

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

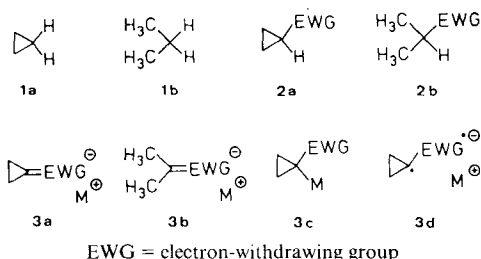
by Robert Häner¹⁾, Thomas Maetzke²⁾, and Dieter Seebach*

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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*-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/H₂O/THF) to the corresponding carboxylic acids or reduced (LiAlH₄/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], SO₂R [4] [5] [8] [9], NO₂ [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 species³⁾.



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.

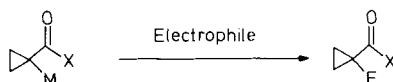
Besides these physical organic aspects, synthetic applications of EWG-substituted cyclopropyl nucleophiles have been studied extensively. A list of leading references to papers in which the successful generation and reactions with electrophiles of metalated

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].

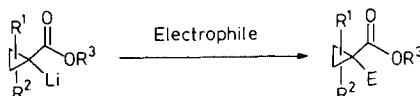
Scheme 1



M	X ^{a)}	Electrophile	Ref.
Li	MeO	Me ₃ SiCl	Ainsworth <i>et al.</i> (1972) [19a]
Li	LiO	Me ₃ SiCl	Ainsworth and Kuo (1972) [19b]
Li	<i>t</i> -BuS	RCOR'	Wemple (1975) [20]
Li	<i>t</i> -BuS	Nitroolefin	Our group (1981) [21]
Li	LiO	RX	Warner and Le (1982) [22]
Bu ₄ N	MeO	RCOR'	Paquette <i>et al.</i> (1984) [23]
NiL _n	Me ₂ N	RCOR'; acrylic ester	Hirao <i>et al.</i> (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 ≠ H (many examples)		Me	RX, MeSSMe	Reichelt and Reissig (1982–1985) [14] [28]
Ph	H	Me, Et	MeI, (Ph) ₂ CO	Feit <i>et al.</i> (1984) [16]

Scheme 3

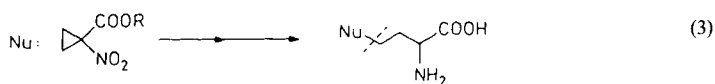
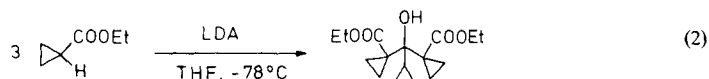
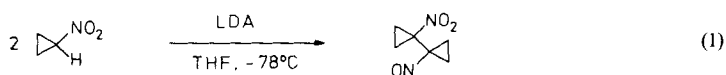
	EWG:	C≡N	Walborsky and Hornyak (1955) [29] Van Cantfort and Coates (1981) [30]
		N=C	Walborsky and Periasamy (1974) [31]
		SO ₂ Ph	Chang and Pinnick (1978) [32] Pohmakotr and Pisutjaroenpong (1985) [33] Padwa and Wannamaker (1986) [34]
		PO(OEt) ₂	Hirao <i>et al.</i> (1985) [35] Haller and Benoist (1921) [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.

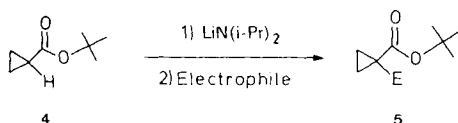
During an investigation aimed at an amino-acid α^4 -reagent, see *Scheme 4*, *Eqn. 3*, we were looking for a method of preparing α -nitrocyclopropanecarboxylic-acid derivatives.

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

Scheme 4

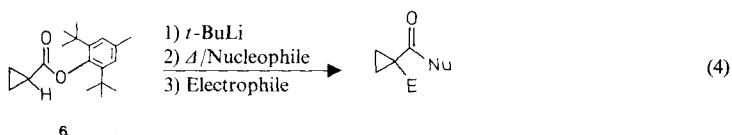


Scheme 5



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

Scheme 6

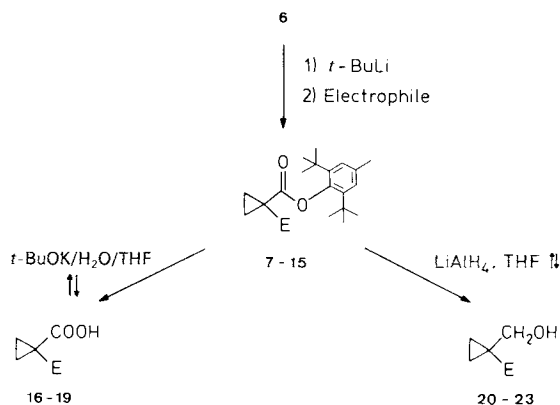


We first examined the reaction of the enolate from the *tert*-butyl ester **4**, the generation of which has been described by *Gorrichon et al.* [15], with various electrophiles including nitrating reagents. Although, a clean reaction occurred with alkyl halides and with carbonyl compounds ($\rightarrow$ **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 ($\rightarrow$ **7–9**), an aldehyde ($\rightarrow$ **10, 11**), an acyl chloride ($\rightarrow$ **12**) as well as a hetero-atom-transferring reagent (isopentyl nitrate, O₂, and I₂ ($\rightarrow$ **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

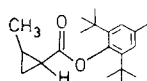


Electrophile	E	Product (Yield [%])		
		Ester	Acid	Alcohol
CH ₃ I	CH ₃	7 (71)	16 (87)	
	CH ₂ CHCH ₂	8 (86)		20 (75)
	C ₆ H ₅ CH ₂	9 (88)	17 (73)	21 (84)
	(CH ₃) ₂ CHCH(OH)	10 (91)	18 (58)	22 (72)
	C ₆ H ₅ CH(OH)	11 (93)	19 (41)	23 (83)
	CH ₃ OCO	12 (88)		
	NO ₂	13 (70)		
O ₂	OH	14 (25)		
I ₂	I	15 (93)		

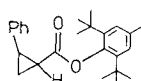
Cleavage to the corresponding carboxylic acids was accomplished by the method of Gassman *et al.* [39] (*t*-BuOK/THF/2 equiv. of H₂O). While no complications arose with the methylated (7) and benzylated (9) esters (→16 and 17, respectively), the allylated derivative 8 underwent partial double-bond shift 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 LiAlH₄ [40] to yield alcohols (20, 21) or diols (22, 23). The α-heterosubstituted esters 13–15 could not be hydrolyzed 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



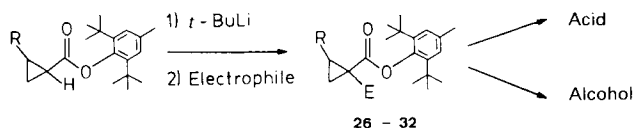
24



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)}
Me (24)	CH ₃ I	CH ₃	26 (90; 2:1)	(73; 2:1)	
	C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₂	27 (70; > 20:1)	(92; 24:1)	
	C ₆ H ₅ CHO	C ₆ H ₅ CH(OH)	28 (84) ^{c)}		(96; 2:2:1)
	C ₆ H ₅ COCl	C ₆ H ₅ CO	29 (80; 3:2)		
Ph (25)	CH ₃ I	CH ₃	30 (68; 1:1)		
	C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₂	31 (62; 2:3)	(11) ^{d)}	
	C ₆ H ₅ CHO	C ₆ H ₅ CH(OH)	32 (53; 5:3:2:2)		(87; 6:3:3:1)

^{a)} Determined by ¹H-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 SOCl₂. 2-Phenylcyclopropanecarbonyl chloride was likewise prepared from the corresponding acid which was obtained by hydrolysis (KOH/H₂O/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*. ¹H-NMR spectra (CDCl₃): *Bruker WM-300-W8* (300 MHz) or *Varian EM-390* (90 MHz); unless otherwise indicated, 300-MHz spectra are reported; ¹³C-NMR spectra (CDCl₃): *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-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. NH₄Cl soln., otherwise the soln. was allowed to warm to r.t. during 4 h. The mixture was poured onto sat. aq. NH₄Cl soln., the layers were separated, and the H₂O phase was twice extracted with Et₂O. The combined org. phases were washed twice with brine, dried (MgSO₄), concentrated, and purified by FC (pentane/Et₂O) followed by bulb-to-bulb distillation.

tert-Butyl 1-Allylcyclopropanecarboxylate (5a). Colorless liquid (79%) after FC (pentane/Et₂O 95:5) followed by bulb-to-bulb distillation, b.p. 100°/15 Torr. IR (CHCl₃): 3090, 2990, 2940, 1710s, 1645, 1480, 1460, 1440, 1425, 1400, 1375, 1360, 1280, 1160s, 1100, 1070, 1035, 1010, 995, 950, 925, 900, 855. ¹H-NMR (CDCl₃): 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, CH₂=CHCH₂); 4.97–5.06 (*m*, 2 olefin. H); 5.79–5.92 (*m*, 1 olefin. H). ¹³C-NMR (CDCl₃): 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*⁺ – 56), 57 (100). Anal. calc. for C₁₁H₁₈O₂: C 72.49, H 9.95; found: C 72.62, H 10.16.

tert-Butyl 1-Benzylcyclopropanecarboxylate (5b). Colorless liquid (82%) after FC (pentane/Et₂O 98:2) followed by bulb-to-bulb distillation, b.p. 80°/0.05 Torr. IR (CHCl₃): 3100, 3080, 2990, 2950, 1710s, 1610, 1590, 1500, 1480, 1460, 1430, 1400, 1375s, 1365s, 1300, 1150s, 1080, 1070, 1035, 1000, 950, 920, 855, 700. ¹H-NMR (CDCl₃): 0.72–0.75 (*m*, 2 ring H); 1.19–1.23 (*m*, 2 ring H); 1.34 (*s*, *t*-Bu); 2.93 (*s*, PhCH₂); 7.15–7.29 (*m*, 5 arom. H). ¹³C-NMR (CDCl₃): 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*⁺), 57 (100). Anal. calc. for C₁₅H₂₀O₂: 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/Et₂O 95:5 to 80:20) followed by bulb-to-bulb distillation, b.p. 105°/0.05 Torr. IR (CHCl₃): 3580 (br.), 3100, 3080, 2990, 2940, 2920, 1730–1700s (br.), 1610, 1500, 1480, 1465, 1400, 1375s, 1150s, 1090, 1040s, 1030s, 980, 970, 950, 920, 905, 865, 850, 705, 650. ¹H-NMR (CDCl₃): 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*, PhCH); 7.24–7.43 (*m*, 5 arom. H). ¹³C-NMR (CDCl₃): 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*⁺ – 56). Anal. calc. for C₁₅H₂₀O₃: 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/Et₂O 95:5) followed by bulb-to-bulb distillation, b.p. 110°/0.01 Torr. IR (CHCl₃): 3570, 3500 (br.), 2990, 2850, 1725–1700s (br.), 1605, 1495, 1480, 1450, 1390, 1375s, 1340, 1310, 1260, 1160s, 1130s, 1090, 1080, 1040, 970, 930, 900, 850, 700, 650. ¹H-NMR (CDCl₃): 0.94–1.00 (*m*, 1 ring H); 1.05–1.17 (*m*, 2 ring H); 1.19 (*s*, *t*-Bu); 1.23 (*s*, CH₃); 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). ¹³C-NMR (CDCl₃): 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*⁺), 121 (100). Anal. calc. for C₁₆H₂₂O₃: 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 I₂, the reaction was quenched with sat. aq. NH₄Cl soln. after 5 min, otherwise the soln. was allowed to warm to r.t. within 4 h. The mixture was diluted with Et₂O, washed with sat. aq. NH₄Cl soln. and brine, dried (MgSO₄), concentrated, and purified by FC (pentane/Et₂O).

2,6-Di(tert-butyl)-4-methylphenyl 1-Methylcyclopropanecarboxylate (7). Colorless crystals (71%) after FC (pentane/Et₂O 97:3), m.p. (MeOH) 96.0–96.8°. IR (CHCl₃): 3000, 2980s, 2920, 2880, 1735s, 1600, 1470, 1425, 1395, 1370, 1330s, 1270, 1190, 1140, 1115s, 1030, 955, 915, 895, 865, 840. ¹H-NMR (CDCl₃): 0.78–0.83 (*m*, 2 ring H); 1.33 (*s*, *t*-Bu); 1.35–1.39 (*m*, 2 ring H); 1.53 (*s*, CH₃); 2.30 (*s*, PhCH₃); 7.08 (*s*, 2 arom. H). ¹³C-NMR (CDCl₃): 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*⁺), 83 (100). Anal. calc. for C₂₀H₃₀O₂: 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/Et₂O 97:3) followed by bulb-to-bulb distillation, b.p. 120°/0.03 Torr. IR (CHCl₃): 3080, 2970, 2920, 2880, 1730s, 1640, 1595, 1480, 1420, 1390, 1360, 1340, 1260s, 1180s, 1130s, 1105s, 1025, 1005, 985, 950, 920, 890, 860, 825. ¹H-NMR (CDCl₃): 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*, PhCH₃); 2.62 (*d*, *J* = 7.1, CH₂=CHCH₂); 5.03–5.12 (*m*, CH₂=CH–CH₂); 5.87 (*ddt*, *J* = 17.1, 10.1, 7.1, CH₂=CHCH₂); 7.08 (*s*, 2 arom. H); ¹³C-NMR (CDCl₃): 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^+), 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/Et₂O 97:3), m.p. (MeOH) 84.2–85.2°. IR (CHCl₃): 2960s, 2920, 2870, 1725s, 1595, 1420, 1390, 1380, 1360, 1350, 1260s, 1175s, 1100s, 1025, 990, 910, 890, 860. ¹H-NMR (CDCl₃): 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, PhCH₃); 3.25 (s, PhCH₂); 7.07 (s, 2 arom. H); 7.20–7.26 (m, 5 arom. H). ¹³C-NMR (CDCl₃): 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^+), 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/Et₂O 80:20), m.p. (pentane) 133.8–134.2°. IR (CHCl₃): 3560 (br.), 2980s, 2930, 2880, 1725s, 1600, 1470, 1425, 1400, 1170, 1150, 1315, 1270, 1180, 1145s, 1110s, 1040s, 990, 970, 955, 930, 905, 895, 870, 610. ¹H-NMR (CDCl₃): 0.97 (d, *J* = 6.7, 3 H, (CH₃)₂CH); 1.01 (d, *J* = 6.6, 3 H, (CH₃)₂CH); 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, (CH₃)₂CH); 2.30 (s, PhCH₃); 2.55–2.77 (m, 2 H, CH–OH; D₂O: 2.57 (d, *J* = 10)); 7.09 (s, 2 arom. H). ¹³C-NMR (CDCl₃): 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 (q); 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/Et₂O 80:20), m.p. (pentane) 122.0–122.8°. IR (CHCl₃): 3600, 3540 (br.), 3000, 2970s, 2920, 2880, 1715s, 1600, 1450, 1420, 1395, 1365, 1355, 1300, 1270, 1180s, 1120s, 1105s, 1080, 1040s, 1030s, 1000, 970, 960, 925, 915, 890, 865. ¹H-NMR (CHCl₃): 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, PhCH₃); 3.47 (br., OH); 5.19 (s, PhCH); 7.08 (s, 2 arom. H); 7.24–7.39 (m, 5 arom. H). ¹³C-NMR (CDCl₃): 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/Et₂O 92:8), m.p. (pentane/Et₂O) 97.2–98.0°. IR (CHCl₃): 3000, 2970s, 2920, 2880, 1735s, 1595, 1480, 1435, 1420, 1395, 1365, 1330, 1310s, 1270, 1180, 1125s, 1105s, 1045, 1005, 970, 950, 905, 890, 865. ¹H-NMR (CDCl₃): 1.33 (s, 2 *t*-Bu); 1.56–1.66 (m, 4 ring H); 2.30 (s, PhCH₃); 3.79 (s, CH₃O); 7.09 (s, 2 arom. H). ¹³C-NMR (CDCl₃): 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^+), 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/Et₂O 1:0 to 75:25), m.p. (pentane) 120.2–121.6°. IR (CHCl₃): 3000, 2970s, 2920, 2880, 1750s, 1680 (br.), 1595, 1545s, 1480, 1415, 1395, 1365, 1335s, 1320, 1270, 1180s, 1150s, 1125, 1100, 1060, 1045, 910, 890, 860. ¹H-NMR (CDCl₃): 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, PhCH₃); 7.11 (s, 2 arom. H). ¹³C-NMR (CDCl₃): 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^+). 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 O₂ (dried by passing through a P₂O₅ 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 O₂ supply was stopped. The mixture was poured onto a 10% aq. soln. of Na₂SO₃, stirred for 10 min, and extracted twice with Et₂O. The org. layers were combined, washed with brine, dried (MgSO₄), concentrated, and purified by FC (pentane/Et₂O 70:30) to give 0.385 g (25%) of 14 as colorless crystals; m.p. (pentane) 78.8–81.2°. IR (CHCl₃): 3600, 3560 (br.), 3000, 2970s, 2920, 2880, 1735s, 1595, 1480, 1420, 1395, 1365, 1310, 1270, 1180s, 1135s, 1105, 1025, 990, 915, 890, 865. ¹H-NMR (CDCl₃): 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, PhCH₃); 3.00 (s, OH); 7.11 (s, 2 arom. H). ¹³C-NMR (CDCl₃): 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^+), 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/Et₂O 98:2), m.p. (pentane) 110.8–111.4°. IR (CHCl₃): 3000, 2970s, 2920, 2880, 1730s, 1595, 1480, 1420, 1395, 1365, 1295s, 1180, 1120s, 1105s, 1045, 920, 890, 865. ¹H-NMR (CDCl₃): 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, PhCH₃); 7.09 (s, 2 arom. H). ¹³C-NMR (CDCl₃): –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^+), 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 H₂O (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 H₂O phase was acidified with conc. HCl, extracted with Et₂O, dried (Na₂SO₄), 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/Et₂O 30:70) gave 73% of **17** as colorless crystals, m. p. (pentane/Et₂O) 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 (CHCl₃): 3580 (br.), 3500–2200 (br.), 1680s, 1460, 1420, 1400, 1365, 1330, 1115, 1070, 1040s, 1030s, 985, 960, 950, 885, 620. ¹H-NMR (CDCl₃): 0.87–1.04 (*m*, 2 ring H); 0.94 (*d*, *J* = 6.8, 3 H, (CH₃)₂CH); 1.03 (*d*, *J* = 6.6, 3 H, (CH₃)₂CH); 1.18–1.25 (*m*, 1 ring H); 1.50–1.57 (*m*, 1 ring H); 2.14–2.26 (*m*, (CH₃)₂CH); 2.57 (*d*, *J* = 8.9, CHOH); 6.10 (br., OH, COOH); 7.26 (*s*, 2 arom. H). ¹³C-NMR (CDCl₃): 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 C₈H₁₄O₃: C 60.74, H 8.92; found: C 60.94, H 9.05.

1-(α-Hydroxybenzyl)cyclopropanecarboxylic Acid (19). FC (pentane/Et₂O 1:1 to 0:1) gave 41% of **19** as colorless crystals, m. p. (pentane/Et₂O) 92.0–93.2°. IR (CHCl₃): 3600 (br.), 3500–2200 (br.), 1680s, 1490, 1450, 1420, 1310, 1170, 1125, 1080, 1075, 1040s, 1025s, 960, 910, 885, 700, 610. ¹H-NMR (CDCl₃, 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). ¹³C-NMR (CDCl₃): 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*⁺), 191 (93), 105 (100). Anal. calc. for C₁₁H₁₂O₃: 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 LiAlH₄ (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 (MgSO₄), concentrated, and the crude product purified as described below.

1-Allylcyclopropanemethanol (20). FC (pentane/Et₂O 60:40) followed by bulb-to-bulb distillation gave 75% of **20** as a colorless liquid, b. p. 70°/15 Torr. IR (CHCl₃): 3690, 3610, 3470 (br.), 3090, 3000, 2930, 2880, 1640, 1600, 1460, 1430, 1400, 1030s, 1005s, 925s, 905, 860, 625. ¹H-NMR (CDCl₃): 0.42 (*s*, 4 ring H); 1.41 (br. *s*, OH); 2.17 (*dt*, *J* = 7.1, 1.2, CH₂=CHCH₂); 3.42 (*s*, CH₂OH); 5.02–5.13 (*m*, CH₂=CHCH₂); 5.85 (*ddt*, *J* = 17.2, 10.1, 7.1, CH₂=CHCH₂). ¹³C-NMR (CDCl₃): 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 C₇H₁₂O: C 74.95, H 10.78; found: C 74.38, H 10.78.

1-Benzylcyclopropanemethanol (21). FC (pentane/Et₂O 40:60) followed by bulb-to-bulb distillation gave 84% of **21** as a colorless liquid, b. p. 100°/0.1 Torr. IR (CHCl₃): 3620, 3460 (br.), 3080, 3000, 2930, 2880, 1605, 1495, 1460, 1430, 1395, 1080, 1030s, 1000s, 945, 925, 910, 860, 700, 610. ¹H-NMR (CDCl₃, 90 MHz): 0.32–0.60 (*m*, 4 ring H); 1.55 (br. *s*, OH); 2.70 (*s*, PhCH₂); 3.30 (*s*, CH₂OH); 7.25 (*s*, 5 arom. H). ¹³C-NMR (CDCl₃): 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*⁺), 91 (100). Anal. calc. for C₁₁H₁₄O: C 81.44, H 8.70; found: C 81.29, H 8.72.

1-[1-(Hydroxymethyl)cyclopropyl]-2-methylpropan-1-ol (22). FC (Et₂O) followed by bulb-to-bulb distillation gave 72% of **22** as a colorless liquid, b. p. 90°/0.05 Torr. IR (CHCl₃): 3670, 3600, 3500 (br.), 3080, 2960s, 2880s, 1600, 1470, 1430, 1390, 1365, 1310, 1115, 1035s, 1020s, 980, 950, 940, 890, 835. ¹H-NMR (CDCl₃): 0.46–0.63 (*m*, 4 ring H); 0.94 (*d*, *J* = 6.7, 3 H, (CH₃)₂CH); 1.06 (*d*, *J* = 6.5, 3 H, (CH₃)₂CH); 2.00–2.07 (*m*, (CH₃)₂CH); 2.48 (*d*, *J* = 9.5, H–C(1)); 2.90 (br. *s*, OH); 2.93 (*d*, *J* = 11.2, 1 H, CH₂OH); 3.03 (br. *s*, OH); 4.26 (*d*, *J* = 11.2, 1 H, CH₂OH). ¹³C-NMR (CDCl₃): 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 C₈H₁₆O₂: C 66.63, H 11.18; found: C 66.53, H 11.10.

α-[1-(Hydroxymethyl)cyclopropyl]benzyl Alcohol (23). FC (Et₂O) gave 83% of **23** as a colorless viscous liquid. IR (CHCl₃): 3600, 3500 (br.), 3060, 3000, 2830, 2780, 1600, 1490, 1450, 1420, 1320, 1080, 1035s, 1015s, 940, 915, 900, 700, 640. ¹H-NMR (CDCl₃): 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, CH₂OH); 3.42 (br. *s*, OH); 3.73 (*d*, *J* = 11.3, 1 H, CH₂OH); 4.47 (*s*, H–C(α)); 7.24–7.40 (*m*, 5 arom. H). ¹³C-NMR (CDCl₃): 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*⁺), 176 (6), 107 (100). Anal. calc. for C₁₁H₁₄O₂: 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 into 70 ml of sat. aq. NH₄Cl soln. After separation of the two layers, the H₂O

phase was extracted once with 170 ml of Et₂O. The org. phases were combined, washed twice each with sat. aq. NaHCO₃ and sat. aq. NaCl, and dried (Na₂SO₄). Evaporation and recrystallization from MeOH gave 45.0 g (81%) of **24** as colorless crystals, m.p. 67–68° (pentane). IR (CHCl₃): 2980s, 2930, 2890, 1743s, 1602, 1411, 1388, 1371, 1331, 1154s, 1119, 1097, 1050, 962, 897, 870, 859. ¹H-NMR (CDCl₃, 90 MHz): 0.80–0.88 (*m*, 1 ring H); 1.19 (*d*, *J* = 4, CH₃–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*, PhCH₃); 7.08 (*s*, 2 arom. H). ¹³C-NMR (CDCl₃): 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 C₂₀H₃₀O₂: 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 (CHCl₃): 2962, 2910, 2875, 1737s, 1595, 1398, 1362, 1336, 1321, 1149s, 1109, 1082, 1077, 1050, 1022, 888, 879. ¹H-NMR (CDCl₃, 90 MHz): 1.35 (*s*, 2 *t*-Bu); 1.42–1.85 (*m*, 2 ring H); 2.00–2.30 (*m*, 1 ring H); 2.31 (*s*, PhCH₃); 2.56–2.83 (*m*, 1 ring H); 7.00–7.40 (*m*, 7 arom. H). ¹³C-NMR (CDCl₃): 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 C₂₅H₃₂O₂: 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/Et₂O 95:5), 90%. First diastereoisomer (62%): colorless liquid, b.p. 110°/0.05 Torr. IR (CHCl₃): 2980s, 2880, 1732s, 1600, 1400, 1369, 1310, 1277, 1150s, 1107s, 1095s, 1044, 895, 868. ¹H-NMR (CDCl₃, 90 MHz): 0.38–0.57 (*m*, 1 ring H); 1.19 (*d*, *J* = 5, CH₃–C(2)); 1.32 (*s*, 2 *t*-Bu); 1.50 (*s*, CH₃–C(1)); 1.1–1.8 (*m*, 3 ring H); 2.31 (*s*, PhCH₃); 7.07 (*s*, 2 arom. H). MS: 316 (1, *M*⁺), 97 (100). Anal. calc. for C₂₁H₃₂O₂: C 79.70, H 10.19; found: C 79.97, H 9.86.

Second diastereoisomer (38%): ¹H-NMR (CDCl₃, 90 MHz): 1.27 (*s*, CH₃–C(2)); 1.33 (*s*, 2 *t*-Bu); 1.54 (*s*, CH₃–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/Et₂O 98:2), 70% of a single diastereoisomer could be isolated as colorless crystals, m.p. (Et₂O/pentane) 109–111°. IR (CHCl₃): 2960s, 2870, 1727s, 1596, 1391, 1362, 1348, 1270, 1129s, 1103s, 1089, 1045, 1030, 1010, 890, 860. ¹H-NMR (CDCl₃): 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, CH₃–C(2)); 1.20–1.30 (*m*, 1 ring H); 1.36 (*s*, *t*-Bu); 2.29 (*s*, PhCH₃); 3.30 (*d'*, *AB*, *J* = 14, 1 H, PhCH₂); 3.55 (*d'*, *AB*, *J* = 14, 1 H, PhCH₂); 7.06–7.12 (*m*, 2 arom. H); 7.18–7.33 (*m*, 5 arom. H). ¹³C-NMR (CDCl₃): 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 C₂₇H₃₆O₂: 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/Et₂O 85:15), 84%. First diastereoisomer (45%): colorless crystals, m.p. (pentane/Et₂O) 142–143°. IR (CHCl₃): 3555, 2993s, 2900, 1721s, 1608, 1459, 1429, 1404, 1375, 1326s, 1279, 1142s, 1114s, 1092, 1059s, 1039, 946, 929, 916, 900, 875, 850, 826. ¹H-NMR (CDCl₃, 90 MHz): 0.93 (*s*, *t*-Bu); 1.28 (*s*, *t*-Bu); 1.56 (*d*, *J* = 6, CH₃–C(2)); 0.7–1.7 (*m*, 2 ring H); 1.95–2.21 (*m*, 1 ring H); 2.24 (*s*, PhCH₃); 4.35 (*AB*, *J* = 12, PhCHOH; D₂O: 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). ¹³C-NMR (CDCl₃): 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 C₂₇H₃₆O₃: 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. (CH₂Cl₂) 59–59.5°.

2,6-Di(tert-butyl)-4-methylphenyl 1-Benzoyl-2-methylcyclopropanecarboxylate (29). After FC (pentane/Et₂O 95:5), 80%. First diastereoisomer (60%): colorless crystals, m.p. (pentane/Et₂O) 92–95°. IR (CHCl₃): 2970s, 2880, 1739s, 1674s, 1600, 1450, 1418, 1396, 1365, 1319, 1289s, 1134s, 1101s, 1055, 1028, 1011, 969, 895, 863. ¹H-NMR (CDCl₃, 90 MHz): 1.07 (*s*, *t*-Bu); 1.22 (*s*, *t*-Bu); 1.36 (*m*, 1 ring H); 1.58 (*d*, *J* = 5, CH₃–C(2)); 1.94 (*m*, 2 ring H); 2.27 (*s*, PhCH₃); 7.01 (*s*, 2 arom. H); 7.30–7.63 (*m*, 3 arom. H); 7.95–8.20 (*m*, 2 arom. H). ¹³C-NMR (CDCl₃): 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 C₂₇H₃₄O₃: C 79.77, H 8.43; found: C 79.48, H 8.54.

Second diastereoisomer (40%): colorless crystals, m.p. (Et₂O/pentane) 114–115°. ¹H-NMR (CDCl₃, 90 MHz): 1.14 (*d*, CH₃–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*, PhCH₃); 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/Et₂O 97:3), 68%. First diastereoisomer (50%): colorless crystals, m.p. (pentane) 101–102°. IR (CHCl₃): 2989s, 2885,

1745s, 1601, 1393s, 1369, 1298, 1145s, 1116s, 1092, 1073, 1056, 970, 909, 892, 869. $^1\text{H-NMR}$ (CDCl_3 , 90 MHz): 1.34 (s, *t*-Bu); 1.43 (s, *t*-Bu); 1.62 (s, $\text{CH}_3\text{-C}(1)$); 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). $^{13}\text{C-NMR}$ (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^{+}), 159 (100). Anal. calc. for $\text{C}_{26}\text{H}_{34}\text{O}_2$: 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): 2970s, 2920, 2875, 1746s, 1598, 1384, 1364, 1137, 1108s, 1078, 1054, 1030, 969, 889, 862. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{32}\text{H}_{38}\text{O}_2$: C 84.54, H 8.42; found: C 84.52, H 8.41.

Second diastereoisomer (42%): $^1\text{H-NMR}$ (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, 2967s, 2915, 2875, 1738s, 1599, 1450, 1419, 1392, 1363, 1124s, 1098s, 1078s, 1060, 1039, 1025, 1003, 988, 951, 887, 861. $^1\text{H-NMR}$ (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, PhCH); 6.93–7.56 (*m*, 12 arom. H). $^{13}\text{C-NMR}$ (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^{+}), 220 (100). Anal. calc. for $\text{C}_{32}\text{H}_{38}\text{O}_3$: 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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