174. Generation and Reactions of Lithiated *tert*-Butyl and 2,6-Di(*tert*-butyl)-4-methylphenyl Cyclopropanecarboxylates

by **Robert Häner**[1]), **Thomas Maetzke**[2]), and **Dieter Seebach***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstrasse 16, CH–8092 Zürich

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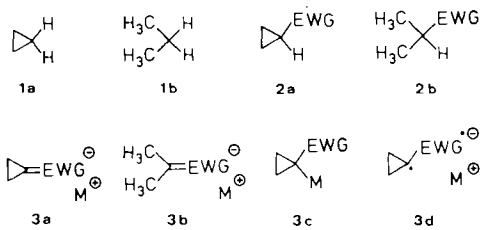
tert-Butyl and 2,6-di(*tert*-butyl)-4-methylphenyl (BHT) cyclopropanecarboxylates (**4**, **6**, **24**, **25**) are lithiated with $LiN(i\text{-}Pr)_2$ and *t*-BuLi, respectively. Reactions with alkyl halides, aldehydes, acyl chlorides, and heteroelectrophiles give α-substituted BHT esters which can be cleaved (*t*-BuOK/H_2O/THF) to the corresponding carboxylic acids or reduced ($LiAlH_4$/THF) to the cyclopropanemethanols.

Though cyclopropane (**1a**) itself is more acidic than the less strained cycloalkanes and open-chain alkanes (*cf.* **1b**) [1] [2], the relative acidity of the corresponding derivatives with conjugatively electron-withdrawing groups (EWG) may be reversed (**2a** less acidic than **2b**), as shown by many mechanistic investigations with various EWG's (COR [3–7], SO_2R [4] [5] [8] [9], NO_2 [4–6] [10], CN [4] [6] [11]). This effect is normally ascribed to the increase in strain upon introduction of a trigonal center into a three-membered ring [12] (compare **3a** with **3b**). Pyramidalized carbanion centers or C-atom rather than heteroatom-metalated structures (compare **3a** with **3c**) are, therefore, discussed for such species[3]).



EWG = electron-withdrawing group

Alternatively, the carbanionoid species can be stabilized by decoupling to a diradical, see **3d** [17] [18]. Hitherto, it was not possible to isolate suitable single crystals for X-ray structure analysis to obtain insight about the bonding in such species.

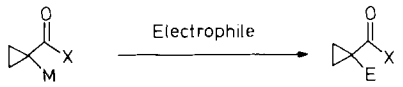
Besides these physical organic aspects, synthetic applications of EWG-substituted cyclopropyl nucleophiles have been studied extensively. A list of leading references to papers in which the successful generation and reactions with electrophiles of metalated

[1]) Part of the projected Ph. D. thesis of *R. H.*, ETH Zürich.

[2]) Part of the Master's thesis of *Th. M.*, ETH Zürich, 1985.

[3]) For the question as to whether a pyramidal ketonic carbanion exists or not, see [13–16].

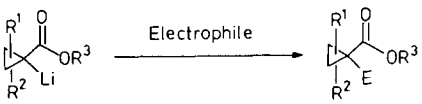
Scheme 1



M	X[a])	Electrophile	Ref.
Li	MeO	Me_3SiCl	*Ainsworth et al.* (1972) [19a]
Li	LiO	Me_3SiCl	*Ainsworth* and *Kuo* (1972) [19b]
Li	*t*-BuS	RCOR'	*Wemple* (1975) [20]
Li	*t*-BuS	Nitroolefin	Our group (1981) [21]
Li	LiO	RX	*Warner* and *Le* (1982) [22]
Bu_4N	MeO	RCOR'	*Paquette et al.* (1984) [23]
NiL_n	Me_2N	RCOR'; acrylic ester	*Hirao et al.* (1985) [24]
Li	BHT/alkyl	PhCHO	Our group (1985) [25]
Li	DBHA	Isopentyl nitrate	Our group (1985) [26]

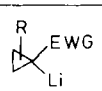
[a]) BHT = 2,6-Di(*tert*-butyl)-4-methylphenoxy; DBHA = 2,6-bis(*tert*-butyl)-4-methoxyphenoxy.

Scheme 2



R^1	R^2	R^3	Electrophile	Ref.
Ph	Ph	Me	D^+	*Ford* and *Newcomb* (1973) [27]
$R^1, R^2 \neq H$ (many examples)		Me	RX, MeSSMe	*Reichelt* and *Reissig* (1982–1985) [14] [28]
Ph	H	Me; Et	MeI, $(Ph)_2CO$	*Feit et al.* (1984) [16]

Scheme 3

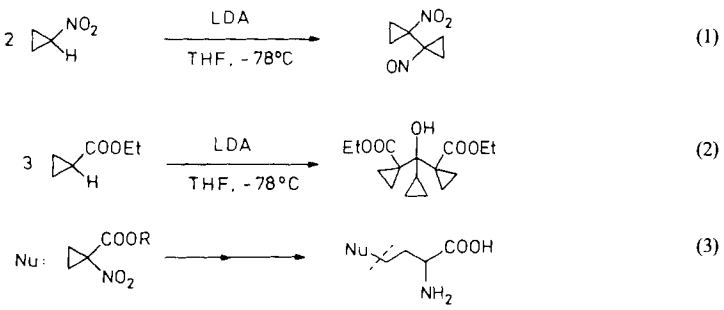
	EWG:	C≡N	*Walborsky* and *Hornyak* (1955) [29]
			Van Cantfort and *Coates* (1981) [30]
		N=C	*Walborsky* and *Periasamy* (1974) [31]
		SO_2Ph	*Chang* and *Pinnick* (1978) [32]
			Pohmakotr and *Pisutjaroenpong* (1985) [33]
			Padwa and *Wannamaker* (1986) [34]
		$PO(OEt)_2$	*Hirao et al.* (1985) [35]
			*Haller* and *Benoist* (1921) [36a]
			Piehl and *Brown* (1953) [36b]

unsubstituted and substituted cyclopropanecarboxylates is described, is given in *Scheme 1* and *2*, respectively. In *Scheme 3*, the studies of some other EWG-substituted cyclopropyl nucleophiles is summarized. Due to the instability and/or extremely high reactivity of such anion derivatives, coupling (see *Scheme 4, Eqn. 1*) [17] [37] and so-called self condensation (see *Eqn. 2*) [17][4]) may occur.

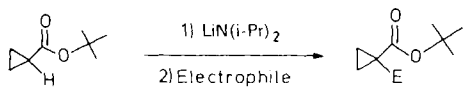
During an investigation aimed at an amino-acid a^4-reagent, see *Scheme 4, Eqn. 3*, we were looking for a method of preparing α-nitrocyclopropanecarboxylic-acid derivatives.

[4]) The dianion of cyclopropanecarboxylic acid has also been shown to undergo dimerization at 50°, see [38].

Scheme 4



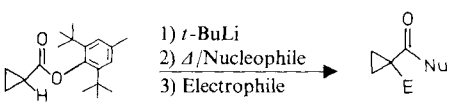
Scheme 5



4 5

	a	b	c	d
Electrophile				
Yield [%]	79	82	81	78

Scheme 6



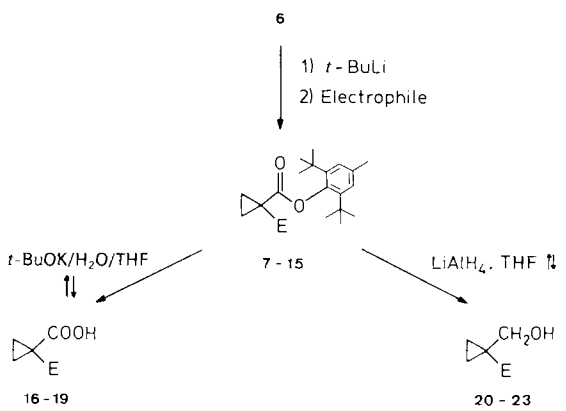
6

We first examined the reaction of the enolate from the *tert*-butyl ester **4**, the generation of which has been described by *Gorrichon et al.* [15], with various electrophiles including nitrating reagents. Although, a clean reaction occurred with alkyl halides and with carbonyl compounds (→**5**, *Scheme 5*), we could not isolate a product of nitration. Similarly, attempts to nitrate the dilithio derivative of cyclopropane carboxylic acid [22] or the enolate of the *tert*-butylthio ester [20] [21] failed.

We found, however, that another lithiated cyclopropane carboxylate can be nitrated in good yield and can be used for reactions with electrophiles quite generally: the BHT ester **6** (see *Scheme 6*) which we have originally employed for *in situ* generation of cyclopropylidene ketene [25].

As shown in *Scheme 7* the electrophile can be an alkyl halide (→**7–9**), an aldehyde (→**10, 11**), an acyl chloride (→**12**) as well as a hetero-atom-transferring reagent (isopentyl nitrate, O_2, and I_2 (→**13–15**)). The ester **6** is quantitatively lithiated within 30 min by treatment with 1 equiv. of *t*-BuLi at −78° in THF to give an amine-free, slightly yellow solution from which the Li derivative precipitates eventually. Subsequent addition of electrophiles gives the products **7–15** in good to excellent yields. All the products were crystalline and were purified by column chromatography and/or recrystallization.

Scheme 7

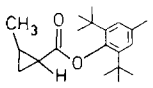


Electrophile	E	Product (Yield [%])		
		Ester	Acid	Alcohol
CH_3I	CH_3	**7** (71)	**16** (87)	
	CH_2CHCH_2	**8** (86)		**20** (75)
	$C_6H_5CH_2$	**9** (88)	**17** (73)	**21** (84)
	$(CH_3)_2CHCH(OH)$	**10** (91)	**18** (58)	**22** (72)
	$C_6H_5CH(OH)$	**11** (93)	**19** (41)	**23** (83)
	CH_3OCO	**12** (88)		
	NO_2	**13** (70)		
O_2	OH	**14** (25)		
I_2	I	**15** (93)		

Cleavage to the corresponding carboxylic acids was accomplished by the method of *Gassman et al.* [39] (*t*-BuOK/THF/2 equiv. of H_2O). While no complications arose with the methylated (**7**) and benzylated (**9**) esters (→**16** and **17**, respectively), the allylated derivative **8** underwent partial double-bond shift under these conditions. Hydrolysis of the aldols **10** and **11** gave the β-hydroxy acids **18** and **19** in lower yields because of competing *retro*-aldol reaction. Alternatively, the BHT-group could be removed by reduction of the esters **8**–**11** with $LiAlH_4$ [40] to yield alcohols (**20**, **21**) or diols (**22**, **23**). The α-heterosubstituted esters **13**–**15** could not be hydrolized or reduced.

For the application outlined in *Eqn. 3 (Scheme 4)*, we eventually used another *o,o'*-di(*tert*-butyl)phenyl ester: the *p*-methoxy derivative, which can be cleaved oxidatively. The preparation of α-aminocyclopropanecarboxylic acid using this ester has been described elsewhere [26] *(Scheme 1)*, and the nucleophilic ring-opening reactions of the nitro ester will be reported in due course.

The substituted cyclopropanecarboxylates **24** and **25** can likewise be lithiated and were found to combine with electrophiles to give the corresponding derivatives



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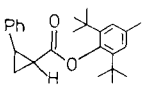
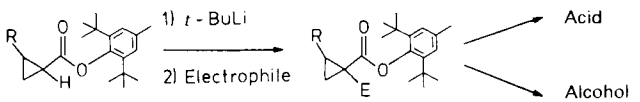


25

26–32 (see *Scheme 8*). In nearly all cases, mixtures of diastereoisomers were obtained and separated chromatographically. Reduction to the alcohols was achieved in the same way as for the less substituted esters **8–11**, whereas hydrolysis under *Gassman* conditions required somewhat higher temperatures (15 h at 120° in diglyme as solvent)[5]).

Scheme 8



26 – 32

R	Electrophile	E	Product Yield [%]; diastereoisomeric ratio[a])		
			Ester	Acid[b])	Alcohol[b])
	CH_3I	CH_3	**26** (90; 2:1)	(73; 2:1)	
	$C_6H_5CH_2Br$	$C_6H_5CH_2$	**27** (70; > 20:1)	(92; 24:1)	
Me (**24**)	C_6H_5CHO	$C_6H_5CH(OH)$	**28** (84)[c])		(96; 2:2:1)
	C_6H_5COCl	C_6H_5CO	**29** (80; 3:2)		
	CH_3I	CH_3	**30** (68; 1:1)		
Ph (**25**)	$C_6H_5CH_2Br$	$C_6H_5CH_2$	**31** (62; 2:3)	(11)[d])	
	C_6H_5CHO	$C_6H_5CH(OH)$	**32** (53; 5:3:2:2)		(87; 6:3:3:1)

[a]) Determined by ^{1}H-NMR.
[b]) Obtained by hydrolysis or reduction of the crude ester.
[c]) Diastereoisomeric ratio not determined.
[d]) Only one diastereoisomer isolated.

Experimental Part

General. All reactions with organometallic reagents were carried out under Ar. THF was freshly distilled from K before use. Commercially available solns. of *t*-BuLi (*ca.* 1.6M in pentane) and BuLi (*ca.* 1.6M in hexane) were standardized by the diphenylacetic-acid method [41]. 2,6-Di(*tert*-butyl)-4-methylphenol was obtained from *Fluka AG* (Buchs) and was of commercial grade. 2-Methylcyclopropanecarbonyl chloride was prepared by treatment of the commercially available acid *(Fluka AG)* with $SOCl_2$. 2-Phenylcyclopropanecarbonyl chloride was likewise prepared from the corresponding acid which was obtained by hydrolysis ($KOH/H_2O/EtOH$) of the ethyl ester [28c]. Flash chromatography (FC) [42]: silica gel *60* (*Fluka AG*, 0.040–0.063 mm, 230–400 mesh, ASTM). M.p.: *Büchi 510* apparatus; not corrected. Bulb-to-bulb distillation: *Büchi GKR-50* oven; b.p. correspond to the air temp. IR spectra: *Perkin-Elmer-297-IR-Spectrometer*. ^{1}H-NMR spectra ($CDCl_3$): *Bruker WM-300-W8* (300 MHz) or *Varian EM-390* (90 MHz); unless otherwise indicated, 300-MHz spectra are reported; ^{13}C-NMR spectra ($CDCl_3$): *Varian CFT-20* (20 MHz); δ [ppm] rel. to TMS as internal standard. MS: *Varian Mat 311*; intensities in brackets in percent relative to the base peak (100%).

[5]) Analytical data of the corresponding acids and alcohols are not given in the *Exper. Part* but can be obtained from the authors.

General Procedure for the Preparation of Esters **5a–d**. To a soln. of $(i\text{-Pr})_2NH$ (6.3 mmol) in 3 ml of THF at 0° was added a soln. of BuLi in hexane (6.0 mmol). After stirring for 10 min, the solvent was evaporated. The residue was again dissolved in 15 ml of THF and cooled to −78°. A soln. of the ester **4** in 2 ml of THF was added, and after stirring for 5 h at −78°, the electrophile (10 mmol, dissolved in 3 ml of THF) was added dropwise. If the electrophile was a carbonyl compound, the reaction was quenched after 5 min at −78° by the addition of 5 ml of sat. aq. NH_4Cl soln., otherwise the soln. was allowed to warm to r.t. during 4 h. The mixture was poured onto sat. aq. NH_4Cl soln., the layers were separated, and the H_2O phase was twice extracted with Et_2O. The combined org. phases were washed twice with brine, dried ($MgSO_4$), concentrated, and purified by FC (pentane/Et_2O) followed by bulb-to-bulb distillation.

tert-*Butyl 1-Allylcyclopropanecarboxylate* (**5a**). Colorless liquid (79%) after FC (pentane/Et_2O 95:5) followed by bulb-to-bulb distillation, b.p. 100°/15 Torr. IR ($CHCl_3$): 3090, 2990, 2940, 1710*s*, 1645, 1480, 1460, 1440, 1425, 1400, 1375, 1360, 1280, 1160*s*, 1100, 1070, 1035, 1010, 995, 950, 925, 900, 855. ^{1}H-NMR ($CDCl_3$): 0.63–0.67 (*m*, 2 ring H); 1.11–1.15 (*m*, 2 ring H); 1.42 (*s*, *t*-Bu); 2.27 (*dt*, J = 6.6, 1.2, CH_2=CHCH_2); 4.97–5.06 (*m*, 2 olefin. H); 5.79–5.92 (*m*, 1 olefin. H). ^{13}C-NMR ($CDCl_3$): 14.57 (*t*); 23.49 (*s*); 28.08 (*q*); 37.64 (*t*); 80.02 (*s*); 115.96 (*t*); 136.07 (*d*); 174.08 (*s*). MS: 126 (69, $M^{+\cdot}$ − 56), 57 (100). Anal. calc. for $C_{11}H_{18}O_2$: C 72.49, H 9.95; found: C 72.62, H 10.16.

tert-*Butyl 1-Benzylcyclopropanecarboxylate* (**5b**). Colorless liquid (82%) after FC (pentane/Et_2O 98:2) followed by bulb-to-bulb distillation, b.p. 80°/0.05 Torr. IR ($CHCl_3$): 3100, 3080, 2990, 2950, 1710*s*, 1610, 1590, 1500, 1480, 1460, 1430, 1400, 1375*s*, 1365*s*, 1300, 1150*s*, 1080, 1070, 1035, 1000, 950, 920, 855, 700. ^{1}H-NMR ($CDCl_3$): 0.72–0.75 (*m*, 2 ring H); 1.19–1.23 (*m*, 2 ring H); 1.34 (*s*, *t*-Bu); 2.93 (*s*, PhCH_2); 7.15–7.29 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 14.71 (*t*); 24.32 (*s*); 27.93 (*q*); 38.69 (*t*); 80.09 (*s*); 125.95 (*d*); 127.99 (*d*); 128.96 (*d*); 140.09 (*s*); 173.96 (*s*). MS: 232 (0.3, $M^{+\cdot}$), 57 (100). Anal. calc. for $C_{15}H_{20}O_2$: C 77.55, H 8.68; found: C 77.33, H 8.78.

tert-*Butyl 1-(α-Hydroxybenzyl)cyclopropanecarboxylate* (**5c**). Colorless, viscous liquid (81%) FC (pentane/Et_2O 95:5 to 80:20) followed by bulb-to-bulb distillation, b.p. 105°/0.05 Torr. IR ($CHCl_3$): 3580 (br.), 3100, 3080, 2990, 2940, 2920, 1730–1700*s* (br.), 1610, 1500, 1480, 1465, 1400, 1375*s*, 1150*s*, 1090, 1040*s*, 1030*s*, 980, 970, 950, 920, 905, 865, 850, 705, 650. ^{1}H-NMR ($CDCl_3$): 0.79–0.94 (*m*, 2 ring H); 1.10–1.17 (*m*, 1 ring H); 1.30–1.37 (*m*, 1 ring H); 1.34 (*s*, *t*-Bu); 3.30 (br. *s*, OH); 4.68 (*s*, PhC*H*); 7.24–7.43 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 12.06 (*t*); 13.47 (*t*); 27.88 (*q*); 74.57 (*d*); 81.29 (*s*); 126.56 (*d*); 127.28 (*d*); 127.96 (*d*); 141.94 (*s*); 173.67 (*s*). MS: 192 (27, $M^{+\cdot}$ − 56). Anal. calc. for $C_{15}H_{20}O_3$: C 72.55, H 8.12; found: C 72.42, H 8.26.

tert-*Butyl 1-(α-Hydroxy-α-methylbenzyl)cyclopropanecarboxylate* (**5d**). Colorless, viscous liquid (78%) after FC (pentane/Et_2O 95:5) followed by bulb-to-bulb distillation, b.p. 110°/0.01 Torr. IR ($CHCl_3$): 3570, 3500 (br.), 2990, 2850, 1725–1700*s* (br.), 1605, 1495, 1480, 1450, 1390, 1375*s*, 1340, 1310, 1260, 1160*s*, 1130*s*, 1090, 1080, 1040, 970, 930, 900, 850, 700, 650. ^{1}H-NMR ($CDCl_3$): 0.94–1.00 (*m*, 1 ring H); 1.05–1.17 (*m*, 2 ring H); 1.19 (*s*, *t*-Bu); 1.23 (*s*, CH_3); 1.53–1.59 (*m*, 1 ring H); 4.30 (br. *s*, OH); 7.18–7.33 (*m*, 3 arom. H); 7.53–7.57 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 11.29 (*t*); 13.03 (*t*); 26.70 (*q*); 27.68 (*q*); 33.01 (*s*); 74.60 (*d*); 81.64 (*s*); 124.99 (*d*); 126.60 (*d*); 128.00 (*d*); 149.06 (*s*); 173.72 (*s*). MS: 262 (0.2, $M^{+\cdot}$), 121 (100). Anal. calc. for $C_{16}H_{22}O_3$: C 73.25, H 8.45; found: C 73.11, H 8.61.

General Procedure for the Preparation of Esters **7–15** *and* **26–32**. To a soln. of the ester **6** [25], **24** or **25** (3–15 mmol) in THF (10–30 ml) was added *t*-BuLi (1.1 equiv.) at −78°. The soln. was stirred under Ar for 30 min (during this time, the Li compound might precipitate), and the electrophile (1.2 equiv., dissolved in 2–5 ml of THF) was added. If the electrophile was a carbonyl compound or I_2, the reaction was quenched with sat. aq. NH_4Cl soln. after 5 min, otherwise the soln. was allowed to warm to r.t. within 4 h. The mixture was diluted with Et_2O, washed with sat. aq. NH_4Cl soln. and brine, dried ($MgSO_4$), concentrated, and purified by FC (pentane/Et_2O).

2,6-Di(tert-*butyl*)*-4-methylphenyl 1-Methylcyclopropanecarboxylate* (**7**). Colorless crystals (71%) after FC (pentane/Et_2O 97:3), m.p. (MeOH) 96.0–96.8°. IR ($CHCl_3$): 3000, 2980*s*, 2920, 2880, 1735*s*, 1600, 1470, 1425, 1395, 1370, 1330*s*, 1270, 1190, 1140, 1115*s*, 1030, 955, 915, 895, 865, 840. ^{1}H-NMR ($CDCl_3$): 0.78–0.83 (*m*, 2 ring H); 1.33 (*s*, 2 *t*-Bu); 1.35–1.39 (*m*, 2 ring H); 1.53 (*s*, CH_3); 2.30 (*s*, PhCH_3); 7.08 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 17.90 (*t*); 19.57 (*s*); 19.66 (*q*); 21.47 (*q*); 31.53 (*q*); 35.28 (*s*); 126.89 (*d*); 134.16 (*s*); 142.02 (*s*); 146.51 (*s*); 175.95 (*s*). MS: 302 (3, $M^{+\cdot}$), 83 (100). Anal. calc. for $C_{20}H_{30}O_2$: C 79.42, H 10.00; found: C 79.64, H 10.08.

2,6-Di(tert-*butyl*)*-4-methylphenyl 1-Allylcyclopropanecarboxylate* (**8**). A colorless, viscous liquid (86%) after FC (pentane/Et_2O 97:3) followed by bulb-to-bulb distillation, b.p. 120°/0.03 Torr. IR ($CHCl_3$): 3080, 2970, 2920, 2880, 1730*s*, 1640, 1595, 1480, 1420, 1390, 1360, 1340, 1260*s*, 1180*s*, 1130*s*, 1105*s*, 1025, 1005, 985, 950, 920, 890, 860, 825. ^{1}H-NMR ($CDCl_3$): 0.93–0.97 (*m*, 2 ring H); 1.32 (*s*, 2 *t*-Bu); 1.43–1.47 (*m*, 2 ring H); 2.30 (*s*, PhCH_3); 2.62 (*d*, J = 7.1, CH_2=CHCH_2); 5.03–5.12 (*m*, CH_2=CH–CH_2); 5.87 (*ddt*, J = 17.1, 10.1, 7.1, CH_2=C*H*CH_2); 7.08 (*s*, 2 arom H); ^{13}C-NMR ($CDCl_3$): 15.24 (*t*); 21.44 (*d*); 23.85 (*s*); 31.48 (*q*); 35.25 (*s*); 36.72 (*t*); 117.56 (*t*); 126.85 (*d*);

134.22 (*s*); 134.79 (*d*); 142.05 (*s*); 146.37 (*s*); 175.27 (*s*). MS: 328 (2, $M^{+\cdot}$), 109 (100). Anal. calc. for $C_{22}H_{32}O_2$: C 80.44, H 9.82; found: C 80.45, H 9.90.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Benzylcyclopropanecarboxylate* (**9**). Colorless crystals (88%) after FC (pentane/Et_2O 97:3), m.p. (MeOH) 84.2–85.2°. IR ($CHCl_3$): 2960*s*, 2920, 2870, 1725*s*, 1595, 1420, 1390, 1380, 1360, 1350, 1260*s*, 1175*s*, 1100*s*, 1025, 990, 910, 890, 860. ^{1}H-NMR ($CDCl_3$): 0.89–0.93 (*m*, 2 ring H); 1.26 (*s*, 2 *t*-Bu); 1.47–1.51 (*m*, 2 ring H); 2.29 (*s*, PhCH_3); 3.25 (*s*, PhCH_2); 7.07 (*s*, 2 arom. H); 7.20–7.26 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 14.88 (*t*); 21.47 (*q*); 24.89 (*s*); 31.44 (*q*); 35.20 (*s*); 37.78 (*t*); 126.47 (*d*); 126.94 (*d*); 128.10 (*d*); 130.26 (*d*); 134.27 (*s*); 138.14 (*s*); 142.10 (*s*); 146.37 (*s*); 175.21 (*s*). MS: 378 (2, $M^{+\cdot}$), 159 (100). Anal. calc. for $C_{26}H_{34}O_2$: C 82.49, H 9.05; found: C 82.52, H 8.98.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-(1-Hydroxy-2-methylpropyl)cyclopropanecarboxylate* (**10**). Colorless crystals (91%) after FC (pentane/Et_2O 80:20), m.p. (pentane) 133.8–134.2°. IR ($CHCl_3$): 3560 (br.), 2980*s*, 2930, 2880, 1725*s*, 1600, 1470, 1425, 1400, 1170, 1150, 1315, 1270, 1180, 1145*s*, 1110*s*, 1040*s*, 990, 970, 955, 930, 905, 895, 870, 610. ^{1}H-NMR ($CDCl_3$): 0.97 (*d*, J = 6.7, 3 H, $(CH_3)_2$CH); 1.01 (*d*, J = 6.6, 3 H, $(CH_3)_2$CH); 1.16–1.20 (*m*, 2 ring H); 1.30 (*s*, *t*-Bu); 1.33 (*s*, *t*-Bu); 1.77–1.89 (*m*, 2 ring H); 2.27–2.38 (*m*, $(CH_3)_2CH$); 2.30 (*s*, PhCH_3): 2.55–2.77 (*m*, 2 H, CH–OH; D_2O: 2.57 (*d*, J = 10)); 7.09 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 14.75 (*t*); 15.54 (*t*); 19.86 (*q*); 20.60 (*q*); 21.41 (*q*); 28.22 (*s*); 31.20 (*q*); 31.46 (*q*); 32.86 (*d*); 35.16 (*s*); 82.57 (*d*); 126.98 (*d*); 134.62 (*s*); 142.09 (*s*); 142.19 (*s*); 145.69 (*s*); 174. 98 (*s*). MS: 220 (100). Anal. calc. for $C_{23}H_{36}O_3$: C 76.62, H 10.06; found: C 76.76, H 10.10.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-(α-Hydroxyphenyl)cyclopropanecarboxylate* (**11**). Colorless crystals (93%) after FC (pentane/Et_2O 80:20), m.p. (pentane) 122.0–122.8°. IR ($CHCl_3$): 3600, 3540 (br.), 3000, 2970*s*, 2920, 2880, 1715*s*, 1600, 1450, 1420, 1395, 1365, 1355, 1300, 1270, 1180*s*, 1120*s*, 1105*s*, 1080, 1040*s*, 1030*s*, 1000, 970, 960, 925, 915, 890, 865. ^{1}H-NMR ($CHCl_3$): 0.91–0.96 (*m*, 1 ring H); 1.20–1.28 (*m*, 1 ring H); 1.22 (*s*, *t*-Bu); 1.30 (*s*, *t*-Bu); 1.62–1.72 (*m*, 2 ring H); 2.30 (*s*, PhCH_3); 3.47 (br., OH); 5.19 (*s*, PhC*H*); 7.08 (*s*, 2 arom. H); 7.24–7.39 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 11.85 (*t*); 14.90 (*t*); 21.47 (*q*); 30.75 (*s*); 31.33 (*q*); 35.09 (*s*); 35.19 (*s*); 74.16 (*d*); 127.03; 127.12; 127.63; 127.96; 134.70 (*s*); 140.32 (*s*); 142.03 (*s*); 142.12 (*s*); 145.78 (*s*); 175.42 (*s*). MS: 220 (100). Anal. calc. for $C_{26}H_{34}O_3$: C 79.15, H 8.69; found: C 79.15, H 8.63.

2,6-Di(tert-*butyl*)-*4-methylphenyl Methyl Cyclopropane-1,1-dicarboxylate* (**12**). Colorless crystals (88%) after FC (pentane/Et_2O 92:8), m.p. (pentane/Et_2O) 97.2–98.0°. IR ($CHCl_3$): 3000, 2970*s*, 2920, 2880, 1735*s*, 1595, 1480, 1435, 1420, 1395, 1365, 1330, 1310*s*, 1270, 1180, 1125*s*, 1105*s*, 1045, 1005, 970, 950, 905, 890, 865. ^{1}H-NMR ($CDCl_3$): 1.33 (*s*, 2 *t*-Bu); 1.56–1.66 (*m*, 4 ring H); 2.30 (*s*, PhCH_3); 3.79 (*s*, CH_3O); 7.09 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 18.10 (*t*); 21.47 (*q*); 29.15 (*s*); 31.35 (*q*); 35.26 (*s*); 52.44 (*q*); 126.88 (*d*); 134.62 (*s*); 142.11 (*s*); 146.19 (*s*); 169.34 (*s*); 170.80 (*s*). MS: 346 (2, $M^{+\cdot}$), 127 (100). Anal. calc. for $C_{21}H_{30}O_4$: C 72.80, H 8.73; found: C 72.53, H 8.48.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Nitrocyclopropanecarboxylate* (**13**). Colorless crystals (70%) after FC (pentane/Et_2O 1:0 to 75:25), m.p. (pentane) 120.2–121.6°. IR ($CHCl_3$): 3000, 2970*s*, 2920, 2880, 1750*s*, 1680 (br.), 1595, 1545*s*, 1480, 1415, 1395, 1365, 1335*s*, 1320, 1270, 1180*s*, 1150*s*, 1125, 1100, 1060, 1045, 910, 890, 860. ^{1}H-NMR ($CDCl_3$): 1.34 (*s*, 2 *t*-Bu); 1.88–1.95 (*m*, 2 ring H); 1.98–2.04 (*m*, 2 ring H); 2.31 (*s*, PhCH_3); 7.11 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 18.35 (*t*); 21.47 (*q*); 31.40 (*q*); 35.30 (*s*); 67.27 (*s*); 127.14 (*d*); 135.39 (*s*); 142.04 (*s*); 145.59 (*s*); 166.54 (*s*). MS: 333 (11, $M^{+\cdot}$). Anal. calc. for $C_{19}H_{27}NO_4$: C 68.44, H 8.16, N 4.20; found: C 68.59, H 8.26, N 4.05.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Hydroxycyclopropanecarboxylate* (**14**). A stream of O_2 (dried by passing through a P_2O_5 column) was bubbled through a soln. of 5.0 mmol of the enolate of ester **6** in THF at −78° for 1 h. After slowly warming to −20°, the O_2 supply was stopped. The mixture was poured onto a 10% aq. soln. of Na_2SO_3, stirred for 10 min, and extracted twice with Et_2O. The org. layers were combined, washed with brine, dried ($MgSO_4$), concentrated, and purified by FC (pentane/Et_2O 70:30) to give 0.385 g (25%) of **14** as colorless crystals; m.p. (pentane) 78.8–81.2°. IR ($CHCl_3$): 3600, 3560 (br.), 3000, 2970*s*, 2920, 2880, 1735*s*, 1595, 1480, 1420, 1395, 1365, 1310, 1270, 1180*s*, 1135*s*, 1105, 1025, 990, 915, 890, 865. ^{1}H-NMR ($CDCl_3$): 1.33 (*s*, 2 *t*-Bu); 1.31–1.36 (*m*, 2 ring H); 1.56–1.60 (*m*, 2 ring H); 2.31 (*s*, PhCH_3); 3.00 (*s*, OH); 7.11 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 17.28 (*t*); 21.48 (*q*); 31.44 (*q*); 35.29 (*s*); 56.24 (*s*); 127.06 (*d*); 134.76 (*s*); 142.03 (*s*); 145.78 (*s*); 174.84 (*s*). MS: 304 (7, $M^{+\cdot}$), 205 (100). Anal. calc. for $C_{19}H_{28}O_3$: C 74.96, H 9.27; found: C 74.72, H 9.62.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Iodocyclopropanecarboxylate* (**15**). Colorless crystals (93%) after FC (pentane/Et_2O 98:2), m.p. (pentane) 110.8–111.4°. IR ($CHCl_3$): 3000, 2970*s*, 2920, 2880, 1730*s*, 1595, 1480, 1420, 1395, 1365, 1295*s*, 1180, 1120*s*, 1105*s*, 1045, 920, 890, 865. ^{1}H-NMR ($CDCl_3$): 1.36 (*s*, 2 *t*-Bu); 1.44–1.48 (*m*, 2 ring H); 1.80–1.85 (*m*, 2 ring H); 2.30 (*s*, PhCH_3); 7.09 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): −8.67 (*s*); 21.52 (*q*); 23.83 (*t*); 31.58 (*q*); 35.33 (*s*); 126.93 (*d*); 134.70 (*s*); 141.87 (*s*); 146.71 (*s*); 170.82 (*s*). MS: 414 (7, $M^{+\cdot}$), 195 (100). Anal. calc. for $C_{19}H_{27}IO_2$: C 55.08, H 6.57; found: C 55.22, H 6.70.

General Procedure for the Preparation of the Carboxylic Acids **16**–**19**. A suspension of the corresponding ester **7**, **9**, **10**, or **11** (2–4 mmol), *t*-BuOK (6 equiv.), and H_2O (2 equiv.) in 10–20 ml of THF was heated under reflux until TLC indicated that the starting material had disappeared (2 h for aldols, 36 h for the other compounds). After extraction with 2N KOH, the H_2O phase was acidified with conc. HCl, extracted with Et_2O, dried (Na_2SO_4), and concentrated. Purification as described below yielded the acids **16**–**19**.

1-Methylcyclopropanecarboxylic Acid (**16**). Bulb-to-bulb distillation (110°/15 Torr) gave 87% of the known **16** as a colorless liquid which solidified upon cooling (m.p. of an authentic sample of *Fluka AG*: 30–32°).

1-Benzylcyclopropanecarboxylic Acid (**17**). FC (pentane/Et_2O 30:70) gave 73% of **17** as colorless crystals, m.p. (pentane/Et_2O) 108–108.8° ([22]: 102–104°).

1-(1-Hydroxy-2-methylpropyl)cyclopropanecarboxylic Acid (**18**). Bulb-to-bulb distillation gave 58% of **18** as a viscous liquid which solidified upon standing, b.p. 150°/0.05 Torr. IR ($CHCl_3$): 3580 (br.), 3500–2200 (br.), 1680*s*, 1460, 1420, 1400, 1365, 1330, 1115, 1070, 1040*s*, 1030*s*, 985, 960, 950, 885, 620. ^{1}H-NMR ($CDCl_3$): 0.87–1.04 (*m*, 2 ring H); 0.94 (*d*, J = 6.8, 3 H, $(CH_3)_2CH$); 1.03 (*d*, J = 6.6, 3 H, $(CH_3)_2CH$); 1.18–1.25 (*m*, 1 ring H); 1.50–1.57 (*m*, 1 ring H); 2.14–2.26 (*m*, $(CH_3)_2CH$); 2.57 (*d*, J = 8.9, CHOH); 6.10 (br., OH, COOH); 7.26 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 14.81 (*t*); 15.76 (*t*); 19.95 (*q*); 26.75 (*s*); 33.65 (*t*); 81.98 (*d*); 180.02 (*s*). MS: 115 (44), 97 (100). Anal. calc. for $C_8H_{14}O_3$: C 60.74, H 8.92; found: C 60.94, H 9.05.

1-(α-Hydroxybenzyl)cyclopropanecarboxylic Acid (**19**). FC (pentane/Et_2O 1:1 to 0:1) gave 41% of **19** as colorless crystals, m.p. (pentane/Et_2O) 92.0–93.2°. IR ($CHCl_3$): 3600 (br.), 3500–2200 (br.), 1680*s*, 1490, 1450, 1420, 1310, 1170, 1125, 1080, 1075, 1040*s*, 1025*s*, 960, 910, 885, 700, 610. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.70–1.50 (*m*, 4 ring H); 4.90 (*s*, PhCH); 7.00 (br. *s*, OH, COOH); 7.15–7.50 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 12.56 (*t*); 15.20 (*t*); 28.51 (*s*); 73.82 (*d*); 126.75 (*d*); 127.68 (*d*); 128.12 (*d*); 140.56 (*s*); 180.76 (*s*). MS: 192 (58, $M^{+\cdot}$), 191 (93), 105 (100). Anal. calc. for $C_{11}H_{12}O_3$: C 68.74, H 6.29; found: C 68.91, H 6.37.

General Procedure for the Preparation of the Cyclopropanemethanols **20**–**23**. A suspension of the corresponding ester **8**, **9**, **10**, or **11** (3–7 mmol) and $LiAlH_4$ (10–20 mmol) in 20–40 ml of THF was heated under reflux until TLC indicated that the starting material had disappeared (12–24 h). After quenching by the N,N,3N method [43], the soln. was dried ($MgSO_4$), concentrated, and the crude product purified as described below.

1-Allylcyclopropanemethanol (**20**). FC (pentane/Et_2O 60:40) followed by bulb-to-bulb distillation gave 75% of **20** as a colorless liquid, b.p. 70°/15 Torr. IR ($CHCl_3$): 3690, 3610, 3470 (br.), 3090, 3000, 2930, 2880, 1640, 1600, 1460, 1430, 1400, 1030*s*, 1005*s*, 925*s*, 905, 860, 625. ^{1}H-NMR ($CDCl_3$): 0.42 (*s*, 4 ring H); 1.41 (br. *s*, OH); 2.17 (*dt*, J = 7.1, 1.2, CH_2=CHCH_2); 3.42 (*s*, CH_2OH); 5.02–5.13 (*m*, CH_2=CHCH$_2$); 5.85 (*ddt*, J = 17.2, 10.1, 7.1, CH_2=CHCH$_2$). ^{13}C-NMR ($CDCl_3$): 9.40 (*t*); 22.10 (*s*); 38.55 (*t*); 68.88 (*t*); 116.53 (*t*); 136.21 (*d*). MS: 84 (67), 41 (100). Anal. calc. for $C_7H_{12}O$: C 74.95, H 10.78; found: C 74.38, H 10.78.

1-Benzylcyclopropanemethanol (**21**). FC (pentane/Et_2O 40:60) followed by bulb-to-bulb distillation gave 84% of **21** as a colorless liquid, b.p. 100°/0.1 Torr. IR ($CHCl_3$): 3620, 3460 (br.), 3080, 3000, 2930, 2880, 1605, 1495, 1460, 1430, 1395, 1080, 1030*s*, 1000*s*, 945, 925, 910, 860, 700, 610. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.32–0.60 (*m*, 4 ring H); 1.55 (br. *s*, OH); 2.70 (*s*, PhCH_2); 3.30 (*s*, CH_2OH); 7.25 (*s*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 9.52 (*t*); 23.19 (*s*); 39.69 (*t*); 68.01 (*t*); 126.16 (*d*); 128.21 (*d*); 129.44 (*d*); 139.79 (*s*). MS: 162 (1, $M^{+\cdot}$), 91 (100). Anal. calc. for $C_{11}H_{14}O$: C 81.44, H 8.70; found: C 81.29, H 8.72.

1-[1-(Hydroxymethyl)cyclopropyl]-2-methylpropan-1-ol (**22**). FC (Et_2O) followed by bulb-to-bulb distillation gave 72% of **22** as a colorless liquid, b.p. 90°/0.05 Torr. IR ($CHCl_3$): 3670, 3600, 3500 (br.), 3080, 2960*s*, 2880*s*, 1600, 1470, 1430, 1390, 1365, 1310, 1115, 1035*s*, 1020*s*, 980, 950, 940, 890, 835. ^{1}H-NMR ($CDCl_3$): 0.46–0.63 (*m*, 4 ring H); 0.94 (*d*, J = 6.7, 3 H, $(CH_3)_2CH$); 1.06 (*d*, J = 6.5, 3 H, $(CH_3)_2CH$); 2.00–2.07 (*m*, $(CH_3)_2CH$); 2.48 (*d*, J = 9.5, H–C(1)); 2.90 (br. *s*, OH); 2.93 (*d*, J = 11.2, 1 H, CH_2OH); 3.03 (br. *s*, OH); 4.26 (*d*, J = 11.2, 1 H, CH_2OH). ^{13}C-NMR ($CDCl_3$): 9.37 (*t*); 10.11 (*t*); 19.45 (*q*); 20.19 (*q*); 24.70 (*s*); 32.90 (*d*); 67.47 (*t*); 85.19 (*d*). MS: 83 (100). Anal. calc. for $C_8H_{16}O_2$: C 66.63, H 11.18; found: C 66.53, H 11.10.

α-[1-(Hydroxymethyl)cyclopropyl]benzyl Alcohol (**23**). FC (Et_2O) gave 83% of **23** as a colorless viscous liquid. IR ($CHCl_3$): 3600, 3500 (br.), 3060, 3000, 2830, 2780, 1600, 1490, 1450, 1420, 1320, 1080, 1035*s*, 1015*s*, 940, 915, 900, 700, 640. ^{1}H-NMR ($CDCl_3$): 0.42–0.48 (*m*, 1 ring H); 0.60–0.73 (*m*, 3 ring H); 2.60 (br. *s*, OH); 3.18 (*d*, J = 11.3, 1 H, CH_2OH); 3.42 (br. *s*, OH); 3.73 (*d*, J = 11.3, 1 H, CH_2OH); 4.47 (*s*, H–C(α)); 7.24–7.40 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 7.85 (*t*); 9.71 (*t*); 27.28 (*s*); 68.16 (*t*); 79.31 (*d*); 126.25 (*d*); 127.35 (*d*); 128.09 (*d*); 142.09 (*s*). MS: 178 (4, $M^{+\cdot}$), 176 (6), 107 (100). Anal. calc. for $C_{11}H_{14}O_2$: C 74.13, H 7.92; found: C 74.03, H 8.18.

2,6-Di(tert-*butyl*)*-4-methylphenyl 2-Methylcyclopropanecarboxylate* (**24**). To an ice-cooled soln. of 2,6-di-(*tert*-butyl)-4-methylphenol (40.4 g, 183 mmol) in 180 ml of THF, stirred under Ar, was added 183 mmol of BuLi. After 10 min, 2-methylcyclopropanecarbonyl chloride (22.4 g, 189 mmol) was added and stirring was continued at r.t. for 24 h. The mixture was poured onto 70 ml of sat. aq. NH_4Cl soln. After separation of the two layers, the H_2O

phase was extracted once with 170 ml of Et_2O. The org. phases were combined, washed twice each with sat. aq. $NaHCO_3$ and sat. aq. NaCl, and dried (Na_2SO_4). Evaporation and recrystallization from MeOH gave 45.0 g (81%) of **24** as colorless crystals, m.p. 67–68° (pentane). IR ($CHCl_3$): 2980*s*, 2930, 2890, 1743*s*, 1602, 1411, 1388, 1371, 1331, 1154*s*, 1119, 1097, 1050, 962, 897, 870, 859. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.80–0.88 (*m*, 1 ring H); 1.19 (*d*, J = 4, CH_3–C(2)); 1.33 (*s*, *t*-Bu); 1.34 (*s*, *t*-Bu); 1.48–1.59 (*m*, 1 ring H); 1.60–1.68 (*m*, 1 ring H); 2.30 (*s*, PhCH_3); 7.08 (*s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 17.25; 17.91; 18.12; 21.49; 22.56; 31.46; 35.27; 126.86; 134.18; 142.14; 146.09; 174.51. MS: 302 (2, M^+), 83 (100). Anal. calc. for $C_{20}H_{30}O_2$: C 79.42, H 10.00; found: C 79.71, H 9.86.

2,6-Di(tert-*butyl*)-*4-methylphenyl 2-Phenylcyclopropanecarboxylate* (**25**). As described above, 14.8 g (82 mmol) of 2-phenylcyclopropanecarbonyl chloride was treated to give 12.6 g (42%) of **25** as colorless crystals, m.p. (pentane) 81°. IR ($CHCl_3$): 2962, 2910, 2875, 1737*s*, 1595, 1398, 1362, 1336, 1321, 1149*s*, 1109, 1082, 1077, 1050, 1022, 888, 879. ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.35 (*s*, 2 *t*-Bu); 1.42–1.85 (2*m*, 2 ring H); 2.00–2.30 (*m*, 1 ring H); 2.31 (*s*, PhCH_3); 2.56–2.83 (*m*, 1 ring H); 7.00–7.40 (*m*, 7 arom. H). ^{13}C-NMR ($CDCl_3$): 16.64; 21.55; 25.19; 27.10; 31.52; 35.34; 126.44; 126.60; 126.73; 126.98; 128.61; 134.48; 139.67; 142.09; 146.06; 173.63. MS: 364 (2, M^+), 145 (100). Anal. calc. for $C_{25}H_{32}O_2$: C 82.37, H 8.85; found: C 82.60, H 8.90.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1,2-Dimethylcyclopropanecarboxylate* (**26**). After FC (pentane/Et_2O 95:5), 90%. First diastereoisomer (62%): colorless liquid, b.p. 110°/0.05 Torr. IR ($CHCl_3$): 2980*s*, 2880, 1732*s*, 1600, 1400, 1369, 1310, 1277, 1150*s*, 1107*s*, 1095*s*, 1044, 895, 868. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.38–0.57 (*m*, 1 ring H); 1.19 (*d*, J = 5, CH_3–C(2)); 1.32 (*s*, 2 *t*-Bu); 1.50 (*s*, CH_3–C(1)); 1.1–1.8 (*m*, 3 ring H); 2.31 (*s*, PhCH_3); 7.07 (*s*, 2 arom. H). MS: 316 (1, M^+), 97 (100). Anal. calc. for $C_{21}H_{32}O_2$: C 79.70, H 10.19; found: C 79.97, H 9.86.

Second diastereoisomer (38%): ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.27 (*s*, CH_3–C(2)); 1.33 (*s*, 2 *t*-Bu); 1.54 (*s*, CH_3–C(1)); 0.92–1.66 (3 ring H); 7.07 (*s*, 2 arom. H).

One of the acids obtained from the crude ester by hydrolysis had b.p. 50–60°/0.05 Torr.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Benzyl-2-methylcyclopropanecarboxylate* (**27**). FC (pentane/Et_2O 98:2), 70% of a single diastereoisomer could be isolated as colorless crystals, m.p. (Et_2O/pentane) 109–111°. IR ($CHCl_3$): 2960*s*, 2870, 1727*s*, 1596, 1391, 1362, 1348, 1270, 1129*s*, 1103*s*, 1089, 1045, 1030, 1010, 890, 860. ^{1}H-NMR ($CDCl_3$): 0.94–1.00 (*m*, 1 ring H); 1.09–1.14 (*m*, 1 ring H); 1.26 (*s*, *t*-Bu); 1.28 (*d*, J = 2, CH_3–C(2)); 1.20–1.30 (*m*, 1 ring H); 1.36 (*s*, *t*-Bu); 2.29 (*s*, PhCH_3); 3.30 (*'d'*, *AB*, J = 14, 1 H, PhCH_2); 3.55 (*'d'*, *AB*, J = 14, 1 H, PhCH_2); 7.06–7.12 (*m*, 2 arom. H); 7.18–7.33 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 11.82 (*q*); 21.43 (*q*); 22.32 (*t*); 22.80 (*d*); 27.93 (*s*); 31.46 (*q*); 31.63 (*q*); 34.98 (*s*); 35.34 (*s*); 38.14 (*t*); 126.48 (*d*); 126.78 (*d*); 127.02 (*s*); 128.20 (*d*); 130.13 (*d*); 134.12 (*s*); 138.00 (*s*); 141.99 (*s*); 146.18 (*s*); 174.17 (*s*). MS: 392 (0.2, M^+), 173 (100). Anal. calc. for $C_{27}H_{36}O_2$: C 82.61, H 9.24; found: C 82.74, H 9.02.

The acid obtained from the crude ester by hydrolysis had b.p. 120°/0.05 Torr.

2,6-Di-(tert-*butyl*)-*4-methylphenyl 1-(α-Hydroxybenzyl)-2-methylcyclopropanecarboxylate* (**28**). After FC (pentane/Et_2O 85:15), 84%. First diastereoisomer (45%): colorless crystals, m.p. (pentane/Et_2O) 142–143°. IR ($CHCl_3$): 3555, 2993*s*, 2900, 1721*s*, 1608, 1459, 1429, 1404, 1375, 1326*s*, 1279, 1142*s*, 1114*s*, 1092, 1059*s*, 1039, 946, 929, 916, 900, 875, 850, 626. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.93 (*s*, *t*-Bu); 1.28 (*s*, *t*-Bu); 1.56 (*d*, J = 6, CH_3–C(2)); 0.7–1.7 (*m*, 2 ring H); 1.95–2.21 (*m*, 1 ring H); 2.24 (*s*, PhCH_3); 4.35 (*AB*, J = 12, PhC*HOH*; D_2O: 4.45 (*s*)); 6.85–7.10 (*m*, 2 arom. H); 7.10–7.35 (*m*, 3 arom. H); 7.35–7.63 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 13.73 (*q*); 21.37 (*q*); 22.31 (*t*); 22.82 (*d*); 31.02 (*q*); 31.21 (*q*); 34.83 (*s*); 35.06 (*s*); 73.74 (*d*); 126.27; 126.74; 126.81; 127.16; 127.72; 134.62 (*s*); 141.86 (*s*); 142.20 (*s*); 142.55 (*s*); 145.28 (*s*); 174.92 (*s*). MS: 220 (100). Anal. calc. for $C_{27}H_{36}O_3$: C 79.37, H 8.88; found: C 79.17, H 8.99.

The other diastereoisomers were not obtained in an anal. pure form. One of the alcohols obtained from the crude ester by reduction had m.p. (CH_2Cl_2) 59–59.5°.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Benzoyl-2-methylcyclopropanecarboxylate* (**29**). After FC (pentane/Et_2O 95:5), 80%. First diastereoisomer (60%): colorless crystals, m.p. (pentane/Et_2O) 92–95°. IR ($CHCl_3$): 2970*s*, 2880, 1739*s*, 1674*s*, 1600, 1450, 1418, 1396, 1365, 1319, 1289*s*, 1134*s*, 1101*s*, 1055, 1028, 1011, 969, 895, 863. ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.07 (*s*, *t*-Bu); 1.22 (*s*, *t*-Bu); 1.36 (*m*, 1 ring H); 1.58 (*d*, J = 5, CH_3–C(2)); 1.94 (*m*, 2 ring H); 2.27 (*s*, PhCH_3); 7.01 (*s*, 2 arom. H); 7.30–7.63 (*m*, 3 arom. H); 7.95–8.20 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 11.47; 21.38; 23.87; 26.19; 31.19; 34.95; 35.10; 37.93; 126.55; 126.84; 128.46; 128.60; 129.53; 130.21; 133.14; 134.57; 137.44; 142.08; 146.0; 170.1; 195.0. MS: 406 (1, M^+), 187 (100). Anal. calc. for $C_{27}H_{34}O_3$: C 79.77, H 8.43; found: C 79.48, H 8.54.

Second diastereoisomer (40%): colorless crystals, m.p. (Et_2O/pentane) 114–115°. ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.14 (*d*, CH_3–C(2)); 1.17 (*s*, *t*-Bu); 1.25 (*s*, *t*-Bu); 1.43–1.67 (*m*, 1 ring H); 1.85–2.05 (*dd*, J = 5, 9, 1 ring H); 2.26 (*s*, PhCH_3); 2.05–2.45 (*m*, 1 ring H); 7.02 (*s*, 2 arom. H); 7.27–7.61 (*m*, 3 arom. H); 7.94–8.17 (*m*, 2 arom. H).

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Methyl-2-phenylcyclopropanecarboxylate* (**30**). After FC (pentane/Et_2O 97:3), 68%. First diastereoisomer (50%): colorless crystals, m.p. (pentane) 101–102°. IR ($CHCl_3$): 2989*s*, 2885,

1745*s*, 1601, 1393*s*, 1369, 1298, 1145*s*, 1116*s*, 1092, 1073, 1056, 970, 909, 892, 869. ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.34 (*s*, *t*-Bu); 1.43 (*s*, *t*-Bu); 1.62 (*s*, CH_3–C(1)); 1.17–1.70 (*m*, 2 ring H); 2.10–2.28 (*m*, 1 ring H); 2.30 (*s*, PhCH_3); 7.10 (*s*, 2 arom. H); 7.20–7.44 (*m*, 5 arom. H). ^{13}C-NMR ($CDCl_3$): 20.35; 21.49; 21.85; 27.76; 31.61; 32.89; 35.22; 35.34; 126.31; 126.72; 126.90; 127.07; 127.73; 128.63; 134.20; 142.10; 145.87; 172.92. MS: 378 (2, $M^{+\cdot}$), 159 (100). Anal. calc. for $C_{26}H_{34}O_2$: C 82.49, H 9.05; found: C 82.30, H 9.14.

The second diastereoisomer was not obtained in an anal. pure form.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-Benzyl-2-phenylcyclopropanecarboxylate* (**31**). After FC (pentane/Et_2O 93:7), 62%. First diastereoisomer (58%): colorless crystals, m.p. (Et_2O/pentane) 127–128°. IR ($CHCl_3$): 2970*s*, 2920, 2875, 1746*s*, 1598, 1384, 1364, 1137, 1108*s*, 1078, 1054, 1030, 969, 889, 862. ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.28 (*s*, 2 *t*-Bu); 1.45–1.70 (*m*, 1 ring H); 1.70–1.93 (*m*, 1 ring H); 2.21 (*s*, PhCH_3); 2.24–2.47 (*m*, 1 ring H); 2.40 (*'d', AB, J* = 14, 1 H, PhCH_2); 3.40 (*'d', AB, J* = 14, 1 H, PhCH_2); 6.87–7.27 (*m*, 12 arom. H). ^{13}C-NMR ($CDCl_3$): 20.71; 21.33; 27.73; 31.57; 31.89; 35.26; 37.98; 46.86; 126.50; 126.65; 126.76; 127.52; 128.03; 129.53; 130.23; 134.02; 137.98; 138.07; 142.07; 145.88; 171.24. MS: 91 (100). Anal. calc. for $C_{32}H_{38}O_2$: C 84.54, H 8.42; found: C 84.52, H 8.41.

Second diastereoisomer (42%): ^{1}H-NMR ($CDCl_3$, 90 MHz): 1.37 (*s*, *t*-Bu); 1.50 (*s*, *t*-Bu); 1.60–1.84 (*m*, 2 ring H); 2.33 (*s*, PhCH_3); 2.28–2.54 (*m*, 1 ring H); 3.03 (*'d', AB, J* = 14, PhCH_2); 3.49 (*'d', AB, J* = 14, 1 H, PhCH_2); 6.77–6.98 (*m*, 2 arom. H); 6.98–7.40 (*m*, 10 arom. H).

One of the acids obtained from the crude ester by hydrolysis had m.p. (Et_2O) 157–159°.

2,6-Di(tert-*butyl*)-*4-methylphenyl 1-(α-Hydroxybenzyl)-2-phenylcyclopropanecarboxylate* (**32**). After FC (pentane/Et_2O 90:10), 53%. First diastereoisomer (43%), colorless crystals, m.p. (Et_2O/pentane) 160–161°. IR ($CHCl_3$): 3605, 2967*s*, 2915, 2875, 1738*s*, 1599, 1450, 1419, 1392, 1363, 1124*s*, 1098*s*, 1078*s*, 1060, 1039, 1025, 1003, 988, 951, 887, 861. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.89–1.23 (*m*, 1 ring H); 1.06 (*s*, *t*-Bu); 1.38 (*s*, *t*-Bu); 1.86–2.13 (*m*, 1 ring H); 2.24 (*s*, PhCH_3); 2.78 (*t*, *J* = 9, 1 ring H); 2.94 (*s*, OH); 6.16 (*s*, PhC*H*); 6.93–7.56 (*m*, 12 arom. H). ^{13}C-NMR ($CDCl_3$): 21.20 (*t*); 21.34 (*q*); 29.49 (*d*); 31.64 (*q*); 35.01 (*s*); 35.26 (*s*); 38.79 (*s*); 27.26 (*d*); 126.55; 126.94; 127.19; 127.42; 127.89; 128.17; 130.18; 134.28; 134.47; 139.71; 141.54; 142.48; 145.85; 171.42. MS: 470 (0.01, $M^{+\cdot}$), 220 (100). Anal. calc. for $C_{32}H_{38}O_3$: C 81.66, H 8.14; found: C 81.74, H 8.17.

The other diastereoisomers were not obtained in an anal. pure form. One of the alcohols obtained from the crude ester by reduction had m.p. 104–105°.

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