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Preparation of New Functionalized Cyclopropylmagnesium Reagents

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Procedures:

The following starting materials were obtained from commercial sources: ethyl propiolate (precursor to **1**), ethyl methacrylate (precursor to **4a** and **4b**).

The following starting materials were prepared according to literature procedures: cis-2-iodo-cyclopropanecarboxylic acid ethyl ester (**1**)[1] , 2,2-dibromo-1-methyl-cyclopropanecarboxylic acid ethyl ester (**4a**)[2] and 2,2-diiodo-1-methyl-cyclopropanecarboxylic acid ethyl ester (**4b**) [3].

General procedure for the halogen-magnesium exchange of cis-cyclopropanic iodoester (Method A):

A dry two-necked flask equipped with a magnetic stirring bar and a septum was charged with the *cis*-2-iodo-cyclopropanecarboxylic acid ethyl ester **1** (1 mmol) in dry THF (4 mL) under argon. The reaction mixture was cooled to –40 ^{o}C and a solution of *i*PrMgCl (0.67 mL, 1.62 M in THF, 1.1 mmol) was slowly added. After 15 min of stirring, the exchange was complete (checked by GC analysis). Electrophile (1.5 mmol) was added and the reaction mixture was allowed to warm up to rt. After 2 h, the reaction mixture was quenched with sat. NH_4Cl-solution (10 mL) and extract with ether. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash chromatography using the specified solvent system.

General procedure for the halogen-magnesium exchange of dihalogen cyclopropanic ester (Method B):

A dry two-necked flask equipped with a magnetic stirring bar and a septum was charged with the 2,2-Dihalogen-1-methyl-

cyclopropanecarboxylic acid ethyl ester **(4a** or **4b**)(1 mmol) in dry ether (4 mL) under argon. The reaction mixture was cooled to –50 ^{o}C and solution of *i*PrMgCl (0.55 mL, 2 M in ether, 1.1 mmol) was slowly added. After 10 min of stirring, the exchange was complete (checked by GC analysis) and electrophile (1.5 mmol) was added and the reaction mixture was allowed to warm up to rt. After 2 h, the reaction mixture was quenched with sat. NH_4Cl-solution (10 mL) and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by flash chromatography using the specified solvent system.

***Cis*-2-trimethylstannanyl-cyclopropanecarboxylic acid ethyl ester** (**3a**)

The reaction was carried out according to Method A using **1** (245 mg, 1.02 mmol), *i*PrMgCl (0.69 mL, 1.12 mmol), Me_3SnCl (1.53 mL, 1 M in THF, 1.53 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 2:1) affording **3a** (191 mg, 67% yield) as a yellow oil.
IR (KBr): 2925 (m), 1717 (s), 1381 (m), 1192 (s) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.12-3.92 (m, 2H), 1.73 (dd, *J* = 7.8Hz, *J* = 4.2 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13-1.06 (m, 1H), 0.82-0.73 (m, 2H), 0.00 (s, 9H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.0, 60.9, 32.3, 30.0, 23.0, 16.6, 14.7, 13.5, 8.0.
MS (EI): 277 (3), 263 (100), 233 (13), 165(40), 135 (10).
HRMS (EI): $C_9H_{18}O_2Sn$ required 278.0329; found 278.0360

***Cis*-2-phenylsulfanyl-cyclopropanecarboxylic acid ethyl ester** (**3b**)

The reaction was carried out according to Method A using **1** (158 mg, 0.65 mmol), *i*PrMgCl (0.44 mL, 0.72 mmol), PhSSPh (215 mg in 3 mL THF, 0.98 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 3:1) affording **3b** (76 mg, 52% yield) as a yellow oil.

IR (KBr): 3448 (w), 2981 (m), 1731 (s), 1381 (m), 1180 (s) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): d 7.39-7.13 (m, 5H), 4.07 (q, *J* = 7.1Hz, 2H), 2.71 (dt, *J* = 6.9, *J* = 7.8, 1H), 2.25 (dt, *J* = 6.7, *J* = 7.8, 1H), 1.50-1.43 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.0, 137.5, 129.1, 127.9, 125.9, 61.2, 22.5, 14.5, 13.6.
MS (EI): 222 (100), 177 (31), 149 (96), 116 (25), 109 (18).
HRMS (EI): $C_{12}H_{14}O_2S$ required 222.0715; found 222.0711.

$C_{12}H_{14}O_2S$	Calcd:	C	64.83	H	6.35	S	14.42
	Found	C	64.87	H	6.39	S	14.67

***Cis*-2-cyano-cyclopropanecarboxylic acid ethyl ester (3c):**

The reaction was carried out according to Method A using **1** (334 mg, 1.39 mmol), *i*PrMgCl (0.94 mL, 1.53 mmol), *p*-toluenesulphonyl cyanide (377 mg in 3 mL THF, 2.08 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 1:1) affording **3c** (131 mg, 67% yield) as a colorless oil.

IR (KBr): 3449 (w), 2986 (m), 2246 (m), 1731 (s), 1385 (m), 1199 (s) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.27 (q, *J* = 7.1Hz, 2H), 2.16-2.09 (m, 1H), 1.85 (dd, *J* = 8.1, *J* = 6.7, 1H), 1.69 (dt, *J* = 5.0, *J* = 6.5, 1H), 1.43 (dd, *J* = 8.1, *J* = 5.0, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.2, 118.0, 62.1, 20.4, 14.5, 13.6, 6.0.
MS (EI): 139 (11), 112 (60), 94 (100), 67 (30).
HRMS (EI): $C_7H_9NO_2$ required 139.1519; found 139.1547.

4-phenyl-3-oxa-bicyclo[3.1.0]hexan-2-one (3d):

The reaction was carried out according to Method A using **1** (107 mg, 0.44 mmol), *i*PrMgCl (0.30 mL, 0.49 mmol), benzaldehyde (71 mg, 0.66 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 1:1) affording **3d** (71 mg, 90% yield) as two diastereoisomers in the ratio of 65:35.

Diastereoisomer 1: 46 mg, yellow oil
IR (KBr): 3492 (w), 2924 (m), 1765 (s), 1455 (m), 1180 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.29 (m, 5H), 5.27 (s, 1H), 2.23-2.14 (m, 2H), 1.30 (dd, *J* = 7.6, *J* = 4.9, 1H), 1.01 (dt, *J* = 3.5, *J* = 4.6, 1H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.3, 140.1, 129.2, 126.0, 82.0, 25.1, 18.2, 13.3.
MS (EI): 174 (100), 145 (10), 129 (36), 117 (36), 104 (22).
HRMS (EI): $C_{11}H_{10}O_2$ required 174.0681; found 174.0678.

Diastereoisomer 2: 25 mg, yellow solid (mp = 110^{o}C)
IR (KBr): 3318 (w), 2920 (m), 1770 (s), 1452 (m), 1191 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.23 (m, 5H), 5.65 (d, *J* = 4.8 Hz, 1H), 2.52-2.45 (m, 1H), 2.18-2.12 (m, 1H), 1.05 (dd, *J* = 7.6, *J* = 5.2, 1H), 0.82-0.78 (m, 1H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 176.0, 137.8, 129.2, 128.8, 126.0, 82.0, 22.6, 19.6, 13.3.
MS (EI): 174 (100), 145 (12), 129 (17), 115 (16), 104 (32).

HRMS (EI): $C_{11}H_{10}O_2$ required 174.0681; found 174.0668.

***Cis*-2-allyl-cyclopropanecarboxylic acid ethyl ester (3e)**:

The reaction was carried out according to Method A using **1** (186 mg, 0.87 mmol), *i*PrMgCl (0.59 mL, 0.96 mmol), CuCN·2LiCl (0.17 mL, 1.0 M in THF, 0.17 mmol), allyl bromide (157 mg, 1.31 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 3:1) affording **3e** (102 mg, 75% yield) as a colorless oil.

IR (KBr): 2981 (m), 1726 (s), 1381 (m), 1180 (s) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.82-5.69 (m, 1H), 5.03-4.87 (m, 2H), 4.05 (q, *J* = 7.1Hz, 2H), 2.34-2.10 (m, 2H), 1.69-1.62 (m, 1H), 1.30-1.23 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.00-0.87 (m, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.2, 137.8, 115.1, 60.6, 31.4, 20.9, 18.4, 14.7.
MS (EI): 155 (12), 125 (33), 109 (100), 107 (9).
HRMS (EI): $C_9H_{14}O_2$ required 154.0994; found 154.0980.

***Cis*-2-(2-Ethoxycarbonyl-allyl)-cyclopropanecarboxylic acid ethyl ester (3f)**:

The reaction was carried out according to Method A using **1** (165 mg, 0.77 mmol), *i*PrMgCl (0.52 mL, 0.85 mmol), CuCN·2LiCl (0.15 mL, 1.0 M in THF, 0.15 mmol), 2-bromomethyl-acrylic acid ethyl ester (225 mg, 1.16 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 4:1) affording **3f** (143 mg, 81% yield) as a colorless oil.

IR (KBr): 2982 (m), 1722 (s), 1404 (m) 1179 (s) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.09 (s, 1H), 5.54 (q, *J* = 1.5Hz, 1H, 1H), 4.17-4.01 (m, 4H), 2.61-2.38 (m, 2H), 1.68 (dd, *J* = 7.8Hz, *J* = 5.6 Hz, 1H), 1.47-1.34 (m, 1H), 1.23 (t, *J* = 7.1Hz, 3H), 1.17(t, *J* = 7.1Hz, 3H), 1.04-0.91 (m, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.1, 167.4, 140.5, 125.2, 61.0, 60.7, 29.6, 20.4, 18.6, 14.7, 14.6, 13.7.
MS (EI): 226 (13), 181 (100), 152 (49), 123 (16), 107 (28).
HRMS (EI): $C_{12}H_{18}O_4$ required 226.1205; found 226.1220

***Cis*-2-benzoyl-cyclopropanecarboxylic acid ethyl ester (3g)**:

The reaction was carried out according to Method A using **1** (166 mg, 0.69 mmol), *i*PrMgCl (0.46 mL, 0.76 mmol), CuCN·2LiCl (0.76 mL, 1.0 M in THF, 0.76 mmol), benzoyl chloride (145 mg, 1.03 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 3:1) affording **3g** (111 mg, 73% yield) as a colorless oil.

IR (KBr): 3621 (w), 2982 (m), 1731 (s), 1597 (m), 1354 (s), 1227 (s) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97-7.94 (m, 2H), 7.51-7.35 (m, 3H), 3.94-3.86 (m, 2H), 2.71 (dd, *J* = 6.8 Hz, *J* = 8.0 Hz, 1H), 2.22 (dd, *J* = 6.4 Hz, *J* = 8.2 Hz, 1H), 1.83 (dt, *J* = 4.7 Hz, *J* = 6.6 Hz, 1H), 1.28 (dt, *J* = 4.7 Hz, *J* = 8.1 Hz, 1H), 0.97 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 194.9, 170.4, 137.5, 133.5, 128.9, 128.7, 61.2, 26.6, 23.5, 14.3, 12.0.
MS (EI): 218 (3), 173 (23), 145 (17), 105 (100).
HRMS (EI): $C_{13}H_{14}O_3$ required 218.0943; found 218.0948

***Trans*-2-benzoyl-cyclopropanecarboxylic acid ethyl ester** (*trans*-**3g**) :

The reaction was carried out according to Method A using *trans*-**1** (57 mg, 0.23 mmol), *i*PrMgCl (0.16 mL, 0.26 mmol), CuCN·2LiCl (0.26 mL, 1.0 M in THF, 0.26 mmol), benzoyl chloride (49 mg, 0.35 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 5:1) affording *trans*-**3g** (33 mg, 65% yield) as a colorless oil.

IR (KBr): 3437 (w), 2982 (m), 1729 (s), 1597 (m), 1333 (s), 1224 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97-7.93 (m, 2H), 7.55-7.38 (m, 3H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.15-3.09 (m, 1H), 2.34-2.28 (m, 1H), 1.58-1.49 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.4, 172.7, 137.4, 133.7, 129.0, 128.6, 61.5, 26.3, 25.0, 18.2, 14.5.
MS (EI): 218 (1), 173 (26), 144 (38), 115 (9).
HRMS (EI): $C_{13}H_{14}O_3$ required 218.0943; found 218.0943

4-(2-ethoxycarbonyl-cyclopropyl)-benzoic acid methyl ester (3h):

The reaction was carried out according to Method A using **1** (274 mg, 1.14 mmol), *i*PrMgCl (0.77 mL, 1.25 mmol), $ZnBr_2$ (0.76 mL, 1.6 M in THF, 1.25 mmol) to give a crude residue which was warm up to rt. Another dry two-necked flask equipped with a magnetic stirring bar and a septum was charged with *bis*-dibenzylidenepalladium ($Pd(dba)_2$) (27.3 mg, 5 mol %) and *tris*-*o*-furylphosphine (tfp) (22.0 mg, 10 mol %) followed by THF (3 mL). The initial red color disappeared after 2 min leading to a yellow solution. The 4-iodo-benzoic acid methyl ester (245 mg, 0.95 mmol) was added followed by the above crude residue. The reaction was stirred for 6h at rt, worked up according to Method A and the residual oil was purified by flash column chromatography on silicagel (pentane/ether 3:1) affording **3h** (215 mg, 92% yield) as a yellow oil.

IR (KBr): 3430 (w), 2983 (m), 1724 (s), 1611 (m), 1280 (s), 1158 (s) cm^{-1}

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88-7.84 (m, 2H), 7.27-7.24 (m, 2H), 3.82 (s, 3H), 3.80 (q, *J* = 7.1Hz, 2H), 2.52 (q, *J* = 8.5Hz, 1H), 2.10-2.02 (m, 1H), 1.68 (dt, *J* = 7.5 Hz, *J* = 5.3 Hz, 1H), 1.30 (dd, *J* = 7.8 Hz, *J* = 5.1 Hz, 1H), 0.91 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.0, 167.4, 142.5, 129.6, 128.9, 60.7, 52.4, 25.7, 22.6, 14.5, 11.8.
MS (EI): 248 (78), 217 (24), 193 (41), 175 (39), 115 (57).
HRMS (EI): $C_{14}H_{16}O_4$ required 248.1049; found 248.1050

$C_{14}H_{16}O_4$					
	Calcd:	C	67.73	H	6.50
	Found	C	68.06	H	6.44

2-bromo-2-iodo-1-methyl-cyclopropanecarboxylic acid ethyl ester (6a):

The reaction was carried out according to Method B using **4a** (345 mg, 1.20 mmol), *i*PrMgCl (0.66 mL, 1.32 mmol), iodine (367 mg, 1.44 mmol in 3 mL ether). After 2 h, the reaction mixture was quenched with sat. NH_4Cl-solution (10 mL) and extracted with ether. The organic layer was washed successively with $Na_2S_2O_3$, with brine, dried over $MgSO_4$ and concentrated under vacuum. The crude residue purified by flash column chromatography on silicagel (pentane/ether 5:1) affording **6a** (345 mg, 85% yield) as a colorless oil

IR (KBr): 3319 (w), 2980 (m), 1731 (s), 1307 (m), 1178 (m), 1026 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.25-4.12 (m, 2H), 2.26 (d, *J* = 7.8 Hz, 1H), 1.58 (d, *J* = 7.8 Hz, 1H), 1.50 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.8, 62.4, 34.8, 34.5, 20.6, 15.7, 14.7.
MS (EI): 333 (10), 259 (11), 179 (100), 149 (46).
HRMS (EI): $C_7H_{10}O_2IBr$ required 331.8909; found 331.8965

$C_7H_{10}O_2IBr$	Calcd:	C	25.25	H	3.03
	Found	C	25.34	H	2.97

2-allyl-2-bromo-1-methyl-cyclopropanecarboxylic acid ethyl ester (6b):

The reaction was carried out according to Method B using **4a** (316 mg, 1.10 mmol), *i*PrMgCl (0.58 mL, 1.16 mmol), CuCN·2LiCl (0.11 mL, 1.0 M in THF, 0.11 mmol), allyl bromide (198 mg, 1.65 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 6:1) affording **6a** (174 mg, 64% yield) as a colorless oil.

IR (KBr): 3429 (w), 2981 (m), 1724 (s), 1290 (m), 1178 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.83-5.70 (m, 1H), 5.07-4.97 (m, 2H), 4.07 (dq, *J* = 1.1 Hz, *J* = 7.1 Hz, 2H), 2.71-2.53 (m, 2H), 1.73 (d, *J* = 6.5 Hz, 1H), 1.51 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.4 Hz, 1H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.0, 134.9, 117.8, 61.6, 47.3, 42.6, 30.2, 28.7, 22.0, 14.6.
MS (EI): 247 (2), 173 (21), 139 (29), 93 (100), 77 (21).
HRMS (EI): $C_{10}H_{15}O_2Br$ required 246.0255; found 246.0334

5-bromo-1-methyl-4-phenyl-3-oxa-bicyclo[3.1.0]hexan-2-one (6c):

The reaction was carried out according to Method B using **4a** (280 mg, 0.97 mmol), *i*PrMgCl (0.53 mL, 1.07 mmol), bezaldehyde (155 mg, 1.46 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 3:1) affording **6c** (157 mg, 60% yield) as a colorless crystal.

mp 100°C
IR (KBr): 3523 (w), 2937 (w), 1790 (s), 1294 (m), 1126 (m), 1019 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.31 (m, 5H), 5.69 (s, 1H), 1.48 (d, *J* = 6.2 Hz, 1H), 1.47 (s, 3H), 1.19 (d, *J* = 6.1 Hz, 1H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.9, 135.2, 129.3, 129.1, 126.1, 84.1, 41.7, 30.3, 24.9, 13.6.
MS (EI): 266 (12), 187 (16), 159 (100), 128 (46), 115 (25), 105 (28).
HRMS (EI): $C_{12}H_{11}O_2Br$ required 265.9942; found 265.9926

$C_{12}H_{11}O_2Br$	Calcd:	C	53.96	H	4.15	Br 29.91
	Found	C	54.11	H	4.12	Br 29.71

X-ray analysis: Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC-171734**. Copies of the data can be obtained free of charge on application to CCDC,12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

5-bromo-1-methyl-4,4-diphenyl-3-oxa-bicyclo[3.1.0]hexan-2-one (6d):

The reaction was carried out according to Method B using **4a** (317 mg, 1.10 mmol), *i*PrMgCl (0.60 mL, 1.21 mmol), bezophenone (242 mg, 1.32 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 10:1) affording **6d** (233 mg, 61% yield) as a colorless oil.

IR (KBr): 3436 (m), 2930 (w), 1771 (s), 1448 (m), 1123 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61-6.90 (m, 10H), 1.53 (s, 3H), 1.50 (d, *J* = 6.4 Hz, 1H), 0.80 (d, *J* = 6.7 Hz, 1H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 173.6, 141.0, 137.8, 127.6, 127.4, 127.0, 126.4, 124.6, 90.3, 45.4, 29.8, 27.6, 12.5.
MS (EI): 342 (3), 263 (20), 235 (100), 202 (13), 160 (11).
HRMS (EI): $C_{18}H_{15}O_2Br$ required 342.0255; found 342.0271

5-bromo-1-methyl-4-cyclopentyl-3-oxa-bicyclo[3.1.0]hexan-2-one (**6e**):

The reaction was carried out according to Method B using **4a** (276 mg, 0.96 mmol), *i*PrMgCl (0.53 mL, 1.06 mmol), cyclopentanone (97 mg, 1.15 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 5:1) affording **6e** (145 mg, 61% yield) as a colorless oil.

IR (KBr): 3530 (w), 2968 (m), 1777 (s), 1341 (m), 1114 (m),960 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.27-1.66 (m, 8H), 1.51 (d, *J* = 5.7 Hz, 1H), 1.43 (s, 3H), 1.27 (d, *J* = 5.7 Hz, 1H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 175.0, 96.5, 44.7, 38.9, 34.5, 30.3, 28.0, 25.1, 24.1, 13.3.
MS (EI): 245 (1), 137 (100), 108 (8).
HRMS (EI): $C_{10}H_{13}O_2Br$ required 244.0099; found 244.0181

$C_{10}H_{13}O_2Br$	Calcd:	C	49.00	H	5.35	Br 32.60
	Found	C	48.95	H	5.07	Br 32.58

2-Bromo-2-iodo-cyclopropanecarboxylic acid ethyl ester (**7a**):

The reaction was carried out according to Method B using **4b** (427 mg, 1.12 mmol), *i*PrMgCl (0.61 mL, 1.23 mmol), 1,2-dibromo-1,1,2,2-tetrachloro-ethane (512 mg, 1.57 mmol) to give a crude residue, which was purified by flash column chromatography on silicagel (pentane/ether 9:1) affording **7a** (301 mg, 80% yield) as a colorless oil.

IR (KBr): 3318 (w), 2980 (m), 1731 (s), 1452 (m), 1270 (m), 1178 (m), 1028 (m) cm^{-1}
^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.25-4.09 (m, 2H), 2.48 (d, *J* = 7.8 Hz, 1H), 1.48 (d, *J* = 7.9 Hz, 1H), 1.46 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.2, 62.3, 34.8, 34.2, 26.0, 14.7.
MS (EI): 332 (4), 289 (13), 259 (12), 177(93), 151 (52).
HRMS (EI): $C_7H_{10}O_2IBr$ required 331.8909; found 331.9001.

$C_7H_{10}O_2IBr$	Calcd:	C	25.25	H	3.03	
	Found	C	25.43	H	2.98	

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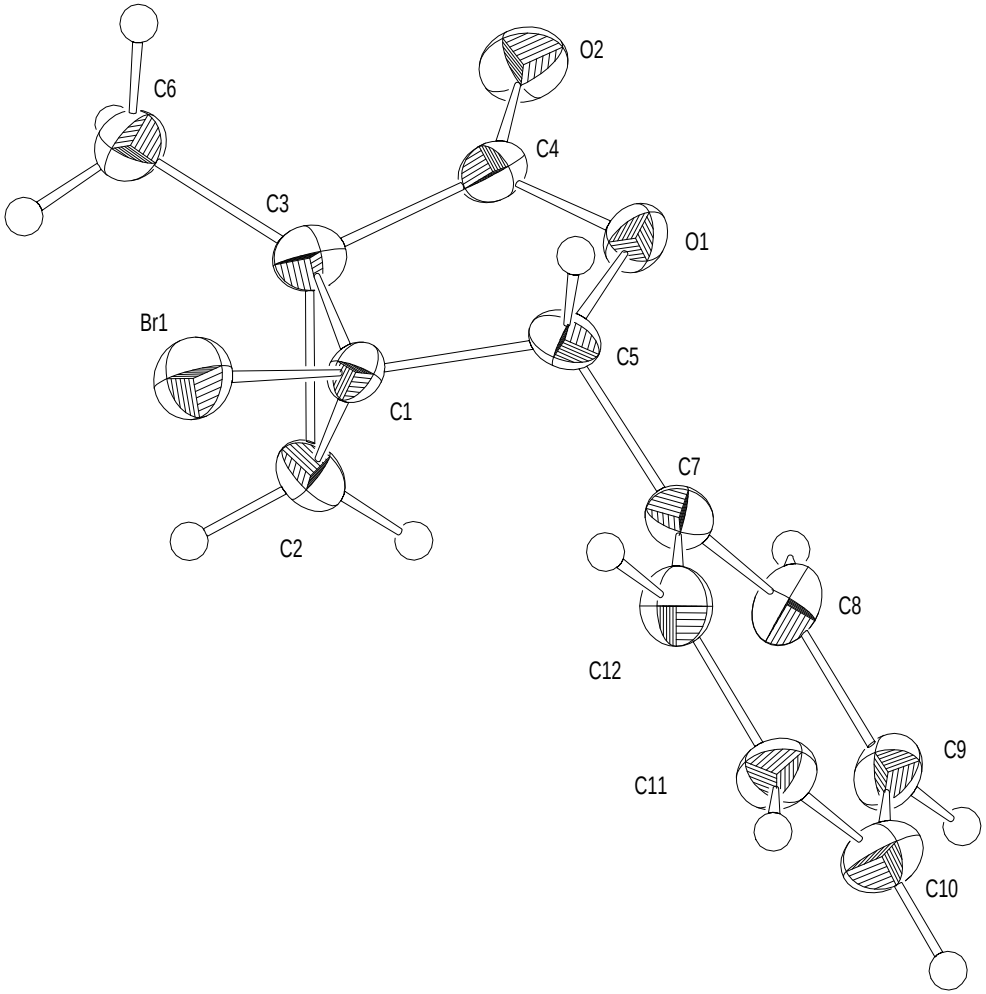

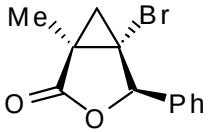

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