 126.9 (CH); 128.1 (CH); 128.6 (CH); 140.6 (C); 140.6 (C); 170.3 (CO); 203.2 (CO); (enol): 10.9 (Me); 18.6 (Me); 66.7 (CH_2); 126.7 (CH); 128.2 (CH); 128.5 (CH); 141.2 (C). EI-MS: 198 (2, $[M - Ph_2CHCH_2OH]^+$), 180 (73), 167 (100), 152 (14), 43 (11). ESI-MS: 314.2 ($[M + NH_4]^+$). Anal. calc. for $C_{19}H_{20}O_3$ (296.37): C 77.00, H 6.80; found: C 77.04, H 6.76.

Benzyl 2-Methyl-3-oxobutanoate (**17**). Synthesized as described in [48] (44% yield), or by the following modification with cat. DMAP: In an open 50-ml round flask, ethyl 2-methylacetoacetate (9.06 g, 62.8 mmol), BnOH (9.0 g, 83 mmol), and DMAP (50 mg) were stirred for 3 h at 135° (conversion: 10% ^{1}H-NMR). The mixture was stirred for another 12 h at 145°, developing a brown color in the course (conversion: 86% ^{1}H-NMR). After distilling off volatiles at 90°/0.016 mbar in a bulb-to-bulb oven (*ca.* 3 ml, mainly BnOH), the residue was separated by CC (^{t}BuOMe/hexanes 1:10), and the product fraction distilled in a bulb-to-bulb oven (130°/0.025 mbar) gave (after discarding a pre-run of *ca.* 1 ml) **17** (7.25 g, 56%). Colorless liquid. ^{1}H-NMR (300 MHz): 1.35 (*d*, *J* = 7.2, 3 H); 2.18 (*s*, 3 H); 3.54 (*q*, *J* = 7.2, 1 H); 5.17 (*s*, 2 H); 7.28–7.41 (*m*, 5 arom. H); (enol, 7.5%): 1.78 (*q*, *J* = 0.7, 3 H); 2.01 (*quint.*, *J* = 0.7, 3 H); 5.20 (*s*, 2 H); 12.62 (*q*, *J* = 0.7, OH). ^{13}C-NMR (75.5 MHz): 12.6; 28.3; 53.4; 66.9; 128.2; 128.3; 128.5; 135.3; 170.2; 203.3. Known compound, CAS No. 37526-93-5.

(Naphthalen-1-yl)methyl 2-Methyl-3-oxobutanoate (**18**). *a*) *By Transesterification*[4]): In a 25-ml vessel with *Vigreux* head (10 cm, air-cooling), open to air, **15** (6.87 g; 90% purity, *ca.* 43 mmol) and (naphthalen-1-yl)methanol (5.58 g, 35.3 mmol) were heated to 180° for 2 h, and further heated to 210° for 2 h. The residue was distilled (bulb-to-bulb; 0.0097 mbar, 200–220°; discarding a pre-run at 0.01 mbar/170°). Purification by CC (*t*BuOMe/hexane 1:20–1:15) and thorough drying in high vacuum gave **18** (6.278 g, 57%). Colorless oil.

b) *By Esterification with Cyanuric Chloride*[4]): To a stirred mixture of (naphthalen-1-yl)methanol (2.0 g, 12.6 mmol), *2-methyl-3-oxobutanoic acid* (**66**; 1.85 g, 15.9 mmol), and **67** (1.16 g, 6.3 mmol) in MeCN (5 ml) at 0°, *N*,*N*-dimethylaniline (1.90 ml, 15 mmol) was slowly added with stirring for 2 h at 0°, followed by stirring for 1 d at r.t. Workup with H_2O/*t*BuOMe, washing the org. phase with HCl (0.2M) and H_2O, and evaporation gave a crude, which was separated by CC (*t*BuOMe/hexane 1:10) to give **18** (2.414 g, 75%). Slightly yellow oil. R_f (*t*BuOMe/hexane 1:5) 0.23. ^{1}H-NMR (250 MHz): 1.34 (*d*, *J* = 7.2, 3 H); 2.12 (*s*, 3 H); 3.53 (*q*, *J* = 7.2, 1 H); 5.62 (*s*, 2 H); 7.38–7.59 (*m*, 4 H); 7.78–7.90 (*m*, 2 H); 7.93–8.02 (*m*, 1 H); (enol, 7.5%): 1.72 (*s*, 3 H); 1.98 (*s*, 3 H); 5.64 (*s*, 2 H); 7.40–7.58 (*m*, 4); 7.81–7.89 (*m*, 2 H); 8.00–8.05 (*m*, 1 H); 12.64 (*s*, 1 H). ^{13}C-NMR (62.9 MHz): 12.7 (Me); 28.4 (Me); 53.5 (CH); 65.4 (CH_2); 123.3 (CH); 125.2 (CH); 126.0 (CH); 126.6 (CH); 127.7 (CH); 128.7 (CH); 129.5 (CH); 130.7 (C); 131.5 (C); 133.6 (C); 170.3 (CO); 203.4 (CO); (enol): 11.3 (Me); 18.9 (Me); 64.3 (CH_2); 123.5 (CH); 125.8 (CH); 126.4 (CH); 127.0 (CH); 128.6 (CH); 129.1 (CH); 172.0 (C). EI-MS: 256 (22, M^+), 141 (100). Anal. calc. for $C_{16}H_{16}O_3$ (256.30): C 74.98, H 6.29; found: C 74.90, H 6.22.

2,3,4,5,6-Pentafluorobenzyl 2-Methyl-3-oxobutanoate (**19**). Obtained from 2,3,4,5,6-pentafluorobenzyl alcohol (0.600 g, 3.03 mmol), **66** (0.549 g, 4.73 mmol), and **67** (0.279 g, 1.51 mmol) in MeCN (2.5 ml) by slow addition of *N*,*N*-dimethylaniline (0.48 ml, 3.79 mmol) at 0°, stirring for 2 h at 0°, and overnight at r.t. Workup with H_2O/*t*BuOMe, washing the org. phase (1 × H_2O, 2 × 0.5M HCl, 1 × H_2O), evaporation and CC (*t*BuOMe/hexane 1:15–1:10) gave **19** (0.941 g, quant.). Slightly yellow oil with sweet odor. R_f (*t*BuOMe/hexane 1:10) 0.26. ^{1}H-NMR (250 MHz): 1.36 (*d*, *J* = 7.2, 3 H); 2.23 (*s*, 3 H); 3.54 (*q*, *J* = 7.2, 1 H); 5.26 (*t*, *J* = 1.5, 2 H); (enol, 4.1%): 12.4 (*s*, OH). ^{13}C-NMR (62.9 MHz): 12.8 (Me); 28.5 (Me); 53.4 (CH); 54.1–54.3 (*m*, CH_2); 109.1 (*m*, C); 135.4–148.0 (*m*, 5 CF)[5]); 170.0 (CO); 203.0 (CO). ^{19}F-NMR (282 MHz): −161.7 (*m*, 2 F); −152.3 (*tt*, *J*(F,H) = 20.8, 2.3, 1 F); −142.3 (*m*, 2 F). EI-MS: 296 (2.4, M^+), 181 (100). Anal. calc. for $C_{12}H_9O_3F_5$ (296.19): C 48.66, H 3.06; found: C 48.70, H 3.05.

4-Nitrobenzyl 2-Methyl-3-oxobutanoate (**20**). Obtained from 4-nitrobenzyl alcohol (2.026 g, 13.23 mmol), **66** (2.40 g, 20.7 mmol), and **67** (1.219 g, 6.61 mmol) in MeCN (10 ml) at 0° by slow addition of *N*,*N*-dimethylaniline (2.005 g, 16.55 mmol), stirring for 2 h, warming to r.t., and stirring overnight. Workup with H_2O/*t*BuOMe, washing the org. phase (2 × 0.5M HCl, 1 × H_2O), evaporation, and CC (*t*BuOMe/hexane 1:3) gave **20** (2.858 g, 86%). Slightly yellow powder. R_f (*t*BuOMe/hexane 1:1) 0.39. M.p. 54°. ^{1}H-NMR (250 MHz): 1.41 (*d*, *J* = 7.2, 3 H); 2.24 (*s*, 3 H); 3.62 (*q*, *J* = 7.2, 1 H); 5.24 (*d*, *J* = 13.4, 1 H); 5.30 (*d*, *J* = 13.4, 1 H); 7.52 (*d*, *J* = 8.8, 2 H); 8.24 (*d*, *J* = 8.8, 2 H); (enol, 13%): 1.82 (*s*, 3 H); 2.04 (*s*, 3 H); 12.46 (*s*, OH). ^{13}C-NMR (62.9 MHz): 13.0 (Me); 28.7 (Me); 53.6 (CH); 65.6 (CH_2); 124.0 (CH); 128.6 (CH); 142.7 (C); 148.0 (C); 170.2 (CO); 203.5 (CO). EI-MS: 251 (1.1, M^+), 90 (100). Anal. calc. for $C_{12}H_{13}NO_5$ (251.24): C 57.37, H 5.22, N 5.58; found: C 57.46, H 5.37, N 5.51.

Phenyl 2-Methyl-3-oxobutanoate (**21**). Obtained from PhOH (500 mg, 5.31 mmol), **66** (1.05 g, 9.04 mmol), and **67** (550 mg, 8.95 mmol) in MeCN (10 ml) at 0° by slow addition of *N*,*N*-dimethylaniline (1.3 ml, 10 mmol), warming to r.t., and standing for 19 h. Workup with H_2O/*t*BuOMe, washing of the org. phase (2 × 2 M HCl, 1 × H_2O), evaporation, and distillation (200–210°/6 mbar) gave **21** (601 mg, 58%). Colorless liquid. R_f (*t*BuOMe/hexane 1:5) 0.19. ^{1}H-NMR (300 MHz): 1.49 (*d*, *J* = 7.1, 3 H); 2.36 (*s*, 3 H); 3.76 (*q*, *J* = 7.1, 1 H); 7.07–7.13 (*m*, 2 H); 7.23–7.28 (*m*, 1 H); 7.35–7.43 (*m*, 2 H). ^{13}C-NMR (75.5 MHz):

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[4]) The product from procedure *a* was contaminated with a few % of the naphthalen-2-yl-isomer; this regioisomeric impurity was present in the commercially available naphthaldehyde used to prepare naphthylmethanol (by $NaBH_4$ reduction). For synthesis *b*, a recrystallized, isomerically pure sample of (naphthalen-1-yl)methanol was used.

[5]) The quaternary C(–F)-nuclei (higher-order spin system) gave rise to 4 *m* signals centered at 135.7, 139.8, 144.0, and 147.8.

13.0 (Me); 28.7 (Me); 53.8 (CH); 121.4 (CH); 126.3 (CH); 129.7 (CH); 150.4 (C); 169.3 (CO); 203.3 (CO). EI-MS: 192 (3, M^+), 94 (100). Known compound, CAS No. 343772-42-9.

3,5-Dimethylphenyl 2-Methyl-3-oxobutanoate (**22**). Obtained from 3,5-dimethylphenol (3.04 g, 24.9 mmol), **66** (4.65 g, 40.0 mmol), and **67** (2.48 g, 40.3 mmol) in MeCN (50 ml) by slow addition of *N,N*-dimethylaniline (6.0 ml, 47 mmol) at 0°, followed by slow warming to r.t. and standing for 46 h. Workup with H_2O/^{t}BuOMe, washing the org. phase (1 × H_2O, 2 × 0.5M HCl), evaporation, and distillation (230–240°/6 torr) gave **22** (2.145 g, 39%). White powder. A second fraction (2.52 g) containing 30–35 mol-% of 3,5-dimethylphenol was collected at 180–200°/7 Torr. R_f (^{t}BuOMe/hexane 1:10) 0.21. M.p. 51–52°. ^{1}H-NMR (300 MHz): 1.47 (*d*, *J* = 7.3, 3 H); 2.31 (*s*, 6 H); 2.36 (*s*, 3 H); 3.73 (*q*, *J* = 7.3, 1 H); 6.71 (*s*, 2 H); 6.88 (*s*, 1 H); (enol, 6%): 12.46. ^{13}C-NMR (75.5 MHz): 13.0 (Me); 21.3 (Me); 28.7 (Me); 53.8 (CH); 118.9 (CH); 128.0 (CH); 139.6 (C); 150.5 (C); 169.5 (CO); 203.3 (CO). EI-MS: 220 (1.7, M^+), 122 (100). Anal. calc. for $C_{13}H_{16}O_3$ (220.27): C 70.89, H 7.32; found: C 70.88, H 7.16.

2,6-Dimethylphenyl 2-Methyl-3-oxobutanoate (**23**). Obtained from 2,6-dimethylphenol (2.03 g, 16.6 mmol), **66** (3.05 g, 26.3 mmol), and **67** (1.59 g, 25.9 mmol) in MeCN (50 ml) by slow addition of *N,N*-dimethylaniline (3.7 ml, 29 mmol) at 0°, slowly warming to r.t., and standing without stirring for 28 h. Workup with H_2O/^{t}BuOMe, washing the org. phase (2 × 0.5M HCl, 1 × H_2O), evaporation, and distillation (220–240°/8 mbar) of the residue gave **23** (1.47 g, 40%). Colorless oil. A second fraction (1.09 g, 180–200°/8 mbar) consisted of product (58 mol-%), 2,6-dimethylphenol (35 mol-%), and **66** (12 mol-%). R_f (^{t}BuOMe/hexane 1:10) 0.20. ^{1}H-NMR (300 MHz): 1.54 (*d*, *J* = 7.2, 3 H); 2.15 (*s*, 6 H); 2.39 (*s*, 3 H); 3.84 (*q*, *J* = 7.2, 1 H); 7.04–7.07 (*m*, 3 H). ^{13}C-NMR (75.5 MHz): 13.3 (Me); 16.5 (Me); 29.1 (Me); 53.5 (CH); 126.3 (CH); 128.9 (CH); 130.2 (C); 148.0 (C); 168.3 (CO); 203.2 (CO). EI-MS: 220 (2.5, M^+), 122 (100). Anal. calc. for $C_{13}H_{16}O_3$ (220.27): C 70.89, H 7.32; found: C 70.74, H 7.31.

2,4,6-Trimethylphenyl 2-Methyl-3-oxobutanoate (**24**). Obtained from 2,4,6-trimethylphenol (2.92 g, 21.4 mmol), **66** (4.20 g, 36.2 mmol), and **67** (2.20 g, 11.9 mmol) in MeCN (20 ml) by slow addition of *N,N*-dimethylaniline (5.1 ml, 40 mmol) at 0°, slowly warming to r.t., and standing without stirring for 20 h. Workup with H_2O/^{t}BuOMe, washing of the org. phase (1 × H_2O, 2 × 0.5M HCl, 1 × H_2O), evaporation, and distillation (220–230°/11 Torr) gave **24** (1.766 g, 35%). Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.14. ^{1}H-NMR (300 MHz): 1.52 (*d*, *J* = 7.2, 3 H); 2.10 (*s*, 6 H); 2.26 (*s*, 3 H); 2.38 (*s*, 3 H); 3.82 (*q*, *J* = 7.2, 1 H); 6.86 (*s*, 2 H). ^{13}C-NMR (75.5 MHz): 13.3 (Me); 16.4 (Me); 20.9 (Me); 29.1 (Me); 53.5 (CH); 129.5 (CH); 129.7 (C); 135.8 (C); 145.7 (C); 168.5 (CO); 203.3 (CO). EI-MS: 234 (2, M^+), 136 (100). Anal. calc. for $C_{14}H_{18}O_3$ (234.29): C 71.77, H 7.74; found: C 71.67, H 7.54.

Ethyl 2-Benzyl-3-oxobutanoate (**25**). Obtained by alkylation of sodium ethyl acetoacetate (from ethyl acetoacetate and NaH in ^{t}BuOMe/triglyme) with BnCl in the presence of cat. NaI. Purification by CC (^{t}BuOMe/hexane 1:25–1:15) gave 42% of **25**. Considerable losses occurred during separation of mono- and dialkylation products. ^{1}H-NMR (300 MHz): 1.19 (*t*, *J* = 7.1, 3 H); 2.18 (*s*, 3 H); 3.16 (*d*, *J* = 7.6, 2 H); 3.78 (*t*, *J* = 7.6, 1 H); 4.14 (*ψ-qd*, *J* = 7.1, 0.8, 2 H); 7.13–7.33 (*m*, 5 H); (enol, 18%): 1.20 (*t*, *J* = 7.1, 3 H); 2.04 (*s*, 3 H); 3.57 (*s*, 2 H); 4.16 (*q*, *J* = 7.1, 2 H); 12.97 (*q*, *J* = 0.8, 1 H). ^{13}C-NMR (75.5 MHz): 13.9 (Me); 29.5 (Me); 33.9 (CH_2); 61.2 (CH); 61.4 (CH_2); 126.6 (CH); 128.5 (CH); 128.7 (CH); 138.0 (C); 169.0 (CO); 202.3 (CO); (enol): 14.0 (Me); 19.0 (Me); 31.5 (CH_2); 60.4 (CH_2); 99.3 (C); 125.7 (CH); 127.7 (CH); 128.1 (CH); 140.9 (C); 173.2 (C); 173.5 (C). Known compound.

Benzyl 2-Acetyl-3-methylbutanoate (**26**). In a round flask with mounted *Vigreux* head (10 cm, air cooling) open to air, ethyl 2-isopropyl-3-oxobutanoate (*Fluka*, purity >90%; 7.88 g, 45 mmol), and BnOH (6.50 g, 60 mmol) were heated to 180° for 15 h. After cooling, the reaction flask was transferred to a bulb-to-bulb oven, and volatiles were removed at 140°/0.13 mbar. The residue was purified by CC (^{t}BuOMe/hexane 1:25–1:10) to give **26** (5.178 g, 49%). Colorless liquid (yellow aspect). R_f (^{t}BuOMe/hexane 1:5) 0.36. ^{1}H-NMR (300 MHz): 0.92 (*d*, *J* = 6.8, 3 H); 0.94 (*d*, *J* = 6.8, 3 H); 2.16 (*s*, 3 H); 2.35–2.50 (*m*, 1 H); 3.23 (*d*, *J* = 9.5, 1 H); 5.15 (*s*, 2 H); 7.27–7.39 (*m*, 5 H); (enol, 0.1%): 12.94 (*q*, *J* = 0.8, 1 H). ^{13}C-NMR (75.5 MHz): 20.3 (Me); 20.3 (Me); 28.6 (Me); 29.1 (CH); 66.7 (CH_2); 67.4 (CH); 128.2 (CH); 128.3 (CH); 128.5 (CH); 135.3 (C); 168.9 (CO); 202.8 (CO). EI-MS: 235 (4, $[M+H]^+$), 91 (100). Anal. calc. for $C_{14}H_{18}O_3$ (234.29): C 71.77, H 7.74; found: C 71.85, H 7.82.

Benzyl 2-Oxocyclopentanecarboxylate (**27**). Synthesis by modified literature procedures [49][50]. A mixture of methyl 2-oxocyclopentanecarboxylate (7.817 g, 96%, *ca.* 55 mmol) and BnOH (6.49 g, 60 mmol) was heated to 215° in a round-bottom flask with mounted *Vigreux* column, open to air. Above

160°, vapors of MeOH were released from the reaction. After 2 h at 215°, the mixture was cooled to r.t., and volatiles were removed in high vacuum (0.07 mbar) at 60°. The residue was purified by CC (*t*BuOMe/pentane 1:10), and the product fraction was distilled in a bulb-to-bulb oven (160°/0.014 mbar). After a pre-run (2.05 g, 17%; with minor impurity), pure **27** (4.09 g, 34%) was obtained. Colorless liquid. R_f (*t*BuOMe/hexane 1:10) 0.15. ^{1}H-NMR (250 MHz): 1.73–1.94 (*m*, 1 CH); 2.01–2.20 (*m*, 1 CH); 2.21–2.36 (*m*, 3 CH); 3.20 (*t*, *J* = 9.1, H–C(1)); 5.17 (ψ-*s*, OCH_2Ph); 7.24–7.44 (*m*, 5 arom. H); (enol, 5.4%): 2.34–2.41 (*m*, 2 CH); 2.47–2.56 (*m*, 4 CH); 5.20 (*s*, OCH_2Ph); 10.37 (*s*, OH). ^{13}C-NMR (62.9 MHz): 20.8 (CH_2); 27.2 (CH_2); 37.9 (CH_2); 54.6 (CH); 66.8 (CH_2); 127.9 (CH); 128.1 (CH); 128.4 (CH); 135.4 (C); 169.1 (C); 212.0 (C); (enol): 18.9 (CH_2); 26.7 (CH_2); 32.4 (CH_2); 65.2 (CH_2). Known compound, data in accordance with those in [50].

Ethyl 2-Methyl-3-oxopentanoate (**28**). This compound was obtained as side product in mixed *Claisen* condensations involving LDA and ethyl propanoate (by self-condensation). Purification was effected by bulb-to-bulb distillation (170–200°/10 mbar). ^{1}H-NMR (300 MHz): 1.08 (*t*, *J* = 7.2, 3 H); 1.27 (*t*, *J* = 7.2, 3 H); 1.34 (*d*, *J* = 7.2, 3 H); 2.44–2.69 (*m*, 2 H); 3.52 (*q*, *J* = 7.2, 1 H); 4.19 (*q*, 2 H). ^{13}C-NMR (62.9 MHz): 7.8 (Me); 13.0 (Me); 14.2 (Me); 34.8 (CH_2); 52.8 (CH); 61.4 (CH_2); 170.8 (CO); 206.6 (CO). Known compound, CAS No. 759-66-0, 138752-69-9 (*R*), 138752-66-6 (*S*).

Benzyl 2-Methyl-3-oxopentanoate (**29**). *(4Z)-4-Ethylidene-3-methyloxetan-2-one* (**75**; 3.65 g, 32.6 mmol) was added dropwise during 30 min with stirring to a mixture of BnOH (3.25 g, 30.05 mmol) and 1*H*-imidazole (2.05 g, 30.1 mmol) in MeCN (10 ml) at 0°. After stirring for 30 min, TFA (2.30 ml, 30 mmol) was added dropwise at 0°, and the mixture was stirred for 1 d at r.t. Workup with sat. $NaHCO_3$/*t*BuOMe, washing with sat. aq. NaCl, evaporation of the org. phase, and CC (*t*BuOMe/hexane 1:15) gave **29** (5.748 g, 87%). Colorless liquid. R_f (*t*BuOMe/hexane 1:5) 0.35. ^{1}H-NMR (300 MHz): 1.02 (*t*, *J* = 7.2, 3 H); 1.35 (*d*, *J* = 7.1, 3 H); 2.46 (*dq*, *J* = 18.2, 7.2, 1 H); 2.56 (*dq*, *J* = 18.2, 7.3, 1 H); 3.57 (*q*, *J* = 7.2, 1 H); 5.15 (*s*, 2 H); 7.27–7.39 (*m*, 5 H); (enol, 4.5%): 1.14 (*t*, *J* = 7.7, 3 H); 1.78 (*s*, 3 H); 2.32 (*qm*, *J* = 7.6, 2 H); 5.19 (*s*, 2 H); 7.27–7.39 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): 7.5 (Me); 12.7 (Me); 34.5 (CH_2); 52.4 (CH); 66.8 (CH_2); 128.0 (CH); 128.2 (CH); 128.4 (CH); 135.3 (C); 170.3 (CO); 206.0 (CO); (enol): 10.5 (Me); 10.7 (Me); 65.7 (CH_2); 127.7 (CH); 127.9 (CH); 128.4 (CH). EI-MS: 220 (0.5, M^+), 91 (100). Anal. calc. for $C_{13}H_{16}O_3$ (220.27): C 70.89, H 7.32; found: C 70.67, H 7.22.

2,4,6-Tris(methylethyl)benzyl 2-Methyl-3-oxopentanoate (**30**). Obtained from [2,4,6-tris(1-methylethyl)phenyl]methanol (2.877 g, 12.27 mmol) and **75** (1.71 g, 15.2 mmol) in CH_2Cl_2 (5 ml), by addition of 1*H*-imidazole (1.02 g, 14.98 mmol) in several portions at r.t., followed by TFA (1.11 ml, 14.5 mmol) at −15° (ice/EtOH). The suspension was stirred overnight at r.t. Workup with H_2O/*t*BuOMe, washing with HCl (0.1 m) and H_2O, drying (Na_2SO_4), and evaporation gave 4.647 g of a yellow oil that was purified by CC (*t*BuOMe/hexane 1:30–1:20) to give **30** (4.022 g, 94.6%). Colorless oil. R_f (*t*BuOMe/hexane 1:10) 0.28. M.p. 8–9°. ^{1}H-NMR (400 MHz): 1.03 (*t*, *J* = 7.2, 3 H); 1.24 (*d*, *J* = 6.8, 6 H); 1.24 (*d*, *J* = 6.8, 6 H); 1.26 (*d*, *J* = 6.8, 6 H); 1.34 (*d*, *J* = 7.2, 3 H); 2.49 (*dq*, *J* = 18.1, 7.2, 1 H); 2.58 (*dq*, *J* = 18.1, 7.2, 1 H); 2.89 (*sept.*, *J* = 6.8, 1 H); 3.17 (*sept.*, *J* = 6.8, 2 H); 3.53 (*q*, *J* = 7.1, 1 H); 5.24 (*d*, *J* = 12.2, 1 H); 5.32 (*d*, *J* = 12.2, 1 H); 7.04 (*s*, 2 H); (enol, 8%): 1.15 (*t*, *J* = 7.6, 3 H); 1.25 (*d*, *J* = 6.8, 12 H); 1.27 (*d*, *J* = 6.8, 6 H); 1.69 (*s*, 3 H); 2.32 (*q*, *J* = 7.5, $MeCH_2$); 2.90 (*sept.*, *J* = 6.9, 1 Me_2CH); 3.25 (*sept.*, *J* = 6.9, 2 Me_2CH); 5.30 (*s*, ArCH_2); 7.06 (*s*, 2 arom. H); 12.80 (*t*, *J* = 1.0, OH). ^{13}C-NMR (100.6 MHz): 7.5; 12.9; 23.9; 23.9; 24.3; 24.3; 29.4; 34.3; 34.6; 52.6; 60.2; 121.1; 125.9; 148.8; 149.8; 170.8 (CO); 206.0 (CO); (enol): 10.7; 10.9; 24.3; 25.7; 29.4; 34.3; 59.2; 94.0; 121.1; 126.4; 148.9; 149.5; 173.7; 176.0. HR-MALDI-MS: 369.238 ([*M* + Na]$^+$; calc. 369.241). Anal. calc. for $C_{22}H_{34}O_3$ (346.50): C 76.26, H 9.89; found: C 76.05, H 10.02.

Diphenylmethyl 2-Methyl-3-oxopentanoate (**31**). Prepared as described in [4].

Phenyl 2-Methyl-3-oxopentanoate (**32**). To a stirred mixture of PhOH (1.22 g, 13.0 mmol) and 1*H*-imidazole (1.60 g, 15.6 mmol) in CH_2Cl_2 (12 ml), **75** (1.74 g, 15.5 mmol) was added at 0°, and the mixture was stirred for 15 min. After addition of TFA (1.4 ml, 18 mmol), the mixture was warmed to r.t. with stirring overnight. The mixture was worked up with *t*BuOMe and H_2O. The org. phase was washed with sat. NaCl (2×), aq. HCl (0.5M; 2×), and H_2O (1×). After drying (Na_2SO_4), filtration, and evaporation, CC (*t*BuOMe/hexane 1:15) of the residue gave **32** (1.904 g, 71%). Faint yellow oil. R_f (*t*BuOMe/hexane 1:10) 0.27. ^{1}H-NMR (300 MHz): 1.15 (*t*, *J* = 7.7, 3 H); 1.48 (*d*, *J* = 7.2, 3 H); 2.68 (*m*, 2 H); 3.77 (*q*, *J* = 7.3, 1 H); 7.09 (*d*, *J* = 8.3, 2 H); 7.24 (*t*, *J* = 7.9, 1 H); 7.40 (*t*, *J* = 8.1, 2 H); (enol, 5%): 12.50 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 7.9 (Me); 13.1 (Me); 34.9 (CH_2); 52.8 (CH); 121.4 (CH); 126.3 (CH); 129.6 (CH); 150.7

(C); 169.4 (CO); 206.1 (CO). EI-MS: 206 (1, M^+), 94 (100). Anal. calc. for $C_{12}H_{14}O_3$ (206.24): C 69.89, H 6.84; found: C 70.02, H 6.91.

4-Methoxyphenyl 2-Methyl-3-oxopentanoate (**33**). Compound **75** (0.401 g, 3.57 mmol) was added to a mixture of 4-methoxyphenol (0.375 g, 3.02 mmol) and 1*H*-imidazole (0.248 g, 3.64 mmol) in CH_2Cl_2 (3 ml) at 0°, followed by warming to r.t. and stirring for 20 min. After cooling to −7°, TFA (0.28 ml, 3.7 mmol) was slowly added, and the mixture was stirred at r.t. for 20 h, and at 50° for 20 h. Addition of ^{t}BuOMe and washing with sat. NaCl (3×), followed by drying ($MgSO_4$), evaporation, and CC (acetone/hexane 1:10) of the residue gave **33** (0.331 g, 46%). Faint yellow oil. R_f (acetone/hexane 1:5) 0.22. ^{1}H-NMR (300 MHz): 1.13 (*t*, *J* = 7.0, 3 H); 1.47 (*d*, *J* = 7.6, 3 H); 2.68 (*m*, 2 H); 3.77 (*q*, *J* = 7.6, 1 H); 3.80 (*s*, 3 H); 6.89 (*d*, *J* = 8.8, 2 H); 7.00 (*d*, *J* = 8.8, 2 H); (enol, 0.5%): 12.53 (*s*, OH). ^{13}C-NMR (62.9 MHz): 7.9 (Me); 13.1 (Me); 34.9 (CH_2); 52.7 (CH); 55.7 (Me); 114.6 (CH); 122.2 (CH); 144.1 (C); 157.6 (C); 169.8 (CO); 206.2 (CO). EI-MS: 236 (2, M^+), 124 (100). Anal. calc. for $C_{13}H_{16}O_4$ (236.27): C 66.09, H 6.83; found: C 65.97, H 6.67.

*2,6-Di-(*tert*-butyl)-4-methylphenyl 2-Methyl-3-oxopentanoate* (**34**). Prepared as described in [4].

*3-Benzoyl-3,4,5,6-tetrahydro-2*H*-pyran-2-one* (**35**). A soln. of δ-valerolactone (1.00 g, 9.98 mmol) in THF (15 ml) and little EtOH (4 drops) was slowly added to a stirred mixture of NaH (1.5 equiv.) and PhCOOEt (9.98 mmol) in THF (15 ml) at 0°. After stirring for 2 h at 5° and overnight at r.t., the reaction was quenched by addition of ice H_2O (20 ml), and the mixture was extracted with Et_2O (2 × 10 ml). The org. phase was washed with H_2O (10 ml) and sat. NaCl (2 × 10 ml), dried ($MgSO_4$), filtered, and evaporated. CC (AcOEt/hexanes 1:1) gave **35** (1.42 g, 69%). Colorless solid. ^{1}H-NMR (300 MHz): (enol, 76%): 1.92–1.98 (*m*, 1 H); 2.58 (*t*, *J* = 6.0, 2 H); 4.40 (*t*, *J* = 5.4, 2 H); 7.44–7.57 (*m*, 5 H); 14.18 (*s*, 1 H); (keto form, 24%): 2.01–2.09 (*m*, 2 H); 2.36–2.42 (*m*, 2 H); 4.27–4.35 (*m*, 2 H); 4.54 (*t*, *J* = 7.1, 1 H); 7.54–7.62 (*m*, 2 H); 7.98–8.07 (*m*, 3 H). ^{13}C-NMR (75.5 MHz): (enol): 22.8 (CH_2); 24.2 (CH_2); 69.2 (CH_2); 94.0 (C); 127.7 (C); 127.9 (C); 130.0 (CH); 134.1 (C); 173.0 (C); 190.7 (C); (keto form): 19.8 (CH_2); 20.9 (CH_2); 51.0 (CH); 67.3 (CH_2); 128.3 (CH); 128.6 (CH); 129.1 (CH); 129.6 (CH); 133.0 (C); 172.9 (CO); 195.4 (CO). EI-MS: 204 (12, M^+), 105 (100). Anal. calc. for $C_{12}H_{12}O_3$ (204.08): C 70.57, H 5.92; found: C 70.45, H 6.01.

*3-(2-Phenylacetyl)-3,4,5,6-tetrahydro-2*H*-pyran-2-one* (**36**). A soln. of δ-valerolactone (1.00 g, 9.98 mmol) in THF (15 ml) and little EtOH (4 drops) was slowly added to a stirred mixture of NaH (1.5 equiv.) and ethyl 2-phenylacetate (9.98 mmol) in THF (15 ml) at 0°. After stirring for 2 h at 5° and overnight at r.t., the reaction was quenched by addition of ice H_2O (20 ml), and the mixture was extracted with Et_2O (2 × 10 ml). The org. phase was washed with H_2O (10 ml) and sat. NaCl (2 × 10 ml), dried ($MgSO_4$), filtered, and evaporated. CC (AcOEt/hexanes 1:1) gave **36** (1.74 g, 75%). Colorless solid. ^{1}H-NMR (300 MHz): (enol, 45%): 1.88–1.92 (*m*, 2 H); 2.48 (*t*, *J* = 6.3, 2 H); 3.64 (*s*, 2 H); 4.28 (*m*, 2 H); 7.26–7.33 (*m*, 5 H); 13.87 (*s*, 1 H); (keto form, 55%): 1.25 (*m*, 2 H); 2.48 (br., 1 H); 3.62 (*s*, 2 H); 4.12 (*m*, 2 H); 4.26–4.30 (*m*, 2 H); 7.26–7.33 (*m*, 5 H). ^{13}C-NMR (75.5 MHz): (enol): 22.0 (CH_2); 22.3 (CH_2); 38.1 (CH_2); 68.8 (CH_2); 93.5 (C); 126.6 (CH); 128.4 (CH); 129.4 (CH); 135.2 (C); 176.0 (C); 192.7 (C); (keto form): 20.3 (CH_2); 21.1 (CH_2); 49.3 (CH_2); 60.1 (CH); 69.4 (CH_2); 126.9 (CH); 128.3 (CH); 129.1 (CH); 134.9 (C); 172.7 (CO); 176.5 (CO). Anal. calc. for $C_{13}H_{14}O_3$ (218.09): C 71.54, H 6.47; found: C 71.66, H 6.49.

*3-Benzoyl-4,5-dihydrofuran-2(3*H*)-one* (**37**). A soln. of γ-butyrolactone (1.00 g, 11.6 mmol) in THF (15 ml) with little EtOH (4 drops) was slowly added to a stirred mixture of NaH (1.5 equiv.) and PhCOOEt (11.6 mmol) in THF (15 ml) at 0°. After stirring for 2 h at 5° and overnight at r.t., the reaction was quenched by addition of ice H_2O (20 ml), and the mixture was extracted with Et_2O (2 × 10 ml). The org. phase was washed with H_2O (10 ml) and sat. NaCl (2 × 10 ml), dried ($MgSO_4$), filtered, and the filtrate was evaporated. CC (AcOEt/hexanes 1:1) gave **37** (1.96 g, 88%). Colorless solid. ^{1}H-NMR (300 MHz): (keto form, 95%): 2.47–2.55 (*m*, 1 H); 2.82–2.89 (*m*, 1 H); 4.41–4.60 (*m*, 3 H); 7.47–7.53 (*m*, 2 arom. H); 7.59–7.62 (*m*, 1 arom. H); 8.06–8.09 (*m*, 2 arom. H); (enol, 5%): 7.59–7.62 (*m*, 2 arom. H); 11.97 (*s*, OH). ^{13}C-NMR (75 MHz): (keto form): 25.7; 47.7; 66.7; 128.5; 129.5; 133.8; 135.2; 172.5; 192.7; (enol): 25.9; 66.1; 107.3; 127.2; 128.1; 130.5; 163.7; 191.4. Anal. calc. for $C_{11}H_{10}O_3$ (190.06): C 69.46, H 5.30; found: C 69.53, 5.32. Known compound, CAS No. 21034-21-9.

*3-(2-Phenylacetyl)-4,5-dihydrofuran-2(3*H*)-one* (**38**). A soln. of γ-butyrolactone (1.00 g, 11.6 mmol) in THF (15 ml) with little EtOH (4 drops) was slowly added to a stirred mixture of NaH (1.5 equiv.) and

ethyl phenylacetate (11.6 mmol) in THF (15 ml) at 0°. After stirring for 2 h at 5° and overnight at r.t., the reaction was quenched by addition of ice H_2O (20 ml), and the mixture was extracted with Et_2O (2 × 10 ml). The org. phase was washed with H_2O (10 ml) and sat. NaCl (2 × 10 ml), dried ($MgSO_4$), filtered, and the filtrate was evaporated. CC (AcOEt/hexanes 1:1) gave **38** (1.42 g, 62%). Colorless solid. ^{1}H-NMR (300 MHz): (keto form, 95%): 2.15–2.25 (*m*, 1 H); 2.71–2.80 (*m*, 1 H); 3.79 (*dd*, *J* = 9.0, 6.9, 1 H); 4.09 (*s*, 1 H); 4.37–4.39 (*m*, 2 H); 7.24–7.34 (*m*, 5 arom. H); (enol, 5%): 11.12 (*s*, OH). ^{13}C-NMR (75.46 MHz): (keto form): 23.8; 48.7; 50.8; 67.4; 127.3; 128.6; 129.6; 133.0; 172.5; 200.0. EI-MS: 204 (12, M^+), 105 (100). Anal. calc. for $C_{12}H_{13}O_3$ (204.08): C 70.57, H 5.92; found: C 69.79, H 5.88. Known compound, CAS No. 34604-99-4.

*3-(2,2-Diphenylacetyl)-4,5-dihydrofuran-2(3*H*)-one* (**39**). A soln. of γ-butyrolactone (1.00 g, 11.6 mmol) in THF (15 ml) with little EtOH (4 drops) was slowly added to a stirred mixture of NaH (1.5 equiv.) and ethyl diphenylacetate (11.6 mmol) in THF (15 ml) at 0°. After stirring for 2 h at 5° and overnight at r.t., the reaction was quenched by addition of ice H_2O (20 ml), and the mixture was extracted with Et_2O (2 × 10 ml). The org. phase was washed with H_2O (10 ml) and sat. NaCl (2 × 10 ml), dried ($MgSO_4$), filtered, and the filtrate evaporated. CC (AcOEt/hexanes 1:1) gave **39** (1.85 g, 56%). Colorless solid. ^{1}H-NMR (300 MHz): 2.17–2.25 (*m*, 1 H); 2.71–2.83 (*m*, 1 H); 3.83 (*dd*, *J* = 9.2, 7.1, 1 H); 4.19–4.25 (*m*, 1 H); 4.37–4.40 (*m*, 1 H); 5.88 (*s*, 1 H); 7.18–7.42 (*m*, 10 H); (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 24.1 (CH_2); 51.3 (CH_2); 62.7 (CH); 67.3 (CH); 127.2 (CH); 127.4 (CH); 128.3 (CH); 128.6 (CH); 129.0 (CH); 129.3 (CH); 136.4 (CH); 137.6 (C); 172.6 (CO); 200.6 (CO). Anal. calc. for $C_{18}H_{16}O_3$ (280.11): C 77.12, H 5.75; found: C 77.06, H 5.97.

(3β)-Cholest-5-en-3-yl 2-Methyl-3-oxobutanoate (**40**). A mixture of cholesterol (2.26 g, 5.84 mmol), **15** (1.596 g, 11.1 mmol), toluene (5 ml) and DMAP (40 mg) was refluxed for 1 d at 140°. Solvents were removed in a rotary evaporator, and the residue was dissolved in ^{t}BuOMe (10 ml). After addition of pentane (10 ml) and standing for 2 d at −20°, mother liquor was decanted, and the colorless crystals were washed with little ^{t}BuOMe and pentane to give **40** (1.851 g, 65%). Faint yellow powder. R_f (^{t}BuOMe/hexane 1:10) 0.31. M.p. 134.6–136.3°. $[\alpha]_D = -26.4$ (*c* = 1.345, CH_2Cl_2). ^{1}H-NMR (300 MHz): 0.67 (*s*, 3 H); 0.86 (*d*, *J* = 6.8, 6 H); 0.9–1.69 (*m*, 21 H); 0.91 (*d*, *J* = 6.6, 3 H); 1.01 (*s*, 3 H); 1.33 (*d*, *J* = 7.1, 3 H); 1.76–2.06 (*m*, 5 H); 2.24 (*s*, 3 H); 2.32 (br. *d*, *J* = 7.8, 2 H); 3.46 (*q*, *J* = 7.1, 1 H); 4.59–4.73 (*m*, 1 H); 5.38 (*d*, *J* = 4.8, 1 H); (enol, 2%): 12.76 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 11.8 (Me); 12.7 (Me); 18.7 (Me); 19.3 (Me); 21.0 (CH_2); 22.5 (Me); 22.8 (Me); 23.8 (CH_2); 24.3 (CH_2); 27.6*[6]) (CH_2); 28.0 (Me); 28.2 (CH_2); 28.3 (CH); 31.8 (CH); 31.9 (CH_2); 35.8 (CH); 36.2 (CH_2); 36.5 (C); 36.9 (CH_2); 37.9* (CH_2); 39.5 (CH_2); 39.7 (CH_2); 42.3 (C); 50.0 (CH); 53.9 (CH); 56.1 (CH); 56.7 (CH); 75.0 (CH); 122.9 (CH); 139.3* (C); 170.0 (CO); 203.7 (CO). HR-MALDI-MS: 507.380 ($[M + Na]^+$; calc. 507.381). Anal. calc. for $C_{32}H_{52}O_3$ (484.76): C 79.29, H 10.81; found: C 79.26, H 10.87.

*2-[(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]ethyl 2-Methyl-3-oxobutanoate* (**41**). In a round-bottom flask with mounted *Vigreux* head (12 cm, air-cooling) open to air, a mixture of 2-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)ethanol (nopol; 6.547 g, 39.4 mmol; *Fluka*), **15** (6.49 g, 45 mmol), and DMAP (34 mg) was refluxed in toluene (7 ml) for 2 d (at *ca.* 140°). After evaporation, the crude was separated by CC (^{t}BuOMe/hexane 1:10), and the product was dried in high vacuum (50°, bulb-to-bulb) to give **41** (7.907 g, 76%). Colorless oil. R_f (^{t}BuOMe/hexane 1:5) 0.45. $[\alpha]_D = -29.0$ (*c* = 2.195, MeOH; after 1 d of equilibration). ^{1}H-NMR (300 MHz): 0.82 (*s*, 3 H); 1.13*[7]) (*d*, *J* = 8.6, 1 H); 1.27 (*s*, 3 H); 1.33* (*d*, *J* = 7.1, 3 H); 2.00–2.17 (*m*, 2 H); 2.19–2.26 (*m*, 2 H); 2.24* (*s*, 3 H); 2.26–2.40 (*m*, 3 H); 3.49 (*q*, *J* = 7.1, 1 H); 4.08–4.23 (*m*, 2 H); 5.26–5.34 (*m*, 1 H); (enol, 12.6%): 0.83 (*s*, 3 H); 1.15 (*d*, *J* = 8.6, 1 H); 1.27 (*s*, 3 H); 1.73 (*m*, 3 H); 1.99 (*m*, 3 H); 12.66 (*q*, *J* ≈ 1, 1 H). ^{13}C-NMR (75.5 MHz): 12.6* (Me); 21.0 (Me); 26.1 (Me); 28.4 (Me); 31.2 (CH_2); 31.5 (CH_2); 35.7 (CH_2); 40.6 (CH); 45.5* (CH); 53.5* (CH); 63.3* (CH_2); 118.9* (CH); 118.9* (CH); 143.6* (C); 170.4 (CO); 203.4

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[6]) The product is a 1:1 mixture of diastereoisomers with almost identical spectroscopic properties. In the ^{13}C-NMR spectrum, only the chemical shifts designated with * show separation of signals by *ca.* 0.1 ppm.

[7]) ^{1}H- and ^{13}C-NMR data are given for a single compound, although two diastereoisomers were present (ratio 1:1). Resonaces designated with * showed separated peaks for individual diastereoisomers ($\Delta\delta < 1$ Hz in ^{1}H-NMR, < 5 Hz in ^{13}C-NMR).

(CO); (enol): 11.1 (Me); 18.8 (Me); 31.3 (CH_2); 31.6 (CH_2); 35.9 (CH_2); 40.6 (CH); 45.6 (CH); 62.6 (CH_2); 118.8 (CH); 118.8 (CH); 144.1 (C); 171.3 (C). EI-MS: 264 (0.04, M^+), 105 (100). Anal. calc. for $C_{16}H_{24}O_3$ (264.36): C 72.69, H 9.15; found: C 72.62, H 9.08.

*(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)cyclohexyl 2-Methyl-3-oxobutanoate* (**42**). (−)-(1*R*)-Menthol (4.502 g, 28.8 mmol; *Fluka*, ee >99%), **15** (5.05 g 35 mmol), and DMAP (24 mg) were refluxed in toluene (7 ml) for 4 d (bath *ca.* 140°), using an open *Vigreux* head with air-cooling (release of EtOH vapors). After evaporation, the residue was separated by CC (^{t}BuOMe/hexane 1:10). The product fractions were distilled (bulb-to-bulb, 120°/0.02 mbar). After a pre-run (1.477 g (20%); >90% purity by NMR), a main fraction of 4.067 g (56%) of pure **42** was obtained. Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.2–0.3. $[\alpha]_D = -71.6$ ($c = 2.065$, MeOH; after 1 d of equilibration). ^{1}H-NMR (300 MHz): (2 diastereomers, 1:1[8])): 0.76, 0.76 (*d*, *J* = 7.0, 3 H); 0.80–0.95 (*m*, 1 H); 0.89, 0.89 (2*d*, *J* = 7.0, 3 H); 0.91 (*d*, *J* = 6.6, 3 H); 0.93–1.15 (*m*, 2 H); 1.33, 1.34 (2*d*, *J* = 7.1, 3 H); 1.35–1.59 (*m*, 2 H); 1.64–1.75 (*m*, 2 H); 1.78–1.94 (*m*, 1 H); 1.96–2.04 (*m*, 1 H); 2.23, 2.23 (2*s*, 3 H); 3.47, 3.49 (2*q*, *J* = 7.2, 1 H); 4.72, 4.73 (2*td*, *J* = 10.9, 4.2, 1 H); (enol, 12%): 0.77 (*d*, *J* = 7.0, 3 H); 0.90 (*d*, *J* = 7.0, 3 H); 1.73 (*q*, *J* = 0.7, 3 H); 2.00 (*quint.*, *J* = 0.7, 3 H); 4.75 (*td*, *J* ≈ 11, 4.4, 1 H); 12.78 (*q*, *J* = 0.7, 1 H). ^{13}C-NMR (75.5 MHz): (2 diastereomers): 12.6, 12.7 (Me); 15.9, 16.1 (Me); 20.6, 20.7 (Me); 21.9, 22.0 (Me); 23.1, 23.3 (CH_2); 26.0, 26.2 (CH); 28.0, 28.0 (Me); 31.3 (CH); 34.1 (CH_2); 40.4, 40.5 (CH_2); 46.8, 46.8 (CH); 53.8, 54.0 (CH); 75.3, 75.3 (CH); 170.1, 170.1 (C); 203.4, 203.5 (C); (enol, selected signals): 11.3 (Me); 16.5 (Me); 18.8 (Me); 22.0 (Me); 23.6 (CH_2); 26.4 (Me); 31.3 (CH); 34.2 (CH_2); 41.0 (CH_2); 47.0 (CH); 74.1 (CH); 95.2 (C); 171.1 (C); 173.0 (C). EI-MS: 254 (0.1, M^+), 95 (100). Anal. calc. for $C_{15}H_{26}O_3$ (254.37): C 70.83, H 10.30; found: C 70.90, H 10.34.

*(1*S*,2*R*,5*S*)-5-Methyl-2-(propan-2-yl)cyclohexyl 2-Methyl-3-oxobutanoate* (**43**). In a round bottom flask with a *Vigreux* head (12 cm, air-cooling) open to air, a mixture of (+)-(1*S*)-menthol (3.13 g, 20 mmol; *Fluka*, ee >97%), **15** (3.61 g, 25 mmol), and DMAP (30 mg) was refluxed for 2 d in toluene (5 ml; bath *ca.* 140°). Solvents were removed with a rotary evaporator and the residue was purified by CC (^{t}BuOMe/hexane 1:15) to give **43** (4.746 g, 93%). Colorless liquid. Anal. data of **43** are identical to those of **42**. $[\alpha]_D = +70.3$ ($c = 1.955$, MeOH; after 1 d of equilibration; value varies by mutarotation). Anal. calc. for $C_{15}H_{26}O_3$ (254.37): C 70.83, H 10.30; found: C 70.99, H 10.39.

*(1*R*)-2-Methoxy-2-oxo-1-phenylethyl 2-Methyl-3-oxopentanoate* (**44**). Compound **75** (1.68 g, 15.0 mmol) was added dropwise with stirring at 0° to a soln. of methyl (*R*)-mandelate (2.135 g, 12.85 mmol) and 1*H*-imidazole (0.885 g, 13.0 mmol) in CH_2Cl_2 (5 ml). After 1 h stirring, TFA (1.0 ml, 13.0 mmol) was added at 0°. The mixture was stirred overnight with warming to r.t. Workup with ^{t}BuOMe/H_2O, washing the org. phase with HCl (0.2M) and H_2O, followed by evaporation, gave a crude, which was purified by CC (^{t}BuOMe/hexane 1:10–1:5) to give **44** (3.041 g, 85%). Colorless liquid. R_f (^{t}BuOMe/hexane 1:5) 0.20. $[\alpha]_D = -99.1$ ($c = 2.51$, MeOH; 1 d of equilibration). ^{1}H-NMR (250 MHz): (2 diastereomers, 1:1): 1.05 (*t*, *J* = 7.3, 3 H); 1.11 (*t*, *J* = 7.2, 3 H); 1.38 (*d*, *J* = 3.9, 3 H); 1.41 (*d*, *J* = 4.0, 3 H); 2.52 (*dq*, *J* = 18.2, 7.2, 1 H); 2.63 (*dq*, *J* = 18.2, 7.3, 1 H); 2.70 (*dq*, *J* = 18.2, 7.3, 1 H); 2.78 (*dq*, *J* = 18.2, 7.2, 1 H); 3.66 (*q*, *J* = 7.2, 1 H); 3.69 (*q*, *J* = 7.1, 1 H); 3.72 (*s*, 3 H); 3.73 (*s*, 3 H); 5.95 (*s*, 1 H); 5.96 (*s*, 1 H); 7.35–7.53 (*m*, 2 × 5 H); (enol, 5%): 1.16 (*t*, *J* = 7.5, 3 H); 1.87 (*s*, 3 H); 2.35 (*qd*, *J* = 7.4, 1.0, 2 H); 3.73 (*s*, 3 H); 5.98 (*s*, 1 H); 12.38 (*t*, *J* = 1.0, 1 H), aromatic H obscured. ^{13}C-NMR (62.9 MHz): (2 diastereomers): 7.6 (Me); 7.6 (Me); 12.7 (Me); 12.8 (Me); 34.5 (CH_2); 34.8 (CH_2); 52.2 (CH); 52.4 (Me); 52.6 (CH); 74.9 (CH); 75.0 (CH); 127.5 (CH); 127.5 (CH); 128.8 (CH); 128.8 (CH); 129.3 (CH); 129.4 (CH); 133.1 (C); 133.2 (C); 168.8 (C); 168.9 (C); 170.0 (C); 170.1 (C); 205.3 (C); 205.5 (C); (enol) 10.6; 10.7; 25.8; 74.2; 127.4; 128.7; 129.1; 169.4; 177.5. EI-MS: 278 (0.6, M^+), 57 (100). Anal. calc. for $C_{15}H_{18}O_5$ (278.30): C 64.74, H 6.52; found: C 64.59, H 6.38.

S-*Ethyl 2-Methyl-3-oxo-3-phenylpropanethioate* (**45**). Prepared from EtSH (0.11 ml, 1.5 mmol), **66** (0.309 g, 1.73 mmol), and **67** (0.238 g, 1.29 mmol) in MeCN (1 ml) at 0° by slow addition of *N*,*N*-dimethylaniline (0.20 ml, 1.6 mmol), warming to r.t., and stirring for 20 h. After workup with H_2O/

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[8]) The ^{1}H-NMR spectrum of the keto form is interpreted as a single compound. In cases where individual signals for the diastereoisomers are separated, two values for the chemical shift are given. Known compound: [51][52]. Literature value of $[\alpha]_D = -69$ ($c = 2$, EtOH, after 1 d) [52] depends on a mutarotation.

^{t}BuOMe, washing the org. phase with HCl (0.5M) (2×) and H_2O (1×), drying (Na_2SO_4), and evaporation, CC (^{t}BuOMe/hexane 1:20–1:15) of the residue gave **45** (0.144 g, 44%). Oil. R_f 0.21 (^{t}BuOMe/hexane 1:10). ^{1}H-NMR (250 MHz): 1.19 (*t*, *J* = 7.5, 3 H); 1.52 (*d*, *J* = 7.5, 3 H); 2.87 (*q*, *J* = 7.5, 2 H); 4.63 (*q*, *J* = 7.5, 1 H); 7.42–7.48 (*m*, 2 H); 7.54–7.56 (*m*, 1 H); 7.97–8.02 (*m*, 2 H); (enol, 12.9%): 1.32 (*t*, *J* = 7.5, 3 H); 1.94 (*s*, 3 H); 2.96 (*q*, *J* = 7.5, 2 H); 13.90 (*s*, OH). ^{13}C-NMR (75.5 MHz): 14.5 (Me); 14.9 (Me); 23.8 (CH_2); 56.7 (CH); 128.8 (CH); 128.9 (CH); 133.7 (CH); 136.1 (C, 4); 195.1 (C); 196.8 (C). EI-MS: 222 (3.8, M^+), 105 (100). Anal. calc. for $C_{12}H_{14}O_2S$ (222.30): C 64.83, H 6.35; found: C 64.81, H 6.38.

S-*Benzyl 2-Methyl-3-oxo-3-phenylpropanethioate* (**46**). Prepared from $PhCH_2SH$ (0.371 g, 2.99 mmol), **66** (0.800 g, 4.49 mmol), and **67** (0.277 g, 1.50 mmol) in MeCN (2.5 ml) at 0° by slow addition of *N,N*-dimethylaniline (0.453 g, 3.7 mmol), stirring for 2 h, warming to r.t., and stirring overnight. After workup with H_2O/^{t}BuOMe, the org. phase was washed with HCl (0.5 m) (2×) and H_2O (1×), and evaporated. CC (^{t}BuOMe/hexane 1:20) of the residue gave **46** (0.603 g, 71%). Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.40. ^{1}H-NMR (250 MHz): 1.55 (*d*, *J* = 7.0, 3 H); 4.13 (*s*, 2 H); 4.65 (*q*, *J* = 7.0, 1 H); 7.20–7.29 (*m*, 5 H); 7.41–7.50 (*m*, 2 H); 7.55–7.62 (*m*, 1 H); 7.96–8.01 (*m*, 2 H); (enol, 3%): 1.95 (*s*, 3 H); 4.24 (*s*, 2 H); 13.80 (*s*, 1 H). ^{13}C-NMR (62.9 MHz): 14.9 (Me); 33.7 (CH_2); 56.4 (CH); 127.5 (CH); 128.8 (CH); 128.8 (CH); 128.9 (CH); 128.9 (CH); 133.7 (CH); 136.0 (C); 137.0 (C); 194.9 (CO); 196.2 (CO). EI-MS: 284 (4, M^+), 105 (100). Anal. calc. for $C_{17}H_{16}O_2S$ (284.38): C 71.80, H 5.67; found: C 71.80, H 5.82.

S-*Benzyl 2-Methyl-3-oxobutanethioate* (**47**). Prepared from $PhCH_2SH$ (0.376 g, 3.03 mmol), **66** (0.549 g, 4.73 mmol), and **67** (0.279 g, 1.51 mmol) in MeCN (2.5 ml) at 0° by slow addition of *N,N*-dimethylaniline (0.459 g, 3.79 mmol), stirring for 2 h, warming to r.t., and stirring overnight. After workup with H_2O/^{t}BuOMe and washing the org. phase with H_2O (1×), HCl (0.5M; 2×), and H_2O (1×), evaporation, CC (^{t}BuOMe/hexane 1:20) of the residue gave **47** (0.598 g, 89%). Slightly yellow oil. ^{1}H-NMR (300 MHz): 1.39 (*d*, *J* = 7.0, *Me*CH); 2.20 (*s*, 3 H); 3.74 (*q*, *J* = 7.1, 1 H); 4.17 (*s*, 2 H); 7.24–7.34 (*m*, 5 H); (enol, 7%): 1.85 (*s*, 3 H); 2.01 (*s*, 3 H); 3.87 (*s*, 2 H); 13.60 (*s*, OH). ^{13}C-NMR (62.9 MHz): 13.5 (Me); 28.4 (Me); 33.6 (CH); 61.9 (CH_2); 127.5 (CH); 128.7 (CH); 128.8 (CH); 136.8 (C); 196.1 (C); 202.5 (C). EI-MS: 222 (8, M^+), 91 (100). Anal. calc. for $C_{12}H_{14}O_2S$ (222.31): C 64.83, H 6.35; found: C 64.98, H 6.21. Known compound, CAS No. 131309-91-6.

S-*Phenyl 2-Methyl-3-oxopentanethioate* (**48**). To PhSH (0.30 ml, 3.0 mmol), and 1*H*-imidazole (0.255 g, 3.75 mmol) in CH_2Cl_2 (1 ml) at 0°, **75** (0.494 g, 4.41 mmol) was added dropwise. After cooling to −7°, TFA (0.37 ml, 4.8 mmol) was slowly added and the mixture was stirred for 3 d at r.t. Additional CH_2Cl_2 (5 ml) was added, and the mixture was heated to 50° for 20 h. The mixture was diluted with ^{t}BuOMe, washed with sat. NaCl (3×), dried ($MgSO_4$), and evaporated. CC (acetone/hexane 1:30–1:2) gave **48** (0.351 g, 54%). Colorless liquid. R_f (^{t}BuOMe/hexane 1:10) 0.24. ^{1}H-NMR (300 MHz): 1.09 (*t*, *J* = 7.2, 3 H); 1.45 (*d*, *J* = 7.2, 3 H); 2.48–2.74 (*m*, 2 H); 3.85 (*q*, *J* = 7.2, 1 H); 7.38–7.44 (*m*, 5 H); (enol, 7.1%): 1.17 (*t*, *J* = 7.6, 3 H); 2.34 (*q*, *J* = 7.6, 2 H); 13.48 (*s*, OH). ^{13}C-NMR (75.5 MHz): 7.9 (Me); 13.9 (Me); 34.9 (CH_2, 2); 61.1 (CH); 127.1 (C, 8); 129.5 (CH); 129.9 (CH); 134.6 (CH); 195.2 (C); 205.2 (C). EI-MS: 222 (7.4, M^+), 57 (100). Anal. calc. for $C_{12}H_{14}O_2S$ (222.30): C 64.83, H 6.30; found: C 64.63, H 6.30.

N,N-*Dibenzyl-2-methyl-3-oxopentanamide* (**49**). To a soln. of **75** (3.65 g, 32.6 mmol) in MeCN (10 ml), Bn_2NH (6.15 ml, 32 mmol) was added dropwise at 0°. After stirring 1 d at r.t., the reaction was quenched with sat. $NaHCO_3$, and the mixture was extracted with ^{t}BuOMe. After washing the org. phase with sat. NaCl and evaporation, the residue was purified by CC (^{t}BuOMe/hexane 1:5) to give **49** (9.111 g, 92%). Faint-yellow liquid. R_f (^{t}BuOMe/hexane 1:2) 0.29. ^{1}H-NMR (250 MHz): 1.02 (*t*, *J* = 7.2, 3 H); 1.42 (*d*, *J* = 7.0, 3 H); 2.43 (*dq*, *J* = 18.2, 7.2, 1 H); 2.57 (*dq*, *J* = 18.2, 7.3, 1 H); 3.69 (*q*, *J* = 7.0, 1 H); 4.37 (*d*, *J* = 17.3, 1 H); 4.42 (*d*, *J* = 14.6, 1 H); 4.58 (*d*, *J* = 17.1, 1 H); 4.86 (*d*, *J* = 14.8, 1 H); 7.12–7.43 (*m*, 10 H); no enol detected. ^{13}C-NMR (62.9 MHz): 7.6 (Me); 14.1 (Me); 33.0 (CH_2); 48.6 (CH_2); 50.1 (CH_2); 50.8 (CH); 126.2 (CH); 127.5 (CH); 127.8 (CH); 128.1 (CH); 128.6 (CH); 129.0 (CH); 136.2 (C); 137.0 (C); 171.4 (CO); 207.6 (CO). EI-MS: 309 (1, M^+), 106 (100). Anal. calc. for $C_{20}H_{23}NO_2$ (309.402): C 77.64, H 7.49, N 4.53; found: C 77.61, H 7.45, N 4.59.

2-Methyl-3-oxo-N,N-*diphenylpentanamide* (**50**). To a soln. of Ph_2NH (3.485 g, 20.6 mmol) and 1*H*-imidazole (1.50 g, 22.0 mmol) in CH_2Cl_2 (5 ml) at 0°, **75** (2.80 g, 25 mmol) was added dropwise. After

stirring 1 h, TFA (1.68 ml, 22 mmol) was added dropwise to the mixture, and stirring was continued overnight at r.t. Evaporation, followed by CC (^{t}BuOMe/hexane 1:3–1:1) and drying (high vacuum/40°, bulb-to-bulb) gave **50** (5.394 g, 93%). Viscous liquid (solidified to an almost colorless mass after two weeks). R_f (^{t}BuOMe/hexane 1:1) 0.30. M.p. 59.5–61.0°. ^{1}H-NMR (300 MHz): 0.95 (*t*, *J* = 7.2, 3 H); 1.35 (*d*, *J* = 7.0, 3 H); 2.16 (*dq*, *J* = 18.1, 7.2, 1 H); 2.40 (*dq*, *J* = 18.2, 7.3, 1 H); 3.66 (*q*, *J* = 7.0, 1 H); 7.06–7.53 (*m*, 10 H). ^{13}C-NMR (75.5 MHz): 7.5 (Me); 13.8 (Me); 33.9 (CH_2); 51.5 (CH); 126.1 (br., 2 CH); 128.2 (br., CH); 128.8 (br., CH); 128.9 (br., CH); 129.9 (br., CH); 142.3 (C); 170.7 (CO); 207.2 (CO). EI-MS: 281 (6, M^+), 169 (100). Anal. calc. for $C_{18}H_{19}NO_2$ (281.35): C 76.84, H 6.81, N 4.98; found: C 76.74, H 6.78, N 4.92.

2-Benzoylcyclopentanone (**51**) *and 2-Benzoylcyclohexanone* (**52**). Synthesized as described in [43].

2-Methyl-1-phenylbutane-1,3-dione (**53**). To a soln. of 1-phenylbutane-1,3-dione (1.00 g, 6.12 mmol) and K_2CO_3 (1.30 g, 12.3 mmol) in acetone, MeI was added (0.96 g, 6.78 mmol). After refluxing (4 h), the mixture was filtered, and the solvents were evaporated. The resulting oil was purified by CC (acetone/hexane 1:7) to give **53** (0.97 g, 90%). Colorless oil. ^{1}H-NMR (250 MHz): 1.40 (*d*, *J* = 7.0, 3 H); 2.12 (*s*, 3 H); 4.47 (*q*, *J* = 7.0, 1 H); 7.40–7.47 (*m*, 2 H); 7.52–7.55 (*m*, 1 H); 7.91–7.95 (*m*, 2 H); (enol, 4%): 1.88 (*s*, 3 H); 2.21 (*s*, 3 H); 7.51–7.90 (*m*, 5 H); 16.59 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 13.5 (Me); 27.9 (CH); 56.5 (Me); 128.6 (CH); 128.8 (CH); 133.6 (CH); 135.8 (C); 197.3 (CO); 204.9 (CO); (enol): 13.9 (Me); 25.8 (Me); 104.9 (C); 127.9 (CH); 128.4 (CH); 130.2 (CH); 136.1 (C); 196.4 (CO); 199.1 (CO). EI-MS: 176 (2.7, M^+), 105 (100). Anal. calc. for $C_{11}H_{12}O_2$ (176.08): C 74.98, H 6.86; found: C 74.80, H 6.92. Known compound, CAS-RN 6668–24–2.

*2-Acetyl-3,4-dihydronaphthalen-1(2*H*)-one* (**54**). Synthesized as described in [43].

*2-Benzoyl-3,4-dihydronaphthalen-1(2*H*)-one* (**55**). Synthesized as described in [43].

2-Benzoylcyclododecanone (**56**). a) *[(Cyclododec-1-en-1-yl)oxy](trimethyl)silane* [53]: To a soln. of cyclododecanone (18.23 g, 100 mmol) and EtN^iPr_2 (18.2 ml, 106 mmol) in CH_2Cl_2 (100 ml) was added dropwise with stirring at 0° TMSOTf (19.0 ml, 105 mmol). The mixture was stirred and warmed to r.t. overnight. Pentane (100 ml) was added, and the soln. was filtered from the precipitated salt ($HNEt^iPr_2$)OTf. Evaporation and distillation of the residue in high vacuum gave **56** (23.346 g, 92%). Colorless liquid. ^{1}H-NMR (300 MHz): 0.20 (*s*, 9 H); 1.26–1.41 (*m*, 12 H); 1.41–1.55 (*m*, 4 H); 2.00–2.10 (*m*, 4 H); 4.57 (*t*, *J* = 7.4, 1 H). ^{13}C-NMR (75.5 MHz): 0.6 (Me); 23.6 (CH_2); 24.6 (CH_2); 24.7 (CH_2); 24.8 (CH_2); 24.8 (CH_2); 25.8 (CH_2); 26.0 (CH_2); 26.3 (CH_2); 26.5 (CH_2); 36.0 (CH_2); 110.9 (CH); 149.4 (C).

b) *Compound* **56** [53]. To $TiCl_4$ (2.20 ml, 20 mmol) in CH_2Cl_2 (20 ml) at −80°, PhCOCl (2.3 ml, 20 mmol) was added dropwise. To the resulting yellow suspension was added dropwise [(cyclododec-1-en-1-yl)oxy](trimethyl)silane (3.65 g, 20 mmol) in CH_2Cl_2 (10 ml; (color change to pink). The cooling bath was removed, and the mixture was stirred 2 h at r.t. The dark red soln. was diluted with Et_2O (200 ml), and the reaction was quenched by addition of sat. $NaHCO_3$ (200 ml). The org. phase was washed twice with H_2O, dried (Na_2SO_4), and evaporated. The resulting solid (3.904 g) still contained some PhCOCl. It sublimed in high vacuum (100–120°/0.003 mbar) to give **56** (2.828 g, 49%). Colorless crystals. R_f (^{t}BuOMe/hexane 1:5) 0.50. ^{1}H-NMR (300 MHz): 1.15–1.49 (*m*, 15 H); 1.66–1.81 (*m*, 1 H); 1.90–2.05 (*m*, 2 H); 2.24–2.40 (*m*, 1 H); 2.88–3.03 (*m*, 1 H); 4.47 (*dd*, *J* = 11.7, 2.9, 1 H); 7.42–7.50 (*m*, 2 H); 7.54–7.61 (*m*, 1 H); 7.95–8.01 (*m*, 2 H); (enol, 2%): 17.06 (*s*, 1 H). ^{13}C-NMR (75.5 MHz): 21.6 (CH_2); 22.2 (CH_2); 22.8 (CH_2); 23.2 (CH_2); 23.9 (CH_2); 25.7 (CH_2); 26.0 (CH_2); 27.1 (CH_2); 36.2 (CH_2); 63.4 (CH); 128.5 (CH); 128.7 (CH); 133.5 (CH); 136.1 (C); 196.1 (CO); 207.5 (CO). Known compound: [54].

13. *Additional Substrates and Fluorination Products* (not discussed in the main text). For some of the following substrates, the synthesis is discussed in *Chapt. 3* of the theoretical part, but no data on asymmetric fluorination were obtained, because no conditions for chiral analysis of the fluorination products could be found.

(Anthracen-9-yl)methyl 2-Methyl-3-oxobutanoate (**60**). A mixture of **15** (3.0 g, 21 mmol) and (anthracen-9-yl)methanol (2.083 g, 10 mmol) in a 25-ml flask with mounted open *Vigreux* column was heated to 160°, and the temp. was increased to 200° over 3 h. The column was removed and distillation head mounted instead. Volatiles were removed by distillation at 210° external temp. at atmospheric pressure, and then in a bulb-to-bulb oven at 100°/0.005 mbar. The residue was purified by CC (^{t}BuOMe/hexanes 1:10) to give a **60** (1.887 g, 62%). Bright yellow, crystalline solid R_f (^{t}BuOMe/hexane 1:10) 0.21.

M.p. 69.5–70.5°. ^{1}H-NMR (300 MHz): 1.30 (*d*, *J* = 7.2, *Me*CH); 2.04 (*s*, MeCO); 3.47 (*q*, *J* = 7.2, MeC*H*); 6.14 (*d*, *J* = 12.6, 1 H of OCH_2Ar); 6.19 (*d*, *J* = 12.6, 1 H of OCH_2Ar); 7.42–7.49 (*m*, 2 arom. H); 7.51–7.58 (*m*, 2 arom. H); 7.97 (*d*, *J ca.* 9, 2 arom. H); 8.27 (*d*, *J ca.* 9, 2 arom. H); 8.44 (*s*, 1 arom. H); (enol, 0.8%): 12.69 (*s*, OH). ^{13}C-NMR (75.5 MHz): 12.7 (Me); 28.3 (Me); 53.4 (CH); 59.7 (CH_2); 123.6 (CH); 125.1 (CH); 125.4 (C); 126.7 (CH); 129.1 (CH); 129.3 (CH); 130.9 (C); 131.2 (C); 170.1 (C); 203.3 (C). EI-MS: 382 (5, [2 $C_{15}H_{11}$]$^+$), 191 (100). Anal. calc. for $C_{20}H_{18}O_3$ (306.36): C 78.41, H 5.92; found: C 78.23, H 5.93.

(Anthracen-9-yl)methyl 2-Fluoro-2-methyl-3-oxobutanoate (**60F**). Prepared according to *GP 1* using **K2**. The product was of limited stability in soln. and could not be obtained sufficiently pure for analysis. ^{19}F-NMR (188.3 MHz): −157.1 (*qq*, *J*(F,H) = 22.2, 4.4).

Diphenylmethyl 2-Methyl-3-oxobutanoate (**61**). a) *Synthesis by Esterification of 2-Methyl-3-Oxobutanoic acid*. To a stirred mixture of Ph_2CHOH (3.00 g, 16.3 mmol), **66** (2.80 g, *ca.* 24 mmol, partially decomposed), and **67** (1.475 g, 8 mmol) in MeCN (5 ml) at 0°, *N*,*N*-dimethylaniline (2.8 ml, 22 mmol) was slowly added, and the mixture was warmed to r.t. during 2 h with stirring. The reaction was quenched with ^{t}BuOMe and H_2O, the org. phase was washed with aq HCl (0.2M) and H_2O. Evaporation of the org. phase gave an oil containing Ph_2CHOH, which was not separable from the product by CC. Thus, the raw material was dissolved in CH_2Cl_2 (10 ml) and acetylated with Ac_2O (1 ml) in the presence of DMAP (40 mg) by stirring for 1 h at r.t. According to TLC, the starting alcohol had been completely transformed to acetate (^{t}BuOMe/hexane 1:10, R_f 0.39). After extraction with sat. $NaHCO_3$ and ^{t}BuOMe, washing with H_2O, and evaporation of the org. phase, the residue was separated by CC (^{t}BuOMe/hexane 1:15) to give **61** (4.037 g, 88%). Colorless oil that crystallized after a few days.

b) *Synthesis by Transesterification.* Ph_2CHOH (5.425 g, 29.4 mmol), **15** (6.44 g, 44.7 mmol), and DMAP (80 mg, 0.66 mmol, 2 mol-%) were stirred in an open 100 ml round bottom flask for 15 h at 130°[9]). After cooling to r.t., the resulting brown oil was dissolved in CH_2Cl_2 (5 ml) and acetylated by addition of Ac_2O (2 ml) and DMAP (40 mg). After stirring for 1 h at r.t., SiO_2 and sufficient CH_2Cl_2 were added, and the mixture was carefully evaporated to dryness. The solid was placed on a chromatography column, and the product was eluted (^{t}BuOMe/hexane 1:15) to give (after drying for 10 h at 40° with stirring) **61** (4.205, 51%). Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.20. M.p. 28–30°. ^{1}H-NMR (300 MHz): 1.38 (*d*, *J* = 7.1, *Me*CH); 2.14 (*s*, MeCO); 3.60 (*q*, *J* = 7.1, MeC*H*); 6.92 (*s*, OC*H*Ph_2); 7.24–7.40 (*m*, 10 arom. H); (enol, 10%): 1.90 (*q*, *J* = 0.7, Me); 2.01 (*quint.*, *J* = 0.7, Me); 6.93 (*s*, OC*H*Ph_2); 12.53 (*q*, *J* = 0.7, OH). ^{13}C-NMR (75.5 MHz): 12.6; 28.4; 53.8; 77.7; 127.0; 127.0; 128.0; 128.1; 128.5; 128.5; 139.5; 139.5; 169.4; 203.2; (enol): 11.4; 19.0; 126.8; 127.8; 128.5. HR-MALDI-MS: 305.115 ([*M* + Na]$^+$; calc. 305.115). Anal. calc. for $C_{18}H_{18}O_3$ (282.34): C 76.57, H 6.43; found: C 76.59, H 6.48.

Diphenylmethyl 2-Fluoro-2-methyl-3-oxobutanoate (**61F**). Prepared according to *GP 1* from **61** [4] (126.6 mg, 0.448 mmol), **K1** (15.9 mg, 5 mol-%), powdered molecular sieves (3 Å; 100 mg), and sat. F-TEDA in MeCN (3.2 ml, 0.464 mmol). Reaction time < 40 min. Purification by CC (^{t}BuOMe/hexanes 1:15–1:10) gave **61F** (125 mg, 93%). Colorless oil that crystallized on standing. R_f (^{t}BuOMe/hexane 1:10) 0.30. M.p. 74.7–75.2°. $[\alpha]_D$ = +17.8 (*c* = 1.115, MeOH; ee not known). ^{1}H-NMR (300 MHz): 1.71 (*d*, *J*(F,H) = 22.0, MeCF); 2.24 (*d*, *J*(F,H) = 4.5, MeCO); 6.92 (*s*, OC*H*Ph_2); 7.26–7.38 (*m*, 10 arom. H). ^{13}C-NMR (75.5 MHz): 19.7 (*d*, *J*(F,C) = 23); 25.0; 78.9; 97.6 (*d*, *J*(F,C) = 194); 126.8; 126.9; 128.3; 128.3; 128.6; 128.6; 138.9; 138.9; 165.9 (*d*, *J*(F,C) = 26); 201.8 (*d*, *J*(F,C) = 28). ^{19}F-NMR (188.3 MHz): −157.4 (*qq*, *J*(F,H) = 22.0, 4.5). EI-MS: 236 (1), 167 (100). ESI-MS: 318.3 ([*M* + NH_4]$^+$). Anal. calc. for $C_{18}H_{17}FO_3$ (300.32): C 71.99, H 5.71; found: C 72.08, H 5.86.

Ethyl 2-Acetyl-3-methylbutanoate (**62**). Commercially available.

Ethyl 3-Cyclohexyl-2-methyl-3-oxopropanoate (**63**). Ethyl 3-cyclohexyl-3-oxopropanoate (1.00 g, 5.04 mmol) was added to a soln. of Na (195 mg, 8.5 mmol) in EtOH (5 ml). After stirring for 10 min at r.t., MeI (0.32 ml, 5.14 mmol) was added, and the mixture was heated to 60° for 20 h (conversion 30%). Another portion of Na (0.070 g, 3 mmol) was dissolved in the mixture, and MeI (0.50 ml, 8.0 mmol) was added. After stirring for 6 h at 60°, the soln. was evaporated, and the residue was dissolved in H_2O (10 ml). Extraction with AcOEt (3×), washing the org. phases with H_2O, drying (Na_2SO_4), filtration,

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[9]) According to TLC (^{t}BuOMe/hexane 1:5; R_f (Ph_2CHOH) 0.22, R_f (product) 0.27) there was no more reaction progress after 5 h.

and evaporation gave a residue, which was separated by CC (*t*BuOMe/hexane 1:12) to give 447 mg of crude, which contained α,α-dimethylated product as impurity. Another CC (*t*BuOMe/hexane 1:12) gave pure **63** (312 mg, 29%). Colorless oil. R_f (*t*BuOMe/hexane 1:5) 0.65. ^{1}H-NMR (250 MHz): 1.19–1.36 (*m*, 4 H of Cy); 1.26 (*t*, *J* = 7.2, *Me*CH_2O); 1.31 (*d*, *J* = 7.0, CH*Me*); 1.62–1.90 (*m*, 6 H of Cy); 2.49–2.62 (*m*, 1 H of Cy); 3.66 (*q*, *J* = 7.0, C*H*Me); 4.17 (*q*, *J* = 7.2, OCH_2Me); (enol, 2.6%): 12.91 (*s*, OH). ^{13}C-NMR (62.9 MHz): 13.1 (Me); 14.2 (Me); 25.6 (CH_2); 25.8 (CH_2); 25.9 (CH_2); 28.4 (CH_2); 29.0 (CH_2); 50.2 (CH); 51.1 (CH); 61.4 (CH_2); 170.8 (C); 209.2 (C). Known compound, *Beilstein* No. 71911-66-5.

Ethyl 3-Cyclohexyl-2-fluoro-2-methyl-3-oxopropanoate (**63F**). Obtained according to *GP 1* from **K1** (8.0 mg, 11.9 µmol), **63** (48 mg, 0.23 mmol), and F-TEDA (2.0 ml, 0.145M in MeCN; 0.29 mmol). Reaction time: 15 min. CC (AcOEt/hexane 1:6) gave **63F** (48 mg, 92%). Oil. Enantioselectivity with **K1**: 14% ee; with **K2**: 44% ee. Chiral GC (*γ-DEX*, 87°): t_R(minor) 166, t_R(major) 169 min. R_f (*t*BuOMe/hexane 1:5) 0.59. ^{1}H-NMR (250 MHz): 1.15–1.40 (*m*, 6 H of Cy); 1.29 (*t*, *J* = 7.1, *Me*CH_2O); 1.68 (*d*, *J*(F,H) = 22.2, CFMe); 1.74–1.87 (*m*, 4 H of Cy); 2.87–3.02 (*m*, 1 H of Cy); 4.26 (*q*, *J* = 7.1, OCH_2Me). ^{13}C-NMR (62.9 MHz): 14.1 (Me); 20.7 (*d*, *J*(F,C) = 22.8, Me); 25.5 (CH_2); 25.6 (CH_2); 25.8 (CH_2); 28.6 (CH_2); 45.8 (CH); 62.6 (CH_2); 98.0 (*d*, *J*(F,C) = 194.3, CF); 167.3 (*d*, *J*(F,C) = 25.3, C); 207.4 (*d*, *J*(F,C) = 26.5, C). EI-MS: 230 (0.3, M^+), 83 (100).

Benzyl 3-Cyclohexyl-2-methyl-3-oxopropanoate (**64**). A mixture **63** (625 mg, 2.94 mmol) and BnOH (2.5 ml, 24 mmol) was heated to 115° for 1.5 h, followed by heating to 150° for 6.5 h. After evaporation (85–105°/3 mbar), the residue was purified by CC (*t*BuOMe/hexane 1:8) to give **64** (132 mg, 16%). Faint-yellow oil. *Note:* Synthesis not optimized; higher reaction temp. may be necessary. ^{1}H-NMR (250 MHz): 1.04–1.44 (*m*, 4 H of Cy); 1.33 (*d*, *J* = 7.0, *Me*CH); 1.59–1.86 (*m*, 6 H of Cy); 2.42–2.58 (*m*, 1 H of Cy); 3.71 (*q*, *J* = 7.0, MeC*H*); 5.15 (*s*, OCH_2Ph); 7.33–7.35 (*m*, 5 arom. H). ^{13}C-NMR (62.9 MHz): 25.4 (CH_2); 25.7 (CH_2); 25.7 (CH_2); 28.2 (CH_2); 28.8 (CH_2); 50.1; 51.0 (2 CH); 67.0 (CH_2); 128.3 (CH); 128.4 (CH); 128.6 (CH); 135.6 (C); 170.5 (C); 208.7 (C). EI-MS: 274 (0.6, M^+), 83 (100). Anal. calc. for $C_{17}H_{22}O_3$ (274.36): C 74.42, H 8.08, O 17.49; found: C 74.26, H 8.10, O 17.51.

Benzyl 3-Cyclohexyl-2-fluoro-2-methyl-3-oxopropanoate (**64F**). Obtained according to *GP 1* with **K1** (6.4 mg, 9.5 µmol), **64** (52.0 mg, 0.19 mmol), and F-TEDA (0.203 mmol) in MeCN. Reaction time: 3 h. CC (*t*BuOMe/hexane 1:7) gave **64F** (56 mg, quant.). Slightly impure material. R_f (*t*BuOMe/hexane 1:5) 0.43. ^{1}H-NMR (250 MHz): 0.85–1.80 (*m*, 10 H of Cy); 1.69 (*d*, *J*(F,H) = 22.2, CFMe); 5.22 (*s*, OCH_2Ph); 7.32–7.37 (*m*, 5 arom. H). ^{13}C-NMR (62.9 MHz): 20.7 (*d*, *J*(F,C) = 22.8, Me); 20.5 (CH_2); 20.6 (CH_2); 20.7 (CH_2); 28.5 (*d*, *J*(F,C) = 1.5, CH_2); 28.6 (*d*, *J*(F,C) = 1.5, CH_2); 45.7 (CH); 68.0 (CH_2); 98.0 (*d*, *J*(F,C) = 194.9, CF); 128.5 (CH); 128.8 (CH); 128.8 (CH); 134.8 (C); 167.2 (*d*, *J*(F,C) = 25.6, C); 207.1 (*d*, *J*(F,C) = 26.5, C). EI-MS: 292 (1.7, M^+), 83 (100).

Methyl 2-Oxocyclopentanecarboxylate (**65**). Commercial compound.

2-Methyl-3-oxobutanoic acid (**66**). See *Section 12*, *a*, for a synthesis.

2-Methyl-3-oxo-3-phenylpropanoic Acid (**68**). Synthesized analogously to **66** by saponification of the ethyl ester, as described in [55].

(Naphthalen-2-yl)methyl 2-Methyl-3-oxobutanoate (**69**). Et_3N (2.50 ml, 18 mmol) was added dropwise to a stirred mixture of (naphthalen-2-yl)methanol (2.013 g, 12.8 mmol), **66** (1.32 g, 20 mmol), and **67** (1.84 g, 10 mmol) in MeCN (10 ml) at 0°. The mixture was warmed to r.t. during 2 h and stirred 1 d. After workup with *t*BuOMe and H_2O, the org. phase was washed with sat. aq. NaCl and evaporated. Purification of the residue by CC (*t*BuOMe/hexane 1:10–1:5) gave **69** (1.301 g, 40%). Colorless liquid. R_f (*t*BuOMe/hexane 1:5) 0.23. ^{1}H-NMR (300 MHz): 1.37 (*d*, *J* = 7.2, *Me*CH); 2.18 (*s*, *Me*CO); 3.56 (*q*, *J* = 7.2, MeC*H*); 5.32 (*s*, OCH_2Ar); 7.40–7.52 (*m*, 3 arom. H); 7.78–7.86 (*m*, 4 arom. H); (enol, 6.5%): 1.78 (*q*, *J* = 0.6, *Me*C=C); 2.00 (*quint*, *J* = 0.7, *Me*CO); 5.34 (*s*, OCH_2Ar); 12.64 (*q*, *J* = 0.7, OH). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 12.7 (Me); 28.4 (Me); 53.5 (CH); 67.1 (CH_2); 125.7 (CH); 126.3 (CH); 126.3 (CH); 127.5 (CH); 127.6 (CH); 127.9 (CH); 128.4 (CH); 132.7 (C); 133.1 (C); 133.1 (C); 170.3 (C); 203.3 (C); (enol) 11.3 (Me); 18.9 (Me); 66.0 (CH_2); 125.6 (CH); 126.1 (CH); 126.2 (CH); 126.9 (CH); 127.9 (CH); 128.3 (CH). EI-MS: 256 (26, M^+), 141 (100). Anal. calc. for $C_{16}H_{16}O_3$ (256.30): C 74.98, H 6.29; found: C 75.00, H 6.28.

(Naphthalen-2-yl)methyl 2-Fluoro-2-methyl-3-oxobutanoate (**69F**). Prepared according to *GP 1* using **K1**; 80% yield. No conditions for HPLC analysis were found in the course of the present work. R_f (*t*BuOMe/hexane 1:5) 0.50. $[\alpha]_D = +11.5$ (*c* = 1.26, MeOH; ee not known). ^{1}H-NMR (300 MHz): 1.71 (*d*,

J(F,H) = 22.1, *Me*CF); 2.28 (*d*, J(F,H) = 4.5, *Me*CO); 5.39 (*s*, OCH_2Ar); 7.42 (*dd*, J = 8.5, 1.7, 1 arom. H); 7.46–7.53 (*m*, 2 arom. H); 7.79–7.88 (*m*, 4 arom. H). ^{13}C-NMR (75.5 MHz): 19.8 (*d*, J(F,C) = 23, Me); 25.0 (Me); 68.1 (CH_2); 97.6 (*d*, J(F,C) = 194, *CF*); 125.5 (CH); 126.4 (CH); 126.5 (CH); 127.7 (CH); 127.7 (CH); 128.0 (CH); 128.6 (CH); 132.0 (C); 133.1 (C); 133.2 (C); 166.7 (*d*, J(F,C) = 26); 202.1 (*d*, J(F,C) = 29). ^{19}F-NMR (188.3 MHz): −157.4 (*qq*, J(F,H) = 22.1, 4.6). ESI-MS: 292.2 ($[M + NH_4]^+$). Anal. calc. for $C_{16}H_{15}FO_3$ (274.29): C 70.06, H 5.51; found: C 69.94, H 5.41.

2,4,6-Tris(1-methylethyl)benzyl 2-Methyl-3-oxobutanoate (**70**). To a stirred mixture of [2,4,6-tris(1-methylethyl)phenyl]methanol (1.50 g, 6.40 mmol), **66** (1.00 g, 8.6 mmol), and **67** (590 mg, 3.2 mmol) in MeCN (5 ml), *N*,*N*-dimethylaniline (1.0 ml, 8.0 mmol) was added dropwise at 0°. After 2 h of stirring, the ice-bath was removed, and the mixture was stirred at r.t. overnight. After workup with H_2O/^{t}BuOMe, and washing with H_2O, aq 0.5M HCl (2×), and H_2O, the org. phase was evaporated and separated by CC (^{t}BuOMe/hexane 1:15) to give **70** (1.989 g, 93.5%). A colorless oil, which slowly crystallized to a semisolid. R_f (^{t}BuOMe/hexane 1:10) 0.24. ^{1}H-NMR (300 MHz): 1.24 (*d*, J = 6.8, 2 *Me*$_2$CH); 1.26 (*d*, J = 7.0, *Me*$_2$CH); 1.35 (*d*, J = 7.2, *Me*CH); 2.21 (*s*, *Me*CO); 2.89 (*sept.*, J = 6.9, Me$_2$C*H*); 3.17 (*sept.*, J = 6.9, 2 Me$_2$C*H*); 3.51 (*q*, J = 7.1, MeC*H*); 5.26 (*d*, J = 12.2, 1 H of ArCH_2); 5.32 (*d*, J = 12.2, 1 H of ArCH_2); 7.04 (*s*, 2 arom. H); (enol, 18%): 1.25 (*d*, J = 6.7, 2 *Me*$_2$CH); 1.27 (*d*, J = 7, *Me*$_2$CH); 1.68 (*q*, J = 0.7, *Me*–C=C); 2.00 (*quint.*, J = 0.7, *Me*–C–NOH); 2.90 (*sept.*, J = 7.0, Me$_2$C*H*); 3.24 (*sept.*, J = 6.9, 2 Me$_2$C*H*); 5.30 (*s*, ArCH_2); 7.05 (*s*, 2 arom. H); 12.72 (*q*, J = 0.7, OH). ^{13}C-NMR (75.5 MHz): 12.8; 23.9; 24.3; 24.3; 24.4; 28.4; 29.4; 34.3; 34.4; 53.6; 60.3; 121.2; 121.2; 125.8; 148.9; 149.9; 170.7; 203.3; (enol): 11.4; 18.9; 34.3; 59.2; 121.1; 126.4; 149.0; 149.5; 171.7. EI-MS: 332 (0.05, M^+), 201 (100). Anal. calc. for $C_{21}H_{32}O_3$ (332.48): C 75.86, H 9.70; found: C 75.88, H 9.63. *Notes:* 2,4,6-Triisopropylbenzyl alcohol was prepared by $NaBH_4$ reduction from the aldehyde; the latter was obtained from 1,3,5-triisopropylbenzene, Cl_2CHOMe, and $TiCl_4$ [56].

2,4,6-Tris(1-methylethyl)benzyl 2-Fluoro-2-methyl-3-oxobutanoate (**70F**). Prepared according to *GP 1* from **70**, using catalyst **K1** and adding powdered molecular sieves (4 Å 150 mg). Reaction time < 40 min. Purification by CC (^{t}BuOMe/hexane 1:15) gave **70F** (84 mg, 95%). Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.43. $[\alpha]_D = +10.2$ (c = 1.12, MeOH; ee not known). ^{1}H-NMR (300 MHz): 1.23 (*d*, J = 7.0, *Me*$_2$CH); 1.24 (*d*, J = 6.9, *Me*$_2$CH); 1.26 (*d*, J = 7.0, *Me*$_2$CH); 1.67 (*d*, J(F,H) = 22.1, *Me*CF); 2.28 (*d*, J(F,H) = 4.6, *Me*CO); 2.89 (*sept.*, J = 6.9, Me$_2$C*H*); 3.14 (*sept.*, J = 6.8, 2 Me$_2$C*H*); 5.35 (*s*, OCH_2Ar); 7.04 (*s*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 19.8 (*d*, J(F,C) = 23, Me); 23.9 (Me); 24.3 (Me); 24.3 (Me); 24.9 (Me); 29.5 (Me); 34.3 (CH); 61.5 (CH_2); 97.6 (*d*, J(F,C) = 194, CF); 121.2 (CH); 125.0 (C); 149.0 (C); 150.1 (C); 167.0 (*d*, J(F,C) = 25, C); 202.1 (*d*, J(F,C) = 29, C). ^{19}F-NMR (188.3 MHz): −157.1 (*qq*, J = 22.1, 4.5). EI-MS: 350 (0.2, M^+), 201 (100). Anal. calc. for $C_{21}H_{31}FO_3$ (350.467): C 71.97, H 8.92; found: C 72.10, H 9.11.

tert-*Butyl 2-Methyl-3-oxobutanoate* (**71**). Prepared by dissolving **66** (7.50 g, 41.8 mmol), BuOH (3.10 g, 41.58 mmol), and **67** (3.94 g, 64.1 mmol) in MeCN (40 ml), and dropwise addition, with stirring at 0°, of *N*,*N*-dimethylaniline (11.0 ml, 86.8 mmol). The mixture was stirred for 2 h at 0°, then warmed to r.t. and stirred overnight. After addition of ^{t}BuOMe (20 ml) and H_2O (10 ml), the aq. phase was extracted with ^{t}BuOMe (30 ml), and the combined org. phase was washed (40 ml of H_2O, 2 × 40 ml of 0.5M aq. HCl, 40 ml H_2O), dried ($MgSO_4$), filtered, and evaporated. The residue was purified by bulb-to-bulb distillation (180°/10 mbar) to give **71** (3.94 g, 35%). Colorless liquid. ^{1}H-NMR (250 MHz): 1.29 (*d*, J = 7.2, *Me*CH); 1.47 (*s*, ^{t}Bu); 2.23 (*s*, MeCO); 3.41 (*q*, J = 7.2, MeC*H*). ^{13}C-NMR (62.9 MHz): 12.7 (Me); 28.0 (Me); 28.5 (Me); 54.8 (CH); 81.9 (C); 169.9 (C); 204.2 (C). EI-MS: 172 (0.4, M^+), 57 (100). Anal. calc. for $C_9H_{16}O_3$ (172.22): C 62.77, H 9.36; found: C 62.75, H 9.14.

tert-*Butyl 2-Fluoro-2-methyl-3-oxobutanoate* (**71F**). Prepared according to *GP 1* using **K2** (29.4 mg, 35.7 μmol), **71** (100.1 mg, 0.581 mmol), and F-TEDA (0.145M in MeCN; 5.4 ml, 0.783 mmol). Reaction time: 7 min. Experiments to determine the ee of the reaction product (without further purification) by chiral GC or by NMR using the shift reagent tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) were not successful. ^{1}H-NMR (300 MHz): 1.49 (*s*, ^{t}Bu); 1.65 (*d*, J(F,H) = 22.1, CFMe); 1.70 (*d*, J(F,H) = 22.1, CFMe); 2.31 (*d*, J(F,H) = 4.5, 3 H, MeCO). Known substance. *Beilstein* No. 487047-94-9, 126583-38-8.

2,4,6-Tris(1-methylethyl)benzyl 2-Methyl-3-oxo-3-phenylpropanoate (**72**). Prepared by dissolving **68** (0.540 g, 3.03 mmol), [2,4,6-tris(1-methylethyl)phenyl]methanol (0.45 g, 1.9 mmol), and **67** (0.184 g,

1.00 mmol) in MeCN (2.5 ml), and dropwise addition, with stirring at 0°, of *N,N*-dimethylaniline (0.30 ml, 2.4 mmol). The mixture was stirred for 2 h at 0°, then warmed to r.t., and stirred overnight. After addition of ^{t}BuOMe and H_2O, the org. phase was washed ($1 \times H_2O$, 2×0.5M aq. HCl, $1 \times H_2O$), dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was purified by CC (^{t}BuOMe/hexane 1:12) to give **72** (0.472 g, 62%). Colorless oil, which slowly crystallized on standing. R_f (^{t}BuOMe/hexane 1:10) 0.25. ^{1}H-NMR (300 MHz): 1.16 (*d*, *J* = 6.9, 2 *Me*$_2$CH); 1.24 (*d*, *J* = 7.0, *Me*$_2$CH); 1.50 (*d*, *J* = 7.1, *Me*CH); 2.87 (*sept.*, *J* = 7.0, Me$_2$C*H*); 3.06 (*sept.*, *J* = 6.9, 2 Me$_2$C*H*); 4.36 (*q*, *J* = 7.1, MeC*H*); 5.20 (*d*, *J* = 12.4, 1 H of OC*H*$_2$Ar); 5.26 (*d*, *J* = 12.4, 1 H of OC*H*$_2$Ar); 7.00 (*s*, 2 arom. H); 7.40–7.47 (*m*, 2 arom. H); 7.52–7.59 (*m*, 1 arom. H); 7.91–7.98 (*m*, 2 arom. H); (enol, 2.5%): 12.99 (*s*, OH). ^{13}C-NMR (75.5 MHz): 14.0 (Me); 24.1 (Me); 24.4, 24.5 (Me); 29.5 (CH); 34.5 (CH); 48.7 (CH); 60.6 (CH_2); 121.3 (CH); 126.0 (C); 128.7; 128.8 (CH); 133.5 (CH); 135.9 (C); 149.0 (C); 149.9 (C); 171.4 (C); 195.5 (C). EI-MS: 394 (0.6, M^+), 216 (100). Anal. calc. for $C_{26}H_{34}O_3$ (394.55): C 79.15, H 8.69; found: C 79.05, H 8.74.

2,4,6-Tris(1-methylethyl)benzyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**72F**). Prepared according to *GP 1* using **K2** (9.5 mg, 12 μmol), **72** (90.5 mg, 0.229 mmol), and F-TEDA (0.145M in MeCN; 1.8 ml, 0.26 mmol). CC (^{t}BuOMe/hexane 1:10) gave **72F** (82.4 mg, 87%). Colorless oil. R_f (^{t}BuOMe/hexane 1:10) 0.53. ^{1}H-NMR (300 MHz): 1.07 (*d*, *J* = 6.9, *Me*$_2$CH); 1.15 (*d*, *J* = 6.8, *Me*$_2$CH); 1.23 (*d*, *J* = 6.9, *Me*$_2$CH); 1.85 (*d*, *J*(F,H) = 22.5, CF*Me*); 2.86 (*sept.*, *J* = 6.9, Me$_2$C*H*); 2.97 (*sept.*, *J* = 6.8, 2 Me$_2$C*H*); 5.24 (*d*, *J* = 12.3, 1 H of OC*H*$_2$Ar); 5.37 (*d*, *J* = 12.3, 1 H of OC*H*$_2$Ar); 6.97 (*s*, 2 arom. H); 7.39–7.47 (*m*, 2 arom. H); 7.54–7.62 (*m*, 1 arom. H); 7.99–8.05 (*m*, 2 arom. H). ^{13}C-NMR (75.5 MHz): 21.0 (*d*, *J*(F,C) = 23.5, Me); 24.0 (Me); 24.3; 24.4 (Me); 29.6 (CH); 34.5 (CH); 61.7 (CH_2); 96.9 (*d*, *J*(F,C) = 194.9, CF); 121.3 (CH); 125.0 (C); 128.7 (CH); 129.8 (*d*, *J*(F,C) = 5.2, CH); 133.4 (*d*, *J*(F,C) = 3.4, C); 134.0 (CH); 149.1 (C); 150.2 (C); 169.0 (*d*, *J*(F,C) = 25.6, C); 191.1 (*d*, *J*(F,C) = 25.0, C). ^{19}F-NMR (282 MHz): –151.8 (*qt*, *J*(F,H) = 22.6, 1.5). EI-MS: 412 (0.14, M^+), 216 (100). Anal. calc. for $C_{26}H_{33}FO_3$ (412.54): C 75.70, H 8.06; found: C 75.77, H 8.04.

4-Nitrobenzyl 2-Methyl-3-oxo-3-phenylpropanoate (**73**). Prepared by dissolving **68** (0.800 g, 4.49 mmol), (4-nitrophenyl)methanol (0.458 g, 1.50 mmol), and **67** (0.277 g, 1.50 mmol) in MeCN (2.5 ml), and dropwise addition, with stirring at 0°, of *N,N*-dimethylaniline (0.453 g, 3.70 mmol). The mixture was stirred for 2 h at 0°, then warmed to r.t., and stirred overnight. After addition of ^{t}BuOMe and H_2O, the org. phase was washed ($1 \times H_2O$, 2×0.5M aq. HCl, $1 \times H_2O$), dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was purified by CC (^{t}BuOMe/hexane 1:30–1:5) to give **73** (0.772 g, 82%). Colorless powder. ^{1}H-NMR (250 MHz): 1.55 (*d*, *J* = 7.1, *Me*CH); 4.49 (*q*, *J* = 7.1, MeC*H*); 5.22 (*s*, OC*H*$_2$Ar); 7.33 (*d*, *J* = 6.9, 2 arom. H); 7.44–7.50 (*m*, 2 arom. H); 7.58–7.62 (*m*, 1 arom. H); 7.95 (*d*, *J* = 7.1, 2 arom. H); 8.13 (*d*, *J* = 6.8, 2 arom. H). ^{13}C-NMR (62.9 MHz): 13.8 (Me); 48.2 (CH); 65.4 (CH_2); 123.7 (C); 123.7 (CH); 128.2 (CH); 128.6 (CH); 128.8 (CH); 133.7 (CH); 135.5 (C); 142.6 (C); 170.4 (C); 195.5 (C). EI-MS: 313 (0.25, M^+), 105 (100). Anal. calc. for $C_{17}H_{15}NO_5$ (313.31): C 65.17, H 4.83, N 4.47; found: C 65.11, H 5.07, N 4.50.

4-Nitrobenzyl 2-Fluoro-2-methyl-3-oxo-3-phenylpropanoate (**73F**). A sample was prepared according to *GP 1*. No chiral analysis conditions were found, thus the compound was not further investigated. ^{1}H-NMR (250 MHz): 1.92 (*d*, *J*(F,H) = 22.5, CFMe); 5.24 (*d*, *J* = 13.0, 1 H of OC*H*$_2$Ar); 5.35 (*d*, *J* = 13.0, 1 H of OC*H*$_2$Ar); 7.26–7.59 (*m*, 5 arom. H); 7.99 (*d*, *J* = 7.8, 2 arom. H); 8.11 (*d*, *J* = 8.8, 2 arom. H).

tert-*Amyl Propionate* (= *1,1-Dimethylpropyl Propanoate*; **74**). Prepared from equimolar amounts of 2-methylbutan-2-ol, propanoyl chloride, and *N,N*-dimethylaniline (stronger bases like Et_3N are not suitable) in ^{t}BuOMe (0°–r.t.).

(4Z)-4-Ethylidene-3-methyloxetan-2-one (**75**). See *Sect. 12*, *a*, for a synthesis.

*1-(1*H*-Imidazol-1-yl)-2-methylpentane-1,3-dione* (**76**). The compound was obtained *in situ* starting from equimolar amounts of **75** and 1*H*-imidazole in CH_2Cl_2 soln. at 0°. It was used without further purification.

*3-(*tert*-Butyl)-1*H*-pyrazole* (**77**). a) *4,4-Dimethyl-3-oxopentanal* [57]. To a suspension of pentane-washed NaH (11.89 g, 495 mmol) in ^{t}BuOMe (250 ml) were added dropwise EtOH (2 ml) and 5 ml of a mixture of ^{t}BuCOMe (49.6 g, 495 mmol) and isopentyl formate (69 g, 594 mmol). The reaction was initiated by heating with a heat-gun (H_2 evolution). The remainder of the mixture was added at a speed (2–3 drops/s), which kept the mixture at slow reflux. After completion of the addition, the mixture was refluxed for 40 min and stirred for 1 h at r.t. H_2O was carefully added (100 ml) to dissolve the precipitated

sodio enolate. Aq. NaOH (2M, 100 ml) was added, and the mixture was stirred for 15 min at r.t. The org. phase was discarded, and the aq. phase washed with *t*BuOMe (2 × 100 ml). The yellow aq. phase was acidified with aq. H_2SO_4 (10%) until acidic (pH < 3). The turbid mixture was extracted with *t*BuOMe (100 ml) and CH_2Cl_2 (2 × 50 ml). The combined org. phase was dried (Na_2SO_4) and evaporated to give 38.45 g (61%) of a yellow liquid, which was sufficiently pure for further use. ^{1}H-NMR (300 MHz): (enol, 90%): 1.10 (*s*, Me_3C); 5.61 (*d*, *J* = 4.4, H–C(2)); 7.93 (*d*, *J* = 4.5, H–C(1)); 14.7 (br. *s*, OH); (keto-form, 10%): 1.06 (*s*, Me_3C); 3.52 (*d*, *J* = 2.8, CH_2); 9.70 (*t*, *J* = 3, *H*–C=O). ^{13}C-NMR (75.5 MHz): 26.8 (Me of *t*Bu); 40.0 (C of *t*Bu); 97.7 (CH, C(2)); 176.5 (CH, C(1)); 205.4 (C, C=O).

b) *Compound* **77** [58]. Most of the above 4,4-dimethyl-3-oxopentanal (38.4 g, 300 mmol) was added in small portions (2 ml) to a stirred soln. of $NH_2NH_2 \cdot H_2O$ (14.6 ml, 300 mmol) in MeOH (100 ml) and *t*BuOMe (50 ml) at 50°; each addition was accompanied by an exothermic reaction and boiling of the mixture. After completion of the addition, the mixture was refluxed at 80° for another 2 h. Evaporation in a rotary evaporator gave a yellow oil, which crystallized at −20°. The solid was dissolved in an equal volume of pentane at 30° and placed for 1 d at −24°. Decanting of the mother liquors and drying of the crystals by pressing between filter paper gave slightly yellowish material (22.50 g). This was recrystallized from pentane (20 ml) by standing for 2 d at −24°. Decanting, drying the crystals on filter paper, and drying in high vacuum gave **77** (20.92 g, 56%). Clear, colorless crystals of peculiar odor. ^{1}H-NMR (250 MHz): 1.35 (*s*, *t*Bu); 6.08 (*d*, *J* = 2.0, H–C(4)); 7.49 (*d*, *J* = 2.0, H–C(5)); 11.96 (br. *s*, H–N). ^{13}C-NMR (62.9 MHz): 30.4 (Me of *t*Bu); 31.2 (C of *t*Bu); 100.9 (CH, C(4)); 135.9 (br., CH, C(5)); 153 (br., C, C(3); weak signal, insecure).

c) *Alternative Synthesis.* Following the outline above (*a* and *b*), but starting from NaH (21.48 g, 895 mmol) in *t*BuOMe (500 ml) and addition of EtOH (5 ml), followed by a mixture of *t*BuCOMe (85.14 g, 850 mmol) and ethyl formate (94.45 g, 1.275 mol), pivaloylacetaldehyde was obtained after reaction and extraction as described above. The crude intermediate was combined with $NH_2NH_2 \cdot H_2O$ (50 ml) in EtOH (150 ml) in an exothermal reaction, and the mixture was set aside overnight. After evaporation, the residue was taken up in CH_2Cl_2, and the org. phase was washed with a little aq. HCl (0.5 m). Evaporation and distillation of the residue in vacuum (103°/12 mbar) gave **77** as a yellow viscous oil, which slowly crystallized at r.t. Yield: 46.09 g (44%), together with 6.0 g of less pure fractions. Additional purification is possible by crystallization from pentane as described above.

*1-[3-(*tert*-Butyl)-1*H*-pyrazol-1-yl]-2-methylpentane-1,3-dione* (**78**). Lactone **75** (2.261 g, 20.16 mmol) was added dropwise over 15 min to a soln. of **77** (2.504 g, 20.16 mmol) in CH_2Cl_2 (30 ml) at −15° (ice/EtOH). The mixture was warmed to r.t. with stirring for 24 h. The mixture was washed with H_2O (200 ml), and the org. phase dried ($MgSO_4$) and evaporated (crude: 4.792 g, 99%). Purification by CC (*t*BuOMe/hexane) gave **78** (3.64 g, 76%). Colorless oil, which crystallized on standing in the fridge. R_f (*t*BuOMe/hexane 1:10) 0.32. M.p. *ca.* 27°. ^{1}H-NMR (300 MHz): 1.09 (*t*, *J* = 7.2, *Me*CH_2); 1.28 (*s*, Me_3C); 1.44 (*d*, *J* = 7.1, *Me*CH); 2.66 (*dq*, *J* = 18.4, 7.3, 1 H of MeCH_2); 2.88 (*dq*, *J* = 18.3, 7.3, 1 H of MeCH_2); 4.66 (*q*, *J* = 7.1, MeC*H*); 6.33 (*d*, *J* = 2.9, H–C(4) of pyrazole); 8.11 (*d*, *J* = 2.9, H–C(5) of pyrazole). ^{13}C-NMR (75.5 MHz): 7.5; 12.8; 29.7; 32.4; 34.9; 51.3; 107.4; 128.7; 166.4; 168.9; 206.9. EI-MS: 237 (0.6, $[M+H]^+$), 236 (0.5, M^+), 109 (100). Anal. calc. for $C_{13}H_{20}N_2O_2$ (236.31): C 66.07, H 8.53, N 11.85; found: C 66.08, H 8.58, N 11.84.

*1-[3-(*tert*-Butyl)-1*H*-pyrazol-1-yl]-2-fluoro-2-methylpentane-1,3-dione* (**78F**). Obtained according to *GP 1* with **K1** (10 mol-%). A maximum conversion of 50% was achieved (^{1}H-NMR). The product was not further investigated. ^{19}F-NMR (188 MHz): −152.9 (*qdd*, *J*(F,H) = 22.8, 3.3, 1.9).

Dimethyl Carbonotrithioate (**79a**) *and Diethyl Carbonotrithioate* (**79b**). Commercial compounds.

Methyl 2-Methyl-3-oxo-3-phenylpropane(dithioate) (**57**). Propiophenone (= 1-phenylpropan-1-one; 1.8 ml, 13.6 mmol) was added dropwise over 45 min to a mixture of **79a** (1.5 ml, 13.6 mmol) and NaH (60% in oil; 0.90 g, 23 mmol) in *t*BuOMe (10 ml) at 0°. After stirring for 3 d at r.t., the mixture was cooled to 0°, and the reaction was quenched with H_2O and acidified to pH *ca.* 2 by addition of aq. HCl (1M). After extraction with Et_2O, the combined org. phases were washed with H_2O and sat. aq. NaCl, dried (Na_2SO_4), filtered, and evaporated to dryness. Purification by CC (AcOEt/hexane 1:20–1:10) gave **57** (1.384 g, 65%). Yellow oil. R_f (AcOEt/hexane 1:20) 0.25. ^{1}H-NMR (250 MHz): 1.65 (*d*, *J* = 7.5, *Me*CH); 2.61 (*s*, MeS); 5.28 (*q*, *J* = 7.5, MeC*H*); 7.39–7.45 (*m*, 2 arom. H); 7.50–7.56 (*m*, 1 arom. H); 7.99–8.03 (*m*, 2 arom. H); (enol, 2.1%): 16.00 (*s*, OH). ^{13}C-NMR (62.9 MHz): 19.9 (Me); 20.1 (Me); 62.4 (CH);

128.7 (CH); 128.9 (CH); 133.3 (CH); 136.1 (C); 194.9 (C); 235.4 (C). Known compound, CAS No. 83392-39-6.

Ethyl 2-Methyl-3-oxo-3-phenylpropane(dithioate) (**58**). Propiophenone (1.6 ml, 12 mmol) was added dropwise over 15 min to a mixture of **79b** (2.1 ml, 12 mmol) and NaH (60% in oil; 0.50 g, 21 mmol) in ^{t}BuOMe (15 ml) at 0°. After stirring for 20 h at r.t., the mixture was cooled to 0°, and the reaction was quenched with H_2O. The aq. phase acidified to pH *ca.* 2 by addition of aq. HCl (1M) and extracted with ^{t}BuOMe. The combined org. phases were washed with H_2O and sat. aq. NaCl, dried ($MgSO_4$), filtered, and evaporated to dryness. Purification by CC (acetone/hexane 1:5–1:4) gave **58** (915 mg, 32%). ^{1}H-NMR (250 MHz): 1.30 (*t*, *J* = 7.7, EtS); 1.64 (*d*, *J* = 7.0, *Me*CH); 3.20 (*q*, *J* = 7.7, MeC*H2*); 5.21 (*q*, *J* = 7.0, MeC*H*); 7.40–7.46 (*m*, 2 arom. H); 7.51–7.58 (*m*, 1 arom. H); 7.99–8.03 (*m*, 2 arom. H); (enol, 0.2%): 16.04 (*s*, OH). ^{13}C-NMR (62.9 MHz): 12.1 (Me); 19.9 (Me); 31.0 (CH_2); 62.7 (CH); 128.7 (CH); 128.9 (CH); 133.3 (CH); 136.2 (C); 194.9 (C); 234.9 (C). EI-MS: 238 (8.1, M^+), 105 (100).

O-*Ethyl* S-*(2-Methylbenzyl) Carbonodithioate* (**80**). EtOH (0.93 ml, 25 mmol) was added dropwise to a suspension of NaH (0.66 g, 27.5 mmol) in DMSO (9 ml). After completion of the addition and cooling to 0°, CS_2 (= methanedithione; 1.5 ml, 25 mmol), followed by 1-(chloromethyl)-2-methylbenzene (3.23 ml, 25 mmol), was added, and the mixture was stirred at r.t. for 2 h. The reaction was quenched with H_2O and CH_2Cl_2. The aq. phase was extracted with additional CH_2Cl_2, and the combined org. phases were washed with H_2O, dried (Na_2SO_4), filtered, and evaporated to give crude **80** (4.11 g, 73%), which was sufficiently pure for further use. R_f (^{t}BuOMe/hexane 1:10) 0.55. ^{1}H-NMR (250 MHz): 1.46 (*t*, *J* = 7.3, *Me*CH_2O); 2.39 (*s*, Ar*Me*); 4.39 (*s*, ArCH_2); 4.69 (*q*, *J* = 7.0, MeCH_2O); 7.15–7.34 (*m*, 4 arom. H). ^{13}C-NMR (62.9 MHz): 13.7 (Me); 19.2 (Me); 38.8 (CH_2); 69.8 (CH_2); 126.1 (CH); 127.9 (CH); 130.0 (CH); 130.5 (CH); 132.9 (C); 137.1 (C); 214.1 (C). EI-MS: 226 (21.1, M^+), 105 (100).

O-*Ethyl 2-Methyl-3-oxo-3-phenylpropanethioate* (**59**). Propiophenone (1.6 ml, 12 mmol) was added over 10 min to a mixture of **80** (2.75 g, 12 mmol) and pentane-washed NaH (509 mg; 17 mmol) in ^{t}BuOMe (15 ml) at 0°. After stirring for 1 d at r.t., ^{t}BuOMe (5 ml) was added, and the mixture was refluxed for 1 d. After cooling to r.t., ice-water was added, and the org. phase was separated. The aq. phase was acidified to pH *ca.* 2 with aq. HCl (1M) and extracted with ^{t}BuOMe. The combined org. phases were dried ($MgSO_4$), filtered, and evaporated. Purification by CC (^{t}BuOMe/hexane 1:40–1:20) gave **59** (624 mg, 23%). R_f (acetone/hexane 1:10) 0.35. ^{1}H-NMR (300 MHz): 1.29 (*t*, *J* = 7.2, *Me*CH_2O); 1.57 (*d*, *J* = 6.9, *Me*CH); 4.47 (*q*, *J* = 7.2, MeCH_2O); 4.80 (*q*, *J* = 6.9, MeC*H*); 7.42–7.49 (*m*, 2 arom. H); 7.54–7.59 (*m*, 1 arom. H); 7.96–8.03 (*m*, 2 arom. H); (enol, 5.5%): 14.57 (*s*, OH). ^{13}C-NMR (62.9 MHz): 13.4 (Me); 17.1 (Me); 58.8 (CH); 68.9 (CH_2); 128.7 (CH); 128.8 (CH); 133.3 (CH); 136.4 (C); 195.4 (C); 219.7 (C). EI-MS: 222 (7.4, M^+), 105 (100).

Ethyl 1-Fluoro-2-oxocyclododecanecarboxylate. Prepared according to *GP 1* from ethyl 2-oxocyclododecanecarboxylate [59]. After workup, 56 mg of crude material, also containing TADDOL ligand, was obtained. Given a lack of UV absorption in the HPLC detector, the product was not further investigated. ^{1}H-NMR (300 MHz): 1.19–1.43 (*m*, 13 H); 1.31 (*t*, *J* = 7.1, *Me*CH_2O); 1.43–1.58 (*m*, 1 H); 1.61–1.76 (*m*, 1 H); 1.81–1.95 (*m*, 1 H); 1.92–2.13 (*m*, 1 H); 2.39 (*dddd*, *J* = 35.6, 14.3, 9.3, 4.1, 1 H); 2.68–2.74 (*m*, CH_2C=O); 4.26 (*q*, *J* = 7.1, MeCH_2O). ^{13}C-NMR (75.5 MHz): 13.9; 20.0 (*d*, *J*(F,C) = 3); 21.1 (*d*, *J*(F,C) = 2); 22.6; 23.4; 23.7; 23.9; 26.0; 26.7; 33.1 (*d*, *J*(F,C) = 22); 34.8; 62.4; 100.8 (*d*, *J*(F,C) = 200); 167.0 (*d*, *J*(F,C) = 25); 204 (*d*, *J*(F,C) = 24). ^{19}F-NMR (282 MHz): –167.3 (br. *d*, *J*(F,H) *ca.* 35).

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